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RELATIONS BETWEEN THE STRUCTURE AND STRENGTH OF CERTAIN ORGANIC BASES IN AQUEOUS SOLUTION

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Introduction

Surprise at the relatively great strength as a base of diethylaniline ($K_B = 3 \times 10^{-8}$) in relation to ethylaniline ($K_B = 1 \times 10^{-9}$)[1] and dimethylaniline ($K_B = 1 \times 10^{-9}$) was the starting point of this study. Bredig[2] had years ago shown that diethylamine is also exceptionally strong among its near homologs, although the differences are not so great as with the anilines. We measured the strength of thirty-eight amines of various types which had not previously been examined. For comparison, we also redetermined, under like conditions, the strength of twenty-two bases that had been previously studied. The new compounds were chosen as far as possible to throw light upon the effect of alkyl substituents in various combinations, but the effects of other groups were also considered.

Cells containing liquid junctions, in which a hydrogen electrode is surrounded by a buffer mixture of the base and its salt, are satisfactory for the purpose in hand, although the results are not as unambiguous as those obtained in cells without transference. The chief difficulties in this method arise when the base studied is very weak, very strong or very insoluble in water. Many of the bases which we examined had very low solubilities in water at 25°, and for these a special extrapolation method had to be used. Michaelis and Mizutani[3] have shown that when the apparent strength of a base (or acid) in logarithmic units is plotted against the alcohol content of the solution for decreasing percentages of alcohol, the form of the curve obtained is always such as to permit a satisfactory extrapolation to the

[1] (a) Pring, *Trans. Faraday Soc.*, **19**, 705–17 (1924); (b) see Hall, THIS JOURNAL, **52**, 5125 (1930).

[2] Bredig, *Z. physik. Chem.*, **13**, 191 (1894).

[3] Michaelis and Mizutani, *ibid.*, **116**, 135–159 (1925); **118**, 318–326, 327–341 (1925).

strength value for pure water. We followed their method in many cases as shown by Fig. 1.

In the course of the work it became desirable to know the effect of temperature on the strength of many of the bases and this was determined in several cases over the range from 19 to 32°.

Experimental

Our cells were mostly of the type

$$\mathrm{Pt} \left| \mathrm{H_2} \right| \begin{matrix} \text{Base, } C = C_B, \\ \text{Salt, } C = C_{BH^+} \end{matrix} \left| \begin{matrix} \mathrm{KCl}, \\ \text{Satd.} \end{matrix} \right| \begin{matrix} \mathrm{KCl}, \text{ satd.} \\ \mathrm{Hg_2Cl_2}, \text{ satd.} \end{matrix} \left| \mathrm{Hg} \right.$$

They were not thermostated, but the temperatures were measured in different parts of the cells and corrections made as described below. The apparatus presented few novel features and its detailed description is omitted.

Most of the bases were purchased from the Eastman Kodak Company—a few from other manufacturers. Several were prepared in the Organic Chemical Laboratory of this University and kindly presented to us.

Liquid bases were redistilled in a carbon dioxide-free atmosphere and characterized by their boiling points. Solid bases were considered of sufficient purity if they gave correct melting points; otherwise they were recrystallized until a constant and correct melting point was reached.

Other materials were of ordinary C. P. grade further purified when necessary.

Notation.—We define an experimental quantity paH in terms of equation 1.

$$paH = \frac{E - E_{cal.}}{0.00001983(273.1 + t)} \qquad (1)$$

where E is the e. m. f. of a cell of the type described, $E_{cal.}$ is taken as $0.2448 - 0.008(t - 25°)$ and t is the centigrade temperature of the calomel electrode.

Letting

$$paH = pcH + pfH \qquad (2)$$

where cH is the stoichiometric concentration of free strong acid in the cell, pfH may be determined with varying concentrations of strong acids and salts in the cells. This has been done by Bjerrum and Unmack,[4] who give cube root interpolation formulas for pfH over a large range of concentrations of sodium chloride and potassium chloride. We made two series of measurements of this type, one in solutions of pure hydrochloric acid and one in mixtures of hydrochloric acid and guanidine chloride. Our results at low concentrations agreed well with Bjerrum and Unmack's but at higher concentrations many individual ion effects were noticeable.

[4] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, IX, 1 (1929).

Every new substance measured constitutes a special case, and it is in principle impossible to be sure that an adopted *pfH* value is the correct one for a given mixture of any particular base and salt. Nevertheless, in rather dilute and nearly neutral solutions there is a very strong presumption that no serious error will be introduced by adopting any of the values of *pfH* given by different authors, while in concentrated, strongly acid or strongly alkaline solutions, unavoidable uncertainties will be introduced by the use of any set of values for *pfH*. In view of these considerations, and in the hope of making our values as self-consistent and comparable among themselves as possible, we decided to use in all cases *pfH* values calculated from the cube-root interpolation formulas of Bjerrum and Unmack. The value 0.2448 for the saturated calomel electrode was used in order to make our practice consistent with that of the Danish investigators as far as possible. Had the value recommended by Clark been used, our values of $pK_{H(c)}$ would have been 0.02 or 0.03 units lower in most cases.

We now define a constant $K_{H(c)} = C_B \times C_{H_3O^+}/C_{BH^+} = K_{H(o)} \times f_{BH^+}/f_{H_3O^+} \times 1/fB$ where $K_{H(o)}$ is the thermodynamic mass action constant $a_B \times a_{H^+}/a_{BH^+}$ for the dissociation in water of the cation acid BH^+. Because of the form of the activity coefficient terms involved $K_{H(c)}$ may be expected to be very nearly independent of salt concentration in dilute solution—much more nearly so than the "constant" K_B usually given to characterize the strength of a base. Moreover, $pK_{H(c)}$ is more directly obtainable from the measurements and involves no assumption concerning the value of K_w. In fact

$$pK_{H(c)} = pcH + pR \qquad (3)$$

where R is the ratio of the stoichiometric concentrations of free base and salt, and *pcH* is obtained from *paH* by (2).

The Effect of Hydrolysis.—If a 1:1 base–salt mixture is found to be acid or alkaline the acid or alkali has been produced at the expense of the salt or base according to (a) or (b).

$$\begin{aligned} &(a) \quad BH^+ + H_2O \rightleftharpoons B + H_3O^+ \\ &(b) \quad B + H_2O \rightleftharpoons BH^+ + OH^- \end{aligned} \qquad (4)$$

It is therefore necessary to calculate *cH* and *cOH* from *paH* and to apply appropriate corrections to the concentrations of base and salt originally introduced.[5] At an ionic strength of 0.01 this correction to *pR* amounts to less than 0.01 between *paH* = 4.2 and *paH* = 9.8 inclusive, but becomes appreciable when the base is very strong or very weak, as well as in more dilute solutions.

Results

For convenience in discussion the bases are divided into several groups. Group I includes rather weak bases (pK_H between 3 and 7), which were

[5] These corrections are illustrated below.

TABLE I

1 No.	2 Name	3 *paH*	4 *t*	5 *c*	6 *pcH*	7 *pR*	8 $pKH_{(t)}$	9	10 $pKH(25°)$	11
1	β-Acetylpyridine	3.26	25	0.0100	3.23	−0.05	3.18	0.011	3.18	
2	N-Methyl-α-naphthylamine	3.82	27	.0010	3.81	− .14	3.67	.013	3.70	
3	α-Naphthylamine	4.10	22	.0005	4.09	− .13	3.96	.013	3.92	3.92[b]
4	β-Naphthylamine	4.25	23	.0005	4.24	− .10	4.14	.013	4.11	4.25[c]
5	*m*-Phenetidine	4.16	28	.0100	4.13	.00	4.13	.013	4.17	
6	*m*-Anisidine	4.27	22	.0100	4.24	.00	4.24	.013	4.20	
7	*o*-Toluidine	4.42	25	.0100	4.39	.00	4.39	.014	4.39	4.43[a]
8	*o*-Phenetidine	4.46	28	.0100	4.43	.00	4.43	.014	4.47	
9	*o*-Anisidine	4.59	20	.0100	4.56	.00	4.56	.014	4.49	
10	Aniline	4.67	21	.0100	4.64	.00	4.64	.014	4.58	4.62[d]
11	N-Methyl-*o*-toluidine	4.65	23	.0100	4.62	.00	4.62	.014	4.59	
12	*m*-Toluidine	4.72	25	.0100	4.69	.00	4.69	.014	4.69	4.71[a]
13	N-Ethyl-*o*-toluidine	4.99	22.5	.0040	4.96	.00	4.96	.015	4.92	
14	N-Methyl-*m*-toluidine	5.03	21	.0100	5.00	.00	5.00	.015	4.94	
15	α-Hydroxy-β-ethylpyridine	5.03	25	.0100	5.00	.00	5.00	.015	5.00	
16	N-Dimethylaniline	5.08	25.5	.0040	5.05	.00	5.05	.015	5.06	5.10[a]
17	*p*-Toluidine	5.11	24	.0100	5.08	.00	5.08	.015	5.07	5.12[a]
18	*p*-Phenetidine	5.23	28	.0100	5.20	.00	5.20	.015	5.25	
19	*p*-Anisidine	5.36	22.5	.0100	5.33	.00	5.33	.015	5.29	
20	N-Methyl-*p* toluidine	5.39	23	.0100	5.36	.00	5.36	.015	5.33	
21	N-Dimethyl-*p*-toluidine	5.58	21.5	.00125	5.56	.00	5.56	.016	5.50	5.55[e]
22	N-Ethyl-*p*-toluidine	5.75	22	.0050	5.72	.00	5.72	.016	5.67	
23	N-Dimethyl-*o*-toluidine	5.90	20	.0025	5.94	.00	5.94	.016	5.86	5.96[e]

[a] *Cf.* Hall, THIS JOURNAL, **52,** 5115 (1930). [b] Farmer and Warth (F. W.), *J. Chem. Soc.*, **85,** 1713 (1904). [c] 4.23 F. W., 4.27 McCoy, private communication. [d] Average from literature. [e] Ley and Grau, *Ber.*, **58B,** 1765–1775 (1925).

sufficiently soluble to be studied in water solution. Results for these are collected in Table I. The columns of the table present in order: (1) a serial number to aid in identifying the base, (2) its name, (3) the value of *paH* as measured, (4) the centigrade temperature, (5) the concentration of the base (and of the salt) added, (6) the value of *pcH* obtained by subtracting from *paH* the appropriate value of *pfH* calculated from Bjerrum and Unmack's formulas, (7) *pR* ($R = \log (c\mathrm{B}/c\mathrm{BH}^+)$), (8) the negative logarithm of the hydrolysis constant calculated for the temperature of the measurement, (9) the negative temperature coefficient of the constant, and (10) the constant corrected to 25°. In column (11) are added for comparison some of the "best" values obtainable from the literature.

Group II contains the stronger bases (pK_H between 7 and 12) of the same solubility class, results for which appear in Table II. In this table the first six and the last five columns are the same as in Table I. Column (7) shows $pK_{w(c)}$ for the appropriate concentration and temperature (from Bjerrum and Unmack) and column (8) $pcOH = pK_{w(c)} - pcH$.

(A sample calculation (for No. 28, 1-ethylpiperidine) is as follows: *paH* at 23° of a mixture made up 0.01 *N* in free base and 0.01 *N* in salt was 10.45. At this concentration of electrolyte we find from Bjerrum and Unmack's tables *pfH* = 0.03, so that *pcH* is 10.42. $pK_{w(c)}$ for this concentration and temperature is 13.97, so that *pcOH* = 3.55. This means an hydroxyl-ion concentration of 0.00029, so that the ratio $R = (0.01 - 0.00029)/(0.01 + 0.00029)$ and *pR* = 0.03. The constant $pK_{H(c)}$ at 23° is then 10.42 + 0.03 or 10.45, and for a base of this strength the temperature coefficient of

TABLE II

1 No.	2 Name	3 paH	4 t	5 c	6 pcH	7 $pK_{w(t)}$	8 $pcOH$	9 pR	10 $pKH_{(t)}$	11 $-\alpha$	12 $pKH(25°)$	13
24	Triethanolamine	7.85	22	0.0100	7.82	14.00	6.18	0.00	7.82	0.018	7.77	
25	Diethanolamine	8.95	23	.0100	8.92	13.97	5.05	.00	8.92	.020	8.88	
26	2-Hydroxy-3-ethylpiperidine	9.12	25	.0050	9.09	13.92	4.83	.00	9.09	.020	9.09	
27	Ethanolamine	9.53	22	.0100	9.50	14.00	4.50	.00	9.50	.020	9.44	
28	1-Ethylpiperidine	10.45	23	.0100	10.42	13.97	3.55	.03	10.45	.021	10.41	
29	1-N-butylpiperidine	10.47	23	.0100	10.44	13.97	3.53	.03	10.47	.021	10.48	
30	N-Methyl-γ-phenyl-*n*-propylamine	10.63	22.5	.0100	10.60	13.99	3.39	.04	10.64	.022	10.58	
31	*n*-Butylamine	10.71	20	.0100	10.68	14.07	3.39	.04	10.72	.022	10.61	
32	Cyclohexylamine	10.65	24	.0100	10.62	13.93	3.31	.04	10.66	.022	10.64	
33	*n*-Amylamine	10.70	22	.0100	10.67	14.00	3.33	.04	10.71	.022	10.64	
34	Isoamylamine	10.70	22	.0100	10.67	14.00	3.33	.04	10.71	.022	10.64	10.60[a]
35	1-Ethyl-2-methylpiperidine	10.64	26	.0100	10.69	13.87	3.26	.05	10.66	.022	10.68	
36	1-*n*-Butyl-2-methylpiperidine	10.54	26	.0020	10.52	13.91	3.39	.18	10.70	.022	10.72	
37	N-Methyl-δ-phenyl-*n*-butylamine	10.78	23	.0100	10.75	13.97	3.22	.05	10.80	.022	10.76	
38	Di-isobutylamine	10.88	21	.0100	10.85	14.04	3.19	.06	10.91	.022	10.82	10.59[a]
39	2-Methylpiperidine	10.97	23.2	.0100	10.94	13.96	3.02	.08	11.02	.022	10.98	
40	Diethylamine	10.92	25	.0100	13.90	13.90	3.01	.09	10.98	.022	10.98	11.00[a]
41	Di-isopropylamine	11.07	21	.0100	11.04	14.04	3.00	.09	11.13	.022	11.05	
42	Di-*n*-butylamine	11.28	21	.0100	11.25	14.04	2.79	.14	11.39	.022	11.31	

[a] Bredig, Ref. 2, as corrected in "International Critical Tables."

TABLE III

1 No.	Name	3 paH	4 t	5 c	6 pcH	7 $pK_{w(o)}$	8 $pcOH$	9 pR	10 $pKH_{(t)}$	11 $-\alpha$	12 $pKH(25°)$	13
43	2-Aminodiphenyl	3.93	22	0.0010	3.92	...	..	−0.10	3.82	0.013	3.78	
44	N-Ethyl-α-naphthylamine	4.28	29	.0010	4.24	...	..	− .05	4.19	.013	4.24	
45	4-Aminodiphenyl	4.28	29	.0010	4.27	...	..	− .05	4.22	.013	4.27	
46	N-Methylaniline	4.85	27	.0100	4.82	...	..	.00	4.82	.015	4.85	4.75[a]
47	N-Dimethyl-α-naphthylamine	4.86	28	.0005	4.85	...	..	.02	4.83	.015	4.88	
48	N-*n*-Propylaniline	5.06	24	.0020	5.04	...	..	.00	5.04	.015	5.02	
49	N-Ethylaniline	5.15	24	.0020	5.15	...	..	.00	5.62	.016	5.11	5.15[a]
50	N-Di-*n*-propylaniline	5.63	23	.0005	5.62	...	..	.00	5.68	.016	5.59	
51	N-Methyl-*n*-propylaniline	5.68	23	.0009	5.67	...	..	.00	5.67	.017	5.64	
52	N-Methylethylaniline	6.04	22	.0020	6.02	...	..	.00	6.02	.016	5.98	
53	N-Ethyl-*n*-propylaniline	6.40	22	.0008	6.39	...	..	.00	6.39	.016	6.34	
54	N-Diethylaniline	6.62	22	.0010	6.61	...	..	.00	6.61	.017	6.56	6.52[a]
55	N-Diethyl-*p*-toluidine	7.14	23	.0005	7.13	14.03	6.90	.00	7.13	.018	7.09	
56	N-Diethyl-*o*-toluidine	7.25	21	.0005	7.24	14.10	4.09	.00	7.24	.018	7.18	
57	Tri-*n*-butylamine	9.87	25	.0010	9.86	13.95	4.09	+ .07	9.93	.021	9.93	
58	s-Diphenylguanidine	10.02	25	.0010	10.01	13.95	3.94	+ .11	10.12	.021	10.12	10.0[a]
59	Di-isoamylamine	10.78	27.8	.0040	10.75	13.82	3.07	+ .19	10.94	.022	11.00	10.89[a]
60	Di-*n*-amylamine	10.82	26	.0020	10.80	13.91	3.11	+ .36	11.16	.022	11.18	

[a] *Cf.* Hall, Ref. 1.

$pKH(c)$ is -0.021. We must therefore subtract 0.04 from the value at 23° to give 10.41 as the final value of the constant at 25°.

All the constants given in Tables I, II and III were calculated similarly.)

Group III, reported in Table III, includes the bases studied in alcoholic solution (either because they were very insoluble in water, or for comparison purposes). The meanings of the various columns in the table correspond to those in Tables I and II. The concentrations were so low in the case of these bases that the corrections for *pfH* are very small. Figure 1 shows the method of obtaining the value of *paH* by extrapolation from solutions progressively less alcoholic. In this figure abscissas represent increasing percentage of alcohol, and ordinates the observed e. m. f. of the cells containing the base–salt mixtures.

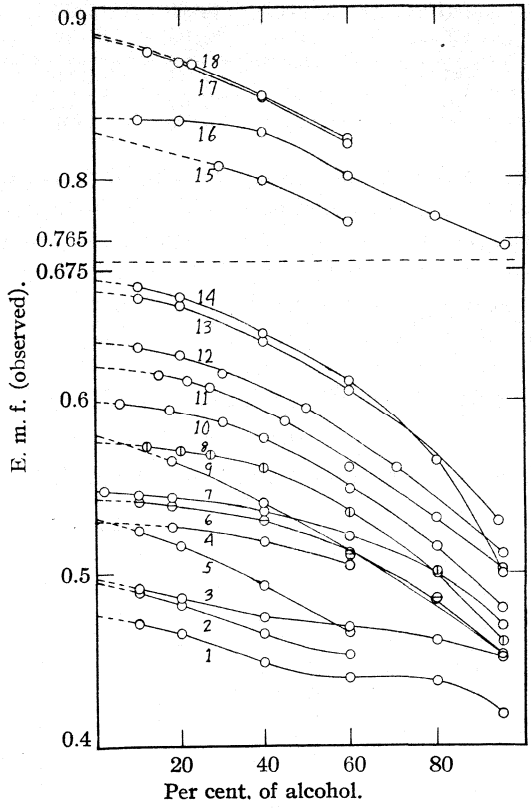

Fig. 1.—Effect of alcohol on apparent strength of bases: ordinates, observed voltages of cells; abscissas, percentage of ethanol by volume. Numbers of curves: 1, 2-aminodiphenyl; 2, ethyl-α-naphthylamine; 3, 4-aminodiphenyl; 4, methylaniline; 5, dimethyl-α-naphthylamine; 6, *n*-propylaniline; 7, ethylaniline; 8, di-*n*-propylamine; 9, methyl-*n*-propylaniline; 10, methylethylaniline; 11, ethyl-*n*-propylaniline; 12, diethylaniline; 13, diethyl-*p*-toluidine; 14, diethyl-*o*-toluidine; 15, tri-*n*-butylamine; 16, diphenylguanidine; 17, di-isoamylamine; 18, di-*n*-amylamine.

Guanidine.—As this proved to be a quite exceptionally strong base, a special method was used to determine its strength.

To 20 cc. of 2 *N* potassium chloride was slowly added an equal volume of 2 *N* potassium hydroxide. The *paH* was determined after each addition of potassium hydroxide. The results are reported in Table IV.

The third line of Table IV is the sum of the first two and is the value of $pK_{w(inc.)} = paH + pcOH$. The exact constancy of this value is surprising even in view of the fact that the ionic strength was maintained constant throughout the experiment. (The value found by Bjerrum and Unmack

TABLE IV

$pK_{w(inc.)}$ IN POTASSIUM HYDROXIDE SOLUTION

pcOH	2.00	1.28	0.97	0.81	0.72	0.57
paH	11.94	12.65	12.96	13.12	13.21	13.36
$pK_{w(inc.)}$	13.94	13.93	13.93	13.93	13.93	13.93
pcOH	0.47	0.34	0.11	0.07	0.03	0.00
paH	13.46	13.59	13.82	13.87	13.90	13.93
$pK_{w(inc.)}$	13.93	13.93	13.93	13.94	13.93	13.93

in 1.5 *N* potassium chloride is 13.91.) A similar experiment was now carried out, using guanidine chloride instead of potassium chloride. From the values of *paH* found corresponding values of *pcOH* were calculated (using 13.91 instead of 13.93 as the value of $pK_{w(inc.)}$, as this series of measurements was made at 24.2° instead of at 23.5°). From these values of *pcOH* (found) and the known amounts of potassium hydroxide added, it was possible to calculate very simply the concentration of free base and of salt. From these data may be calculated a constant

$$pK_{H(inc.)} = pK_{H(c)} + pfH = paH + pR$$

The values of this constant are reported in Table V.

TABLE V

STRENGTH CONSTANT OF GUANIDINE

(*x* = concn. of potassium hydroxide introduced)

x	0.1422	0.1966	0.2817	0.4305	0.5454
paH	12.37	12.53	12.73	12.97	13.13
cOH found	0.0288	0.0417	0.0660	0.1147	0.1660
R	0.065	0.094	0.145	0.252	0.352
$pK_{H(inc.)}$	13.56	13.56	13.57	13.57	13.58
x	0.6760	0.7895	0.8880	0.9441	1.000
paH	13.27	13.42	13.50	13.56	13.60
cOH found	0.2290	0.3235	0.3890	0.4465	0.5246
R	0.507	0.625	0.828	0.896	0.905
$pK_{H(inc.)}$	13.56	13.62	13.58	13.64	13.64
				Mean =	13.59

To calculate $pK_{H(c)}$ from this constant it would be necessary to know the value of *pfH*. This cannot be calculated from our data. Bjerrum and Unmack's formula is not supposed to be valid above 1.5 normal, or in as strongly alkaline solutions as ours. On the very doubtful assumption that their formula is valid in solutions 2 *N* in electrolyte and up to 1 *N* in potassium hydroxide, we find $pfH = -0.09$, from which we calculate for guanidine $pK_{H(c)} = 13.68$ at 24.2°. We have no information on the temperature coefficient for such a strong base, but we may perhaps assume as the most probable value of the constant at 25° $pK_{H(c)} = 13.6_5$.

The Temperature Coefficient of pK_H.—The information in the literature regarding the effect of temperature on the dissociation of bases is

meager. As we needed some rational means of reducing our own results and those of others to a single standard temperature, we measured the constants of several bases at temperatures ranging from 19 to 32°. Three significant conclusions may be drawn from the results: (1) in all cases the value of pK_H diminished with rising temperature, (2) the change with temperature increased with the value of pK_H, (3) where sufficient data were obtained to test the question, the change of pK_H with temperature appears to be linear. The value of pK_H was calculated at each temperature as indicated in the tables. The results are reproduced in Fig. 2, where, however, through error the lower point of curve 8 has been placed 0.01 unit too low. The results are assembled in Table VI.

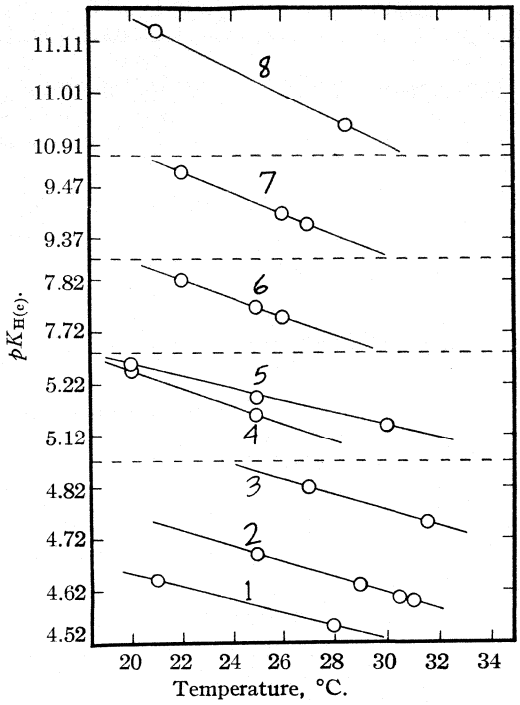

Fig. 2.—Temperature coefficient of $pK_{H(c)}$: ordinates, $pK_{H(c)}$; abscissas, temperature in °C. Numbers of curves: 1, aniline; 2, *m*-toluidine; 3, methylaniline; 4, dimethylaniline; 5, pyridine; 6, triethanolamine; 7, ethanolamine; 8, di-isopropylamine.

The values of the temperature coefficient were plotted against $pK_{H(25°)}$ and a straight line was drawn through the points. From this graph were read the values of $-\alpha$ used in Table I (column 9) and Tables II and III (column 11).

TABLE VI

Base	*t*, °C.	pK_H	$\Delta pK_H/\Delta t$	No. of curves in Fig. 2
Aniline	21.0	4.65		
	28.0	4.55	−0.0129	1
m-Toluidine	25.0	4.69		
	29.0	4.63		
	30.5	4.61		
	31.0	4.60	− .0150	2
Methylaniline	27.0	4.82		
	31.5	4.75	− .0156	3
Dimethylaniline	20.0	5.25		
	25.0	5.16	− .0180	4[a]

TABLE VI (*Concluded*)

Base	t, °C.	pK_H	$\Delta pK_H/\Delta t$	No. of curves in Fig. 2
Pyridine	20.0	5.26		
	25.0	5.19		
	30.0	5.14	−0.0120	5[b]
Triethanolamine	22.0	7.82		
	25.0	7.77		
	26.0	7.75	− .0175	6
Ethanolamine	22.0	9.50		
	26.0	9.42		
	27.0	9.40	− .0200	7
Di-isopropylamine	21.0	11.13		
	28.5	10.96	− .0227	8

[a] Goldschmidt and Keller, *Ber.*, **35**, 3534–3549 (1902). [b] Hahn and Klockman, *Z. physik. Chem.*, **146**, 373–403 (1930).

Discussion of Results

Positive Groups.—Bredig[2] showed that the introduction of one alkyl group into ammonia increased the pK_H by approximately 1.3, while a second alkyl group had a much smaller effect (*ca.* 0.4 of a pK_H unit) and that except in the case of the methyl amines, the tertiary compound was of about the same strength as the primary. We have made only a few additions to the values already known for this class of compounds, and our results confirm the earlier data for the most part. Table VII gives the data at present available, and shows that the behavior of the methylamines referred to above is paralleled by the *n*-butylamines.

TABLE VII

NH_3 pK_H = 9.27

R	$\Delta pK_H(1)$	RNH_2	$\Delta pK_H(2)$	R_2NH	$\Delta pK_H(3)$	R_3N
CH_3	1.37	10.64	0.07	10.71	−0.91	9.80
					$(CH_3(C_2H_5)_2)$	10.34
C_2H_5	1.40	10.67	.31	10.98	−0.24	10.74
n-C_3H_7	1.31	10.58	.33	10.91	− .26	10.65
iso-C_3H_7	1.36	10.63	.42	11.05*	....	...
n-C_4H_9	1.34	10.61*	.70	11.31*	−1.38	9.93*
iso-C_4H_9	1.15	10.42	.40	10.82	−0.50	10.32
sec.-C_4H_9	1.29	10.56	...	...	....	...
tert.-C_4H_9	1.18	10.45	...	...	....	...
n-C_5H_{11}	1.37	10.64*	.54	11.18*	....	...
iso-C_5H_{11}	1.37	10.64	.36	11.00	....	...
cyclo-C_6H_{13}	1.37	10.64*	...	...	....	...
Average	1.32		.39		−0.66	

In Table VII the values marked * refer to compounds which we believe we have measured for the first time. For the other figures we have used our

own results where available, or made the best selection we could from the values in the literature.[6]

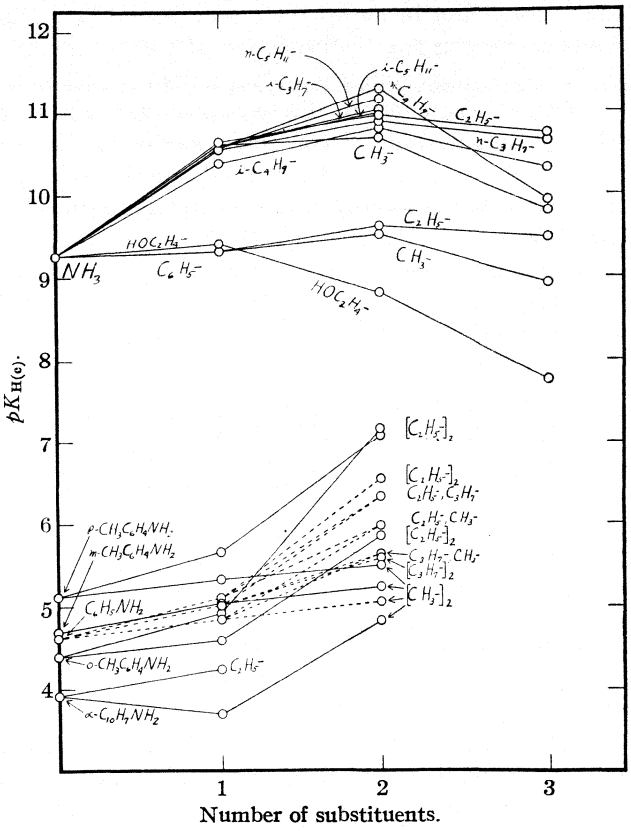

Fig. 3.—Effect of alkyl groups on strength of aliphatic and aromatic amines: ordinates, $pK_{H(c)}$; abscissas, number of substituent groups.

The data are also reproduced in Fig. 3, which clearly shows the high relative base strength of the secondary amines. Very similar relations are observed among the N-alkyl benzylamines, as Table VIII shows.

TABLE VIII

STRENGTH OF BENZYLAMINES

	pK_H		pK_H		pK_H
$C_6H_5CH_2NH_2$	9.34[a,b]	$C_6H_5CH_2NHCH_3$	9.58[b]	$C_6H_5CH_2N(CH_3)_2$	8.93[a]
		$C_6H_5CH_2NHC_2H_5$	9.68[b]	$C_6H_5CH_2N(C_2H_5)_2$	9.48[a]

Average $\Delta pK_H = +0.29$.

[a] "International Critical Tables," Vol. VI. [b] Carothers, Bickford and Hurwitz, THIS JOURNAL, **49**, 2908 (1927).

[6] *Cf.* Hall, THIS JOURNAL, **52**, 5115–5128 (1930).

Although the replacement of one H in CH_3 by C_6H_5 makes the benzylamine as weak as ammonia, the substitution of methyl and ethyl for the other hydrogen atoms first increases the strength and then markedly decreases it in the tertiary amines. Inspection of the last two tables shows that a single alkyl group has almost exactly the same effect on the strength, whatever its nature. The effect of the second alkyl group increases with length and degree of branching of the chain as far as the normal butyl radical, and then falls off again. A third alkyl group weakens the secondary amine in all cases, but especially in the methyl and *n*-butyl compounds.

Effect of Methyl.—The following Table IX shows the very constant positive effect of the methyl group as a second substituent on the nitrogen atom, and also the decreasing effect of an additional CH_2 group as the hydrocarbon chain is lengthened.

TABLE IX

	pK_H	ΔpK_H		pK_H
Aniline	4.62	+0.23	N-Methylaniline	4.85
$\Delta pK_H = +4.72$			$\Delta pK_H = +4.73$	
Benzylamine	9.34*	+ .24	N-Methylbenzylamine	9.58*
$\Delta pK_H = +0.49$			$\Delta pK_H = +0.56$	
β-Phenylethylamine	9.83*	+ .31	N-Methyl-β-phenylethylamine	10.14*
$\Delta pK_H = +0.37$			$\Delta pK_H = +0.44$	
γ-Phenyl-*n*-propylamine	10.20*	+ .38	N-Methyl-γ-phenyl-*n*-propylamine	10.58
$\Delta pK_H = +0.20$			$\Delta pK_H = +0.17$	
δ-Phenyl-*n*-butylamine	10.40*	+ .35	N-Methyl-δ-phenyl-*n*-butylamine	10.75
$\Delta pK_H = +0.09$				
ε-Phenyl-*n*-amylamine	10.49*			

The starred values are from Carothers' paper,[7] while aniline and methylaniline are average values from the literature. The last two values in the right-hand column are from our own data. Similar effects of the methyl group appear below in the discussion of the piperidines, anilines, toluidines, etc.

Alkyl Piperidines.—Our measurements on this class of compounds show clearly two effects, portrayed in Table X. (1) The introduction of a methyl group in the 2-position increases the base strength by 0.3 unit except in the case of piperidine itself. (2) The introduction of an alkyl group on the nitrogen of the secondary amine has a weakening effect of about 0.7 unit quite comparable to the introduction of a third alkyl group into dimethyl- or diethylamine. The weakness of methylpiperidine in rela-

TABLE X

	pK_H		pK_H
Piperidine	11.13	2-Methylpiperidine	10.98
1-Ethylpiperidine	10.40	1-Ethyl-2-methylpiperidine	10.68
1-*n*-Butylpiperidine	10.42	1-*n*-Butyl-2-methylpiperidine	10.72

[7] Carothers, Table VIII, Ref. *b*.

tion to piperidine is surprising, and is comparable to the case of N-methyl-α-naphthylamine.

N-Alkylanilines, N-Alkyltoluidines and N-Alkyl-α-naphthylamines.—Although substitution of one alkyl group for one of the hydrogens attached to the nitrogen atom in these compounds usually (with the exception of methyl-α-naphthylamine) causes a moderate increase in the base strength as is to be expected, the surprising thing is the extent of the increase caused by the *second* alkyl substitution, particularly when the substituents are ethyl groups. This is the effect referred to in the introduction as the starting point of the investigation. As shown by Table XI and Fig. 3, the positive effect seems to reach a decided maximum with the ethyl group, although unfortunately measurements have not been made on the butyl or amyl derivatives.

TABLE XI

ANILINE $pK_H = 4.62$

	pK_H		pK_H
N-Methylaniline	4.85	N-Diethylaniline	6.56
N-Ethylaniline	5.11	N-Methyl-*n*-propylaniline	5.64
N-*n*-Propylaniline	5.02	N-Ethyl-*n*-propylaniline	6.34
N-Dimethylaniline	5.06	N-Di-*n*-propylaniline	5.59
N-Methylethylaniline	5.98		

The toluidines show many similarities to the anilines as will be seen from Table XII.

TABLE XII

	pK_H		pK_H		pK_H
o-Toluidine	4.39	N-Methyl-*o*-toluidine	4.59	N-Dimethyl-*o*-toluidine	5.86
m-Toluidine	4.69	N-Methyl-*m*-toluidine	4.94	N-Dimethyl-*m*-toluidine	5.24
p-Toluidine	5.12	N-Methyl-*p*-toluidine	5.33	N-Dimethyl-*p*-toluidine	5.50
		N-Ethyl-*o*-toluidine	4.92	N-Diethyl-*o*-toluidine	7.18
		N-Ethyl-*m*-toluidine	..	N-Diethyl-*m*-toluidine	..
		N-Ethyl-*p*-toluidine	5.67	N-Diethyl-*p*-toluidine	7.09

In every case we see a moderate increase in base strength due to the first N-methyl, a greater increase due to ethyl, or two methyl groups, and a very marked increase indeed for two ethyl groups. This effect is especially great in the ortho isomer. Dimethyl-*o*-toluidine is, surprisingly enough, stronger than dimethyl-*p*-toluidine. The average increase in strength due to a single methyl group is 0.2 unit, which is to be compared to the value 0.23 given above for methylaniline. An ethyl group produces an increase of about 0.5 unit. The data are included in Fig. 3.

The following few data are available on the derivatives of α-naphthylamine.

TABLE XIII

	pK_H		pK_H
α-Naphthylamine	3.92	N-Ethyl-α-naphthylamine	4.24
N-Methyl-α-naphthylamine	3.70	N-Dimethyl-α-naphthylamine	4.88

Here the methyl group produces an anomalous *decrease* in the strength, while two methyl groups produce a surprisingly large *increase.*

Anisidines and Phenetidines.—A single methoxy or ethoxy group decreases the strength of aniline when it is ortho or meta to the amino group, and increases it in the para position, as the following table shows. It is noteworthy that for both types of bases $\Delta pK_H(o-m)/\Delta pK_H(p-o) = {}^3/_8$, very nearly.

TABLE XIV

Anisidines	pK_H	Phenetidines	pK_H
p-	5.29	*p*-	5.25
$-\Delta pK_H = 0.80$		$-\Delta pK_H = 0.78$	
o-	4.49	*o*-	4.47
$-\Delta pK_H = 0.29$		$-\Delta pK_H = 0.30$	
m-	4.20	*m*-	4.17

Effect of Saturation on the Aromatic Nucleus.—As is well known, piperidine is a much stronger base than pyridine. We have also found that cyclohexylamine is much stronger than aniline, as would be expected.

TABLE XV

Aniline	4.62	Pyridine	5.21
Cyclohexylamine	10.61	Piperidine	11.13
pK_H =	5.99		5.92

Ethanolamines.—The ethanol group appears to be intermediate in character between the positive alkyl groups and the much more strongly negative groups such as phenyl. Thus the first ethanol group makes ammonia slightly stronger, but the second and third have the opposite effect (see Fig. 3).

TABLE XVI

	pK_H		pK_H
Ammonia	9.27	Diethanolamine	8.88
Ethanolamine	9.44	Triethanolamine	7.77

Negative Groups

Effect of Phenyl.—The strongly negative influence of this group is well known, and may be recognized in the following data. (*Cf.* also Fig. 4.)

TABLE XVII

	pK_H		pK_H
Ammonia	9.27	Diphenylamine	0.85
Aniline	4.62	Triphenylamine	<0.0[a]

[a] Estimated from unpublished work on acetic acid solutions.

We have also secured evidence of its effect on the strength of guanidine, as will appear from Table XVIII.

TABLE XVIII

	pK_H		pK_H
Guanidine	13.65	Diphenylguanidine	10.12[b]
Phenylguanidine	10.77[a]	Triphenylguanidine	9.10

[a] Davis and Elderfield, THIS JOURNAL, **54**, 1499 (1932). [b] We calculate the value 10.01 at 18° from the work of Walden and Ulich, *Z. Electrochem.*, **34**, 25 (1928).

Other Negative Groups.—The negative effect of the nitro group appears to be especially strong on guanidine since α-nitroguanidine appears to have a constant in the neighborhood of zero, while guanidine itself has a value above thirteen.

The effect of chlorine, bromine, etc., is well known. It is not always realized, however, how entirely similar are the effects of these groups on acids and on bases (or more properly, on uncharged and cation acids). This is brought out in Figs. 4 and 5. Here we have shown the effect of phenol on guanidine, succinic acid and ammonia, and of chlorine on phenol, acetic acid and aniline. The data on the chlorophenols are from Tiessens'[8] paper except that the values of Hantzsch and of Mizutani[9] are used for *p*-chlorophenol instead of the very old and improbable value given by Bader.[10] The latter's value for *o*-chlorophenol is not included. The values for the chloroacetic and phenylsuccinic acids are taken from Landolt and Börnstein's Tables. The values given by Hall for the chloroanilines are used.

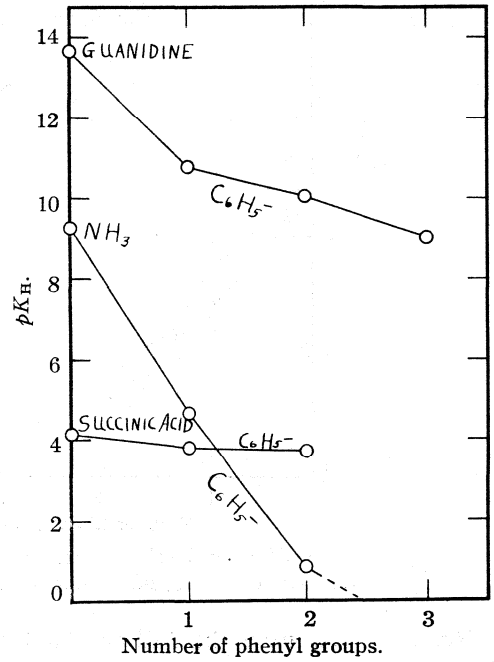

Fig. 4.—Effect of phenyl group on strength of guanidine, ammonia and succinic acid: ordinates, pK_H; abscissas, no. of phenyl groups.

The new facts reported in this paper seem to introduce no radically new principles into the doctrine of the effect of substituents on acid strength, although the great relative strength of *diethyl* compounds is perhaps of special significance, and the existing data have been supplemented at many points. Data of this type should be interpreted with caution for two reasons. In the first place

[8] Tiessens, *Rec. trav. chim.*, **48**, 1068 (1929).

[9] Landolt-Börnstein, "Tabellen."

[10] Bader, *Z. physik. Chem.*, **6**, 295 (1890).

the quantum theoretical basis for the reactions involved is still so obscure as to render discussions of "relative electron sharing ability" and the like of small significance, and in the second place any conclusions based on small variations of the constants (less than one logarithmic unit) are likely to have significance relative to a single solvent or class of solvents only.[1b,11]

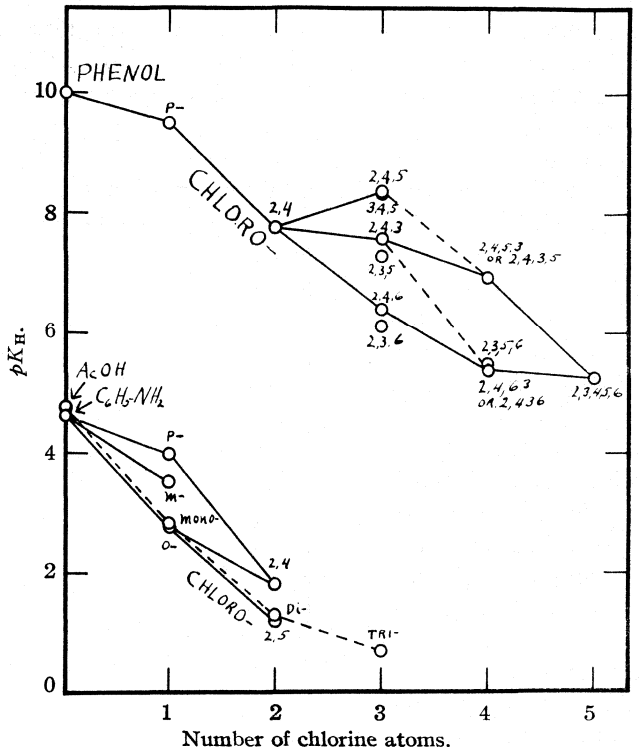

Fig. 5.—Effect of chlorine on strength of phenol, acetic acid and aniline: ordinates, pK_H; abscissas, no. of chlorine atoms.

Financial aid from the Milton Fund of Harvard University and the Research Fund of the University of Wisconsin is gratefully acknowledged, as is the kindness of many workers in the organic chemistry Laboratory of this University, who have supplied purified specimens of bases.

Summary

1. First determinations have been made of the ionization constants of thirty-eight organic derivatives of ammonia, and the constants of twenty-two bases have been redetermined as a control.

[11] See also Halford, THIS JOURNAL, **53**, 2939, 2944 (1931): Conant and Wheland, *ibid.*, **54**, 1213–1221 (1932).

2. One of the bases studied (guanidine) is stronger than any other for which a constant has been given.

3. The temperature coefficient of the constant K_w/K_B has been determined for six bases of different strength and found to vary in a regular manner with the base strength.

4. The effect of substituents on the strength of bases has been shown to be strictly comparable to their effects on the strength of acids.

5. Attention is directed for the first time to the effect of two ethyl groups in enhancing base strength.

6. Many other special effects have been exhibited by means of tables and diagrams.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BUREAU OF MINES, U. S. DEPARTMENT OF COMMERCE]

THEORY OF THE ERROR OF ACID–BASE TITRATION[1]

BY PAUL S. ROLLER[2]

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The origin of the error of acid–base titration lies in the finite sensitivity of the end-point indicator. For a given sensitivity, the magnitude of the titer error increases with decrease in rate of change of P_H at the end-point. A weak acid is thus less accurately titrated than a strong one.

Formulation of the titer error permits one to predict the accuracy and limiting conditions of titration without laborious experimental trial and error. Furthermore, by comparison of the actual with the theoretical error, it can be decided whether or not complications that are not considered in the ideal case, such as side reactions, indicator decomposition, adsorption, etc., play a part.

In this paper formulations are presented for the theoretical titer error of the acid–base colorimetric and electrometric titration. For the latter the condition of the appearance of an inflection point and the magnitude of its deviation from the stoichiometric point are given. Owing to the practical utility of the results these are presented in their final form; at the end of the paper derivation is made for a simple case as illustrative of the general method.

Previous Results

McCoy[3] expressed the error in titrating a weak acid by a strong base with phenolphthalein as indicator. Noyes[4] and Tizard and Boeree[5] have

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Original manuscript received January 30, 1931.

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[3] McCoy, *Am. Chem. J.*, **31**, 512 (1904).

[4] Noyes, THIS JOURNAL, **32**, 815 (1910).

[5] Tizard and Boeree, *J. Chem. Soc.*, **119**, 132 (1921).

deduced particular equations for the error of the color indicator titration of one or two weak acids or bases. Bjerrum[6] derived an equation that was general but left in an unfinished form. Beyond this, Bjerrum's interpretation of his equation is incorrect; he states that although one ends the titration precisely at the stoichiometric point there will nevertheless be a titer error due to the fact that there can be "no partial compensation of errors." This is contrary to the explicit statement of the equation itself.

Eastman[7] came to the conclusion that in an electrometric titration the inflection point may deviate from the stoichiometric point or might not appear at all. His numerical result for the condition of the appearance of an inflection point was shown to be erroneous;[8,9] his other numerical results are also in error as shown below.

The Titer Error.—The percentage titer error E of an acid–base titration is given by equation (1)

$$E = \pm 200 \sqrt{\kappa} \sinh \Delta \qquad (1)$$

Δ is the known error of the end-point indicator.

κ, which is a function of the ionization constants and concentrations, is defined by equation (2) in the titration of an acid solution by a strong base, and (2′) in the titration of a basic solution by a strong acid.

$$\kappa_A = \frac{1}{(C_{HA,A} + \ldots + C_{B,BOH} + \ldots)^2} \left(K_w + C_{HA}K_A + \ldots + C_B \frac{K_w}{K_B} + \ldots\right) \left(1 + C_A \frac{1}{K_A} + \ldots + C_{BOH} \frac{K_B}{K_w} + \ldots\right) \qquad (2)$$

$$\kappa_B = \frac{1}{(C_{BOH,B} + \ldots + C_{A,HA} + \ldots)^2} \left(K_w + C_{BOH}K_B + \ldots C_A \frac{K_w}{K_A} + \ldots\right) \left(1 + C_B \frac{1}{K_B} + \ldots + C_{HA} \frac{K_A}{K_w} + \ldots\right) \qquad (2')$$

If the reagent solution is complex and contains not only a strong acid or base but also weak acids, bases, and salts, the second factor in parentheses in equations (2) and (2′) is replaced, respectively, by the following

$$K_w + C_{HA}K_A + \ldots + C_B \frac{K_w}{K_B} + \ldots + \frac{(C_{HA,A} + \ldots + C_{B,BOH} + \ldots)}{(C_{BOH',B'} + \ldots + C_{A',HA'} + \ldots)} \left(C_{BOH',B'} \frac{K_w}{K_B} + \ldots + C_{A',HA'}K_A + \ldots\right)$$

$$K_w + C_{BOH}K_B + \ldots + C_A \frac{K_w}{K_A} + \ldots + \frac{(C_{BOH,B} + \ldots + C_{A,HA} + \ldots)}{(C_{HA',A'} + \ldots + C_{B',BOH'} + \ldots)} \left(C_{HA',A'} \frac{K_w}{K_A} + \ldots + C_{B',BOH'} K_B + \ldots\right)$$

In the equations for κ, C stands for concentration at the end-point in moles per liter of a component present at the end-point in the form of

[6] Bjerrum, *Herz Sammlung*, **21**, 1 (1914).

[7] Eastman, THIS JOURNAL, **47**, 332 (1925).

[8] Roller, *ibid.*, **50**, 1 (1928).

[9] Eastman, *ibid.*, **50**, 418 (1928).

HA, A, BOH, or B, depending upon the subscript to C. For example, C_{HA} is the molar concentration at the end-point of the component HA; C_A is the molar concentration at the end-point of the weak acid salt component, A, etc. The separate dissociation products of a polybasic acid or base are considered components just as a simple weak acid or base.

$C_{HA,A}$, $C_{B,BOH}$, etc., have a slightly different significance. $C_{HA,A}$ stands for the concentration referred to the end-point volume of component HA that has been titrated to its normal salt component, A; ordinarily, with the titration product remaining in solution, $C_{HA,A} = C_A$, where C_A is the concentration of the salt derived from HA. $C_{B,BOH}$ stands for the concentration referred to the end-point volume of component B that has been titrated to component, BOH; ordinarily $C_{B,BOH} = C_{BOH}$, where C_{BOH} is the concentration of base derived from B.

In the form taken by equation (2) or (2′) when weak acids, bases and salts are present in the reagent solution, the primed subscripts refer to components contained in the latter solution. For example, $C_{BOH',B'}$ stands for the molar concentration in the reagent solution of component BOH′ that in titration goes over to the weak base salt component, B′.

For the simple cases of the titration by a strong base of a weak acid, of a weak acid in the presence of a second acid, of the first H of a dibasic acid, etc., κ reduces substantially to the following, respectively, $\sqrt{\frac{K_w}{C_A K_A}}$, $\sqrt{\frac{C_{A_2} K_{A_2}}{C_{A_1} K_{A_1}}}$, $\sqrt{\frac{K_{A_2}}{K_{A_1}}}$, etc.

Δ in equation (1) for the titer error is defined as follows

$$\Delta = 2.30\ \Delta P_H \text{ for the color indicator titration} \quad (3)$$

$$\Delta = 0.158\ \Delta \text{ m. v. for the inflection point electrometric titration} \quad (4)$$

$$\Delta = 0.0396\ \Delta \text{ m. v. for the absolute electrometric titration} \quad (5)$$

In titrating to the stoichiometric point, ΔP_H in (3) is the error of the color indicator corresponding to its sensitivity. In titrating with an indicator that turns at a P_H different from that at the stoichiometric point, ΔP_H is equal to the deviation in P_H from the stoichiometric point plus the error in P_H (corresponding to its sensitivity) of the indicator.

With an indicator which does not turn at the stoichiometric point, the procedure might also be adopted of correcting the titer for the difference in P_H at which the indicator turns and the P_H at the stoichiometric point. It is not practically desirable to do this, however, because the calculations involved for the titration correction and net titer error are complicated, and because the net titer error, corresponding to the finite sensitivity of the indicator, is greater than that incurred in using an indicator that turns at the stoichiometric point P_H, the qualitative explanation of this fact being that the rate of change of P_H is a maximum in the neighborhood of the stoichiometric point, and the error consequently a minimum.

Δ m. v. in equations (4) and (5) is the error of the e. m. f. measuring instrument. It is seen that the absolute electrometric titration which is made to the e. m. f. at the stoichiometric point is more sensitive than the inflection point titration,[10] and actually four times as sensitive as may be inferred from the work of Hahn.[11] This result may be derived as follows. Numerical evaluation of the inflection point is by definition possible with reference only to the second differences of the e. m. f., and not to the e. m. f. itself. A zero value of the second difference determines the value of the e. m. f. at the inflection point. The error of the e. m. f. so determined is the error of the second difference, or four times the error of an e. m. f. measurement itself.

P_H at Stoichiometric Point.—The P_H at the stoichiometric point to which one titrates for optimum accuracy may be calculated from the ionization constants and concentrations. In the titration of an acid solution by a strong base, or of a basic solution by strong acid, P_{H_S} is given, respectively, by equations (6) and (6′).

$$P_{H_S} = -\tfrac{1}{2}\log \sigma_A \qquad (6)$$

$$P_{H_S} = -\log K_w + \tfrac{1}{2}\log \sigma_B \qquad (6')$$

σ_A and σ_B in (6) and (6′) are defined, respectively, as

$$\sigma_A = \frac{(K_w + C_{HA}K_A + \ldots + C_B\frac{K_w}{K_B} + \ldots)}{(1 + C_A\frac{1}{K_A} + \ldots + C_{BOH}\frac{K_B}{K_w} + \ldots)} \qquad (7)$$

$$\sigma_B = \frac{(K_w + C_{BOH}K_B + \ldots + C_A\frac{K_w}{K_A} + \ldots)}{(1 + C_B\frac{1}{K_B} + \ldots + C_{HA}\frac{K_A}{K_w} + \ldots)} \qquad (7')$$

If weak acids, bases and salts are present in the reagent solution, the following expressions are to be added to the numerator on the right-hand side of equations (7) and (7′), respectively

$$\frac{(C_{HA,A} + \ldots + C_{B,BOH} + \ldots)}{(C_{BOH',B'} + \ldots + C_{A',HA'} + \ldots)}(C_{BOH',B'}\frac{K_w}{K_B} + \ldots + C_{A',HA'}K_A + \ldots)$$

$$\frac{(C_{BOH,B} + \ldots C_{A,HA} + \ldots)}{(C_{HA',A} + \ldots C_{B',BOH'} + \ldots)}(C_{HA',A'}\frac{K_w}{K_A} + \ldots + C_{B',BOH'}K_B + \ldots.)$$

In the simple cases of titration by a strong base of a weak acid, a weak acid in the presence of a second acid, of the first H of a dibasic acid, etc., σ reduces substantially to the following, respectively, $\sqrt{\frac{K_AK_w}{C_A}}$, $\sqrt{\frac{C_{A_2}}{C_{A_1}}K_{A_2}K_{A_1}}$, $\sqrt{\frac{K_{A_2}}{K_{A_1}}}$, etc.

Graphical Expression of Results.—Referring to equation (1) for the titer error, it is seen that if $-\log \kappa$ is plotted against $\log \sinh \Delta$ a series of

[10] Cavanagh, *J. Chem. Soc.*, 2207 (1927); 843, 855 (1928).

[11] Hahn, *Z. physik. Chem.*, **A146**, 363 (1930); Hahn and Weiler, *Z. anal. Chem.*, **70**, 417 (1926).

straight lines is obtained corresponding to different values of the percentage titer error, E. If in place of log sinh Δ, one substitutes ΔP_H and Δ m. v. by equations (2), (3) and (4), the desired graph of the titer error is obtained as shown in Fig. 1.

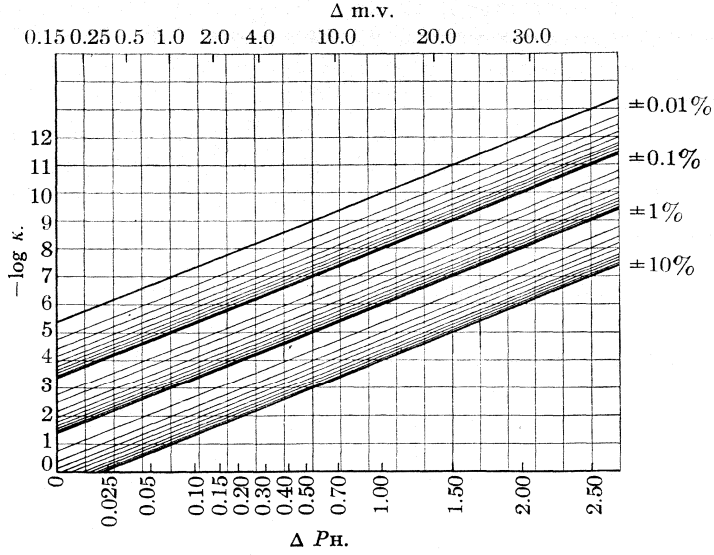

Fig. 1.—Percentage titer error of colorimetric and electrometric inflection point titration.

To construct this graph a basic line is drawn for a given value of E, say $\pm 0.1\%$, only two plotted points being necessary. These are given in Table I. All other straight lines are drawn parallel to the basic line at a vertical distance from it equal to $2 \log E'/E''$, where E' is equal to $\pm 0.1\%$, and E'' is the percentage error of the line in question.

Table II gives the data necessary to convert the abscissa scale, log sinh Δ, to ΔP_H for the colorimetric, and to Δ m. v. for the inflection point electrometric titration. Δ m. v. for the absolute electrometric titration has been omitted since this titration is at the present time infrequently used. However, the abscissa scale is for this titration at once obtained by multiplying by four the abscissa values of Δ m. v. for the inflection point titration.

It is convenient also to graph equations (6) or (6′) for the P_H at the stoichiometric point. A plot of $-\log \sigma_A$ and $-\log \sigma_B$ against P_{H_S} gives two straight lines intersecting at $P_H = {}^1/_2 pK_W$.

Effect of Concentration of the Components.—The concentration of the components enters directly in the expressions given above for the titer error and for the P_H at the stoichiometric point. On close examination it is seen that the concentration substantially affects the results only in the case of the unsymmetrical titration, as of a weak acid by a strong base,

but not in the case of the symmetrical titration as of a weak acid by a weak base or of the second H of a dibasic acid by a strong base.

For the unsymmetrical titration the titer error is substantially proportional to the square root of the molar concentration at the end-point. This result is of significance for acidimetry, because it is at times possible to artificially diminish the concentration of components at the end-point, and thus to enhance the accuracy, by precipitation, complex formation, extraction, heat, etc. Empirical application of this principle has been made in a few instances in volumetric practice, as in boiling off carbonic acid, in the formaldehyde titration of amino acids (Sörenson), in the precipitation of $CO_3^=$ as barium carbonate (Winkler titration), etc. The last titration is discussed in detail below.

TABLE I

DATA FOR CONSTRUCTING BASIC LINE ($E = \pm 0.1\%$)

log sinh Δ	−0.634	0.024	1.699
$-\log \kappa$	5.334	6.650	10.000

TABLE II

DATA FOR CONVERTING LOG SINH Δ TO ΔP_H AND Δ M. V.

ΔP_H	Log sinh Δ	Δ m. v.	Log sinh Δ
0.025	−1.240	0.15	−1.623
.05	−0.939	.25	−1.398
.10	− .635	0.5	−1.102
.20	− .322	1.0	−0.796
.30	− .127	2.0	− .491
.40	.024	4.0	.168
.50	.153	10.0	.370
.70	.381	20	1.080
1.00	.694	30	1.769
1.5	1.196		
2.0	1.700		
2.5	2.195		

TABLE III

MAXIMUM POSSIBLE PERCENTAGE TITER DEVIATION OF THE INFLECTION POINT FROM THE STOICHIOMETRIC POINT

κ	K_A for weak acid C_A = 0.1 molar	Maximum possible percentage titer deviation	Percentage titer error for e. m. f. error of ±0.5 m. v.
10^{-5}	10^{-8}	0.009	0.05
10^{-4}	10^{-9}	.03	.16
$10^{-3.5}$	$10^{-9.5}$	.09	.28
10^{-3}	10^{-10}	.3	.50
$10^{-2.5}$	$10^{-10.5}$	.9	.89
10^{-2}	10^{-11}	3.0	1.6
$10^{-1.5}$	$10^{-11.5}$	9.5	2.8

Dilution of the reagent solution results in a lower concentration of the components at the end-point, and consequently in an increased titer error for the unsymmetrical titration.

Sensitivity of Color Indicator, and Comparison with Electrometric Measurement.—Tizard and Boeree[5] and Kolthoff[12] have performed diversified color indicator titrations, the former without and the latter with a comparison solution containing the indicator at P_{H_S}. Applying equation (1) for the titer error to the results obtained by these authors, it is found that the average color indicator error is, when titrating with the unaided eye, ± 0.2 P_H and when using a comparison solution ± 0.1 P_H. These results are in agreement with previous estimates of ± 0.3 P_H[5,6] and ± 0.2 P_H[13] in titrating with the unaided eye, and of ± 0.1 P_H[6,13] in titrating with a comparison solution.

Assuming that the e. m. f. error is ± 0.5 m. v., and the color indicator error ± 0.1 P_H, it is seen from the equations given above that the absolute electrometric titration is intrinsically about twelve times as sensitive, and the inflection point titration three times as sensitive, as the color indicator titration.

Example.—In the titration by 0.1 M strong acid ($K_A = \infty$) of 0.1 M sodium hydroxide ($K_B = \infty$) in the presence of 0.1 M sodium carbonate ($K_{A_1} = 10^{-6.5}$, $K_{A_2} = 10^{-10.2}$), it is found by calculation from equations (6′) and (2′) that σ_B and κ_B are equal to $10^{-5.2}$ and $10^{-2.6}$, respectively. From a graphical plot of equation (6′) the P_H at the stoichiometric point to which one titrates is found to be 11.5. The value of the titer error is from Fig. 1 for $\kappa_B = 10^{-2.6}$ found to be 4.7% with $\Delta P_H = \pm 0.2$, and 2.2% with $\Delta P_H = \pm 0.1$. The titration is therefore essentially inaccurate as regards the ordinary color indicator titration.

If the concentration at the end-point of the component $C_A = C_{CO_3^=}$ is reduced by precipitation with excess barium chloride, the titration (Winkler) becomes quite accurate. From the solubility product of barium chloride the concentration of $CO_3^=$ is, in the presence of 0.1 M barium chloride, equal to $10^{-7.1}$ mole/liter. σ_B is now $10^{-11.0}$, and P_{H_S} therefore 8.6. κ_B is calculated to be $10^{-8.4}$, and the titer error is therefore less than 0.01% with $\Delta P_H = \pm 0.2$.

This theoretical result of an enhanced titration accuracy obtained by precipitating the component $CO_3^=$ with barium chloride has been amply confirmed by experiment.[14,15,16]

The Electrometric Inflection Point.—A good insight into the nature of the electrometric inflection point is obtained by plotting the rate of change of P_H against quantity of reagent. In such a graph a maximum or minimum corresponds to an inflection point, the meaning of the minimum being that the concave and convex portions of the titration curve are re-

[12] Kolthoff, *Z. anorg. allgem. Chem.*, **115**, 168 (1921).

[13] Kolthoff and Furman, "Indicators," John Wiley and Sons, New York, 1926.

[14] Küster, *Z. anorg. Chem.*, **13**, 127 (1897).

[15] Poethke and Manicke, *Z. anal. Chem.*, **79**, 241 (1929).

[16] Partridge and Schroeder, *Ind. Eng. Chem., Anal. Ed.*, **4**, 271 (1932).

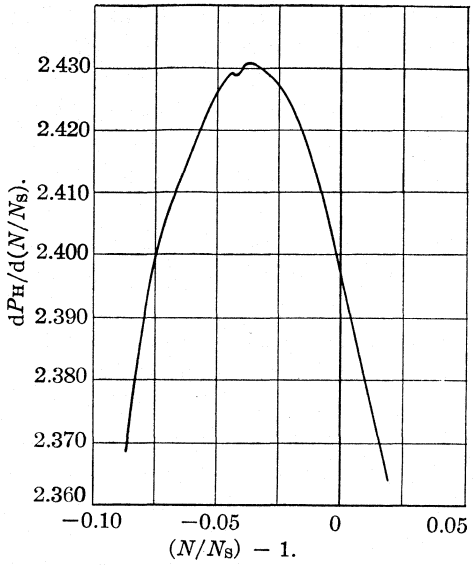

Fig. 2.—Electrometric titration of a weak acid, $K_w/C_AK_A = 10^{-2}$.

versed from their order at the usual inflection point.

By differentiation of an equation similar to equation (11) below, such a plot has been constructed in Figs. 2, 3 and 4 for the unsymmetrical titration of a simple weak acid by a strong base, and in Figs. 5, 6, 7 and 8 for the symmetrical titration of the first H of a dibasic acid by a strong base. In these figures $dP_H/d(N/N_S)$, the rate of change of P_H with fraction of reagent required at the stoichiometric point, has been plotted against $[N/(N_S-1)]$, the fractional difference between reagent added and titer at the stoichiometric point.

In Fig. 2 for $K_w/C_AK_A = 10^{-2}$, there is a prominent maximum corresponding to the ordinary inflection point, with a secondary small maximum and minimum corresponding to secondary trivial inflection points. When the acid is weaker so that K_w/C_AK_A is $10^{-1.5}$, the secondary inflection points are quite pronounced and merge into a broad maximum with the primary inflection point as shown in Fig. 3. For a very weak acid such that K_w/C_AK_A is only 10^{-1}, there are no maxima or minima and therefore no inflection points (Fig. 4).

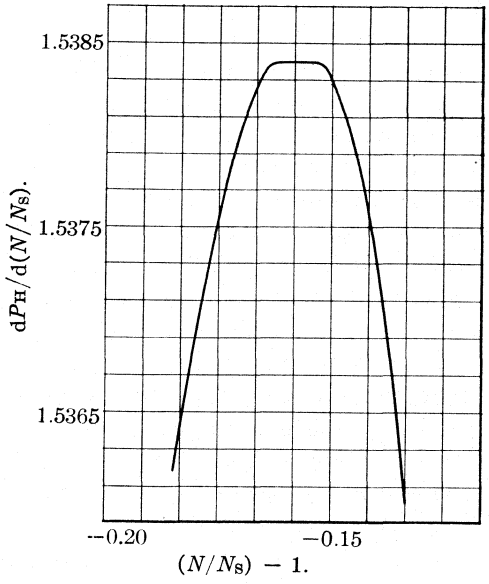

Fig. 3.—Electrometric titration of a weak acid, $K_w/C_AK_A = 10^{-1.5}$.

For the unsymmetrical titration of the first H of a weak acid (Figs. 5 to 8) there is in every case seen to be a maximum or minimum, and therefore an inflection point, precisely at the stoichiometric point. As shown especially in Fig. 7 for $K_{A_2}/K_{A_1} = 10^{-1.28}$, there is for this titration also a

secondary inflection point but it is generally of quite small significance compared to the secondary inflection points in the unsymmetrical titration of a simple weak acid by a strong base.

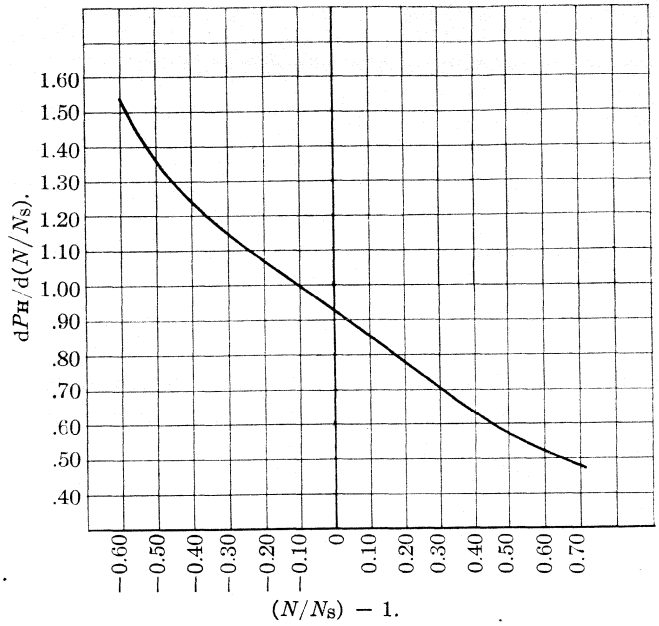

Fig. 4.—Electrometric titration of a weak acid, $K_w/C_AK_A = 10^{-1}$.

Deviation of the Inflection Point from Stoichiometric Point.—By extension of a method of derivation previously employed[8] the general condition that an inflection point shall appear is given in equations (8) and (8′) for the titration of an acid solution and basic solution, respectively.

$$\sqrt{\sigma_A}\left(\frac{1}{K'_A}+\ldots+\frac{K'_B}{K_w}+\ldots+0\right)-\sqrt{\frac{1}{\sigma_A}}\left(K''_A+\ldots+\frac{K_w}{K''_B}+\ldots+0\right)<10^{-0.71} \quad (8)$$

$$\sqrt{\sigma_B}\left(\frac{1}{K'_B}+\ldots+\frac{K'_A}{K_w}+\ldots+0\right)-\sqrt{\frac{1}{\sigma_B}}\left(K''_B+\ldots+\frac{K_w}{K''_A}+\ldots+0\right)<10^{-0.71} \quad (8')$$

In these equations K'_A refers to the ionization constant of an acid or weak acid salt that has been titrated at the end-point, and similarly for K'_B. K''_A refers to the ionization constant of an untitrated acid or weak acid salt, and also to a weak acid salt derived from the reagent solution, and similarly for K''_B.

Equation (8) reduces to the condition that an inflection point shall appear in the titration of a simple weak acid by a strong base that was previously derived,[8] *i. e.*, $K_w/C_AK_A < 10^{-1.42}$. Examination of the general condition given by (8) or (8′) shows, in conformity with the graphical analysis, that in the symmetrical titration an inflection point will always

appear, but may not appear in the unsymmetrical titration. The conclusion of Eastman[7] that an inflection point may not appear in the (symmetrical) titration of a weak acid by a weak base is in the light of these results seen to be incorrect.

The deviation in P_H of the inflection point from the stoichiometric point in the titrations, respectively, of an acid and basic solution is given by equations (9) and (9′).

$$P_{H_S} - P_{H_E} = 0.65\left[\sqrt{\sigma_A}\left(\frac{1}{K'_A}+\ldots+\frac{K'_B}{K_w}+\ldots+0\right)-\frac{1}{\sqrt{\sigma_A}}\left(K''_A+\ldots+\frac{K_w}{K''_B}+\ldots+0\right)\right] \quad (9)$$

$$P_{H_S} - P_{H_E} = 0.65\left[\sqrt{\sigma_B}\left(\frac{1}{K'_B}+\ldots+\frac{K'_A}{K_w}+\ldots+0\right)-\frac{1}{\sqrt{\sigma_B}}\left(K''_B+\ldots+\frac{K_w}{K''_A}+\ldots+0\right)\right] \quad (9')$$

In terms of the percentage titer, the deviation of the inflection point from the stoichiometric point is given, respectively, by equations (10) and (10′).

$$100\frac{(N_S - N_E)}{N_S} = 300\sqrt{\kappa_A}\left[\sqrt{\sigma_A}\left(\frac{1}{K'_A}+\ldots+\frac{K'_B}{K_w}+\ldots+0\right)-\frac{1}{\sqrt{\sigma_A}}\left(K''_A+\ldots+\frac{K_w}{K''_B}+\ldots+0\right)\right] \quad (10)$$

$$100\frac{(N_S - N_E)}{N_S} = 300\sqrt{\kappa_B}\left[\sqrt{\sigma_B}\left(\frac{1}{K'_B}+\ldots+\frac{K'_A}{K_w}+\ldots+0\right)-\frac{1}{\sqrt{\sigma_B}}\left(K''_B+\ldots+\frac{K_w}{K''_A}+\ldots+0\right)\right] \quad (10')$$

Inspection of equations (10) and (10′) shows that the percentage titer deviation may be positive or negative depending upon the sign of the expression in brackets, or it may be zero; in other words, the inflection point may precede, follow or coincide with the stoichiometric point. More explicitly it is seen in agreement with the graphical analysis that the inflection point deviates from the stoichiometric point in the unsymmetrical titration, but coincides with the stoichiometric point in the symmetrical titration. The deduction of Eastman[7] that for the symmetrical titration of a weak acid by a weak base there is a titer deviation of the inflection point from the stoichiometric point is seen

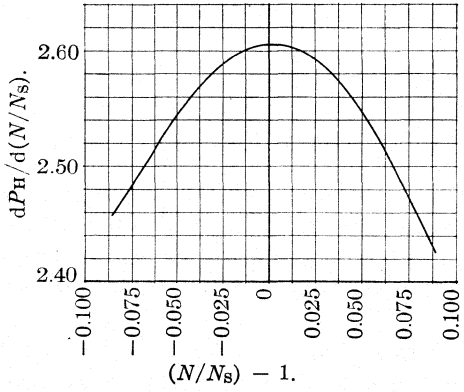

Fig. 5.—Electrometric titration of first H of a dibasic acid, $K_{A_2}/K_{A_1} = 10^{-2}$.

to be erroneous; his estimate of the titer deviation in the unsymmetrical titration by a strong base of a 1 molar weak acid with $K_A = 10^{-12}$ is about ten-fold too low, and his conclusion that the titer deviation for this titration does not vary with concentration of weak acid between 1 and 10^{-3} mole/liter is plainly in error.

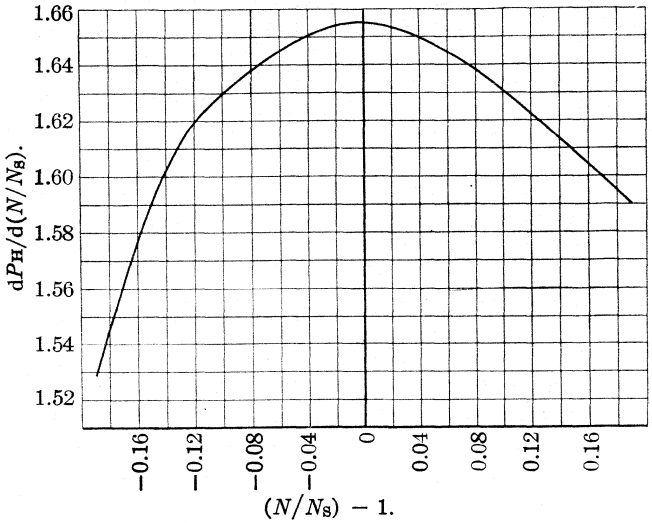

Fig. 6.—Electrometric titration of first H of a dibasic acid, $K_{A_2}/K_{A_1} = 10^{-1.5}$.

Analysis of equations (10) and (10′) for the percentage titer deviation of the inflection point from the stoichiometric point shows that the maximum possible percentage titer deviation in any titration is that previously given[8] for the deviation in the unsymmetrical titration of a simple weak acid by a strong base, namely $100\,\frac{N_S - N_E}{N_S} = 300\,\frac{K_W}{C_A K_A}$. This maximum possible titer deviation is shown in the third column of Table III for values of κ shown in the first column, while the second column gives the corresponding ionization constant of a 0.1 molar weak acid titrated by a strong base. The last column of Table III gives by equation (1), for an e. m. f. error of ± 0.5 m. v., the percentage titer error of estimating the inflection point.

It is seen from Table III that if $\kappa < 10^{-2.5}$, the percentage titer error of the electrometric titration is, for an e. m. f. error of ± 0.5 m. v., greater than the maximum possible titer deviation of the inflection point from the end-point. Nevertheless, for greatest accuracy the correction for the percentage titer deviation logically should be made, for otherwise it will be added as an error to the percentage titer error resulting from inaccuracy of the e. m. f. measurement.

For values of $\kappa > 10^{-2.5}$ the maximum possible titer deviation exceeds the titer error of estimating the inflection point. Because of this fact, and

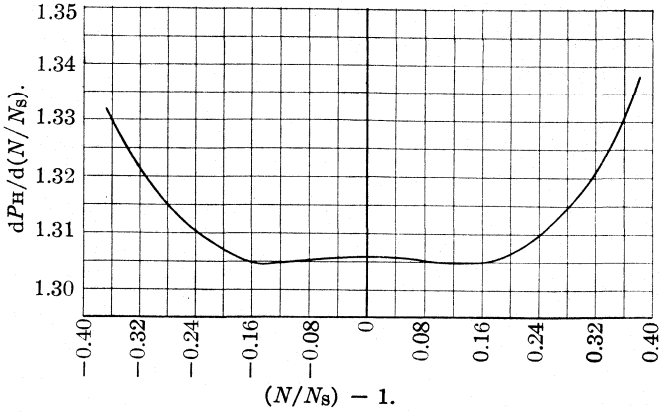

Fig. 7.—Electrometric titration of first H of a dibasic acid, $K_{A_2}/K_{A_1} = 10^{-1.28}$.

the fact that the titer error is now greater than 1%, for $\kappa > 10^{-2.5}$ the inflection point titration might advantageously be replaced by the absolute electrometric titration.[17] As already pointed out, the absolute titration

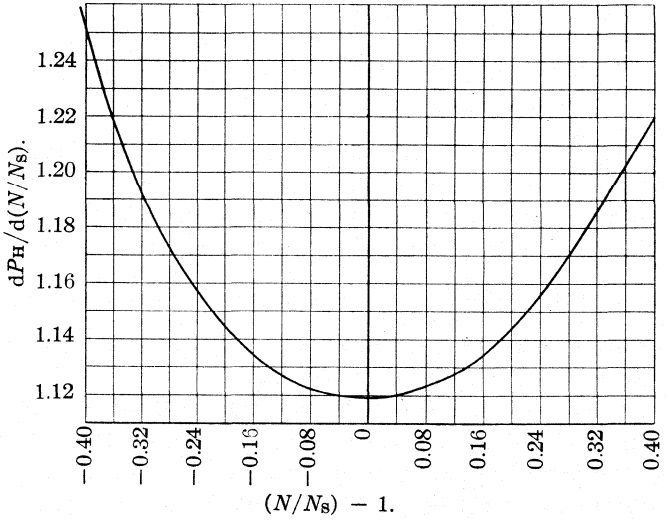

Fig. 8.—Electrometric titration of first H of a dibasic acid, $K_{A_2}/K_{A_1} = 10^{-1}$.

which is made to the e. m. f. at the stoichiometric point is inherently four times as sensitive as the inflection point titration.

[17] *Cf.* Kolthoff, *Rec. trav. chim.*, **47**, 397 (1928); Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, New York, 1931.

Derivation of Equations.—As an example of the method of derivation, the titration of the stronger of two weak acids by a strong base is considered. In the general case, all terms corresponding to different acids and bases are grouped into one or two categories of which the first and second weak acids in the particular example are representative types.

The initial procedure is exactly analogous to that employed in a previous publication,[8] and results in the following equation connecting the cc. of reagent, N and H.

$$C_{OH'}\frac{N}{V} = C^{\circ}_{HA_1} + C^{\circ}_{HA_2} - (V+N)/V\left(H - \frac{K_w}{H}\right) - \frac{C^{\circ}_{HA_1}\,H}{K_{A_1}+H} - \frac{C^{\circ}_{HA_2}\,H}{K_{A_2}+H} \qquad (11)$$

$C^{\circ}_{HA_1}$ and $C^{\circ}_{HA_2}$ are the initial concentrations of the acids in volume V. If concentrated solutions are considered, correction for the ion activities may be made to the ionization constants.

When each acid has been 50% neutralized the H-ion concentration is equal to the K_{A_1} or K_{A_2} as the case may be. Therefore, at the normal salt or stoichiometric point of the first acid, $K_{A_1} > H_S > K_{A_2}$. Expanding then in a binomial series the last two terms on the right-hand side of equation (11) and remembering that at the normal salt or stoichiometric point $C_{OH'}\,N_S/V = C^{\circ}_{HA_1,\,A_1} = C^{\circ}_{HA_1}$, the P_H at the stoichiometric point in titrating the first acid is found to be

$$P_{H_S} = -{}^1/_2 \log\left(\frac{K_w + C_{HA_2}K_{A_2}}{1 + C_{A_1}\,1/K_{A_1}}\right) \qquad (12)$$

In (12) the concentrations now refer to the volume at the end-point and C_{A_1} is written for C_{HA_1} since only the salt of HA_1 now exists.

The generalized form of equation (12) is given by equation (6). For the general case the error due to neglect of powers of H_S/K_A or K_A/H_S can be expressed in terms of κ. It is found that for the extreme case of $\kappa = 10^{\circ}$, P_{H_S} calculated by equation (6) or (6′) is in error at the most by 0.3 P_H. This corresponds to the unsymmetrical titration and the sign may be positive or negative; for the symmetrical titration the error is virtually nil. For $\kappa = 10^{-1}$, the maximum error of the calculated result is 0.04 P_H, and for $\kappa = 10^{-2}$ it is only 0.005 P_H.

To determine the titer error the differential of equation (11) is taken and two of the terms expanded in a binomial series as before. With $dN = \Delta N$, and $dH = \Delta H = \pm(H_E - H_S)$, where H_E is the hydrogen-ion concentration to which one on the average titrates in attempting to titrate to H_S, and taking H as the geometric mean of H_S and H_E (or P_H the arithmetic mean of P_{H_S} and P_{H_E}), the following expression is obtained for the titer error of titrating the first acid

$$\frac{\Delta N}{N_S} = \pm\frac{1}{C_{HA_1,A_1}}\left(1 + \frac{K_w}{H_S H_E} + \frac{C_{A_1}}{K_{A_1}} + C_{HA_2}\frac{K_{A_2}}{H_S H_E}\right)(H_S - H_E) \qquad (13)$$

If in equation (13) we substitute for H_S from equation (12), and transform in the reduced equation the factor $(1/H_S + 1/H_E)\,(H_E - H_S)$ into the

transcendental form by virtue of the definition of the P_H ($= -\log H$), the following simplified form of equation (13) for the titer error is obtained.

$$100\frac{\Delta N}{N_S} = \pm\frac{200}{C_{HA_1,A_1}}\sqrt{(K_w + C_{HA_2}K_{A_2})\left(1 + C_{A_1}\frac{1}{K_{A_1}}\right)}\sinh 2.30(P_{H_E} - P_{H_S}) \quad (14)$$

The general form of equation (14) is given by equation (1), E being written for $100\ \Delta N/N_S$.

The error in E due to neglect of powers of H_S/K_A or K_A/H_S is in general quite small and may be estimated in terms of κ. It is found that E calculated by equation (1) is always greater than the exact value; for the extreme case of $\kappa = 10^\circ$ the calculated titer error is at the most four times as great as the exact value, for $\kappa = 10^{-1}$ it is at the most 1.25, and for $\kappa = 10^{-2}$ it is at the most only 1.02 times as great as the exact value.

If an indicator is chosen that turns not at P_{H_S} but at P_{H_E}, equation (14), while expressing the error in terms of the P_H deviation, may also be considered as a titer correction. The net titer error, due to the finite sensitivity of the indicator, is obtained by a derivation analogous to that above and is

$$100\frac{\Delta N}{N_S} = \pm 400\frac{1}{C_{HA,A_1}}\sqrt{(K_w + C_{HA_2}K_{A_2})\left(1 + C_{A_1}\frac{1}{K_{A_1}}\right)}\cosh 2.30\left(P_{H_S} - P_{H_E} + \frac{\Delta P_H}{2}\right)\sinh 1.15\ \Delta P_H \quad (15)$$

Examination of equation (15) shows that the net titer error is greater than the error incurred in titrating with an indicator that turns at the stoichiometric point.

Summary

The theoretical titer error of the colorimetric and electrometric acid-base titration has been formulated analytically and graphically. The titer error is a simple function of the known error of the color indicator or e. m. f. measuring instrument, and of the concentrations and ionization constants.

For the unsymmetrical titration the error is proportional to the square root of the concentration of the product at the end-point, so that the accuracy of the titration may be enhanced by artificially diminishing the end-point concentration. This procedure has been empirically applied to a few titrations.

The nature of the electrometric inflection point is examined and discussed with reference to the symmetrical and unsymmetrical acid–base titration. For the symmetrical titration the primary inflection point will always appear, and coincides precisely with the stoichiometric point. For the unsymmetrical titration the inflection point may not appear, and does not coincide with the stoichiometric point. The percentage titer deviation may be as high as 11% as for instance in the unsymmetrical titration of a

weak acid by a strong base. The titer deviation is compared with the titer error due to inaccuracy of e. m. f. measurement.

The absolute titration since it is inherently four times as sensitive as the inflection point titration might advantageously replace the latter when the titer error is above about 1%.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY THE IODINE–IODIDE COUPLE. II AND III. THE RATE OF OXIDATION IN NEUTRAL, AND IN ACID, SOLUTION OF HYDROGEN PEROXIDE BY IODINE

BY HERMAN A. LIEBHAFSKY

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II. THE RATE OF OXIDATION, IN NEUTRAL SOLUTION, OF HYDROGEN PEROXIDE BY IODINE

In certain investigations of the catalytic decomposition of hydrogen peroxide by the iodine–iodide couple,[1] it has been postulated that the reaction

$$I_2 + H_2O_2 = 2H^+ + 2I^- + O_2 \quad (1)$$

proceeds through the rate-determining steps

$$IO^- + H_2O_2 \xrightarrow{k_2 = 3(10^{11})} I^- + H_2O + O_2 \quad (2)$$

and

$$HIO + H_2O_2 \xrightarrow{\kappa_2 < 10^4} H^+ + I^- + H_2O + O_2 \quad (3)$$

The concentrations of hypoiodite ion and of hypoiodous acid are governed at the steady state by the equilibria

$$I_2 + H_2O \underset{}{\overset{K = 3(10^{-13})}{\rightleftharpoons}} HIO + H^+ + I^- \quad (4)$$

$$I_2 + H_2O \underset{}{\overset{K' = 6(10^{-24})}{\rightleftharpoons}} IO^- + 2H^+ + I^- \quad (5)$$

Whether or not the hydrolysis equilibrium of iodine (Reaction 4 or 5) is maintained as the steady state is approached through the progress of Reaction 1 has been questioned by Abel.[1a,2]

[1] (a) Abel, *Z. physik. Chem.*, **136**, 16 (1928); (b) Liebhafsky, THIS JOURNAL, **54**, 1792 (1932). References to earlier work may be found in Ref. 1a. Ref. 1b is the first paper of this series and will be referred to as I. The values of k_2, κ_2, and k_1 are taken from I, where references will also be found for the values of K, K' and $(I_2)(I^-)/I_3^-$ given above. ($k_2 = 3(10^{11})$ is an average value deduced from I, Table Ib, Expts. 155–151 incl.; for these experiments the buffer solutions were identical in composition with those employed in the present investigation.) Numerical values of all constants are for 25°. As in other communications, $\longrightarrow$ denotes that the reaction may be rate-determining and ( ) means "concentration of" in moles/liter.

[2] *Cf.* also (a) Liebhafsky, *Z. physik. Chem.*, **155**, 289 (1931); (b) THIS JOURNAL, **53**, 2074 (1931); (c) *J. Phys. Chem.*, **35**, 1648 (1931).

The study of Reaction 2 at a distance from the steady state might settle this difficulty: if the value of k_2 thus obtained agrees even approximately with the value $3(10^{11})$ calculated from steady state measurements, then—since this equilibrium is established at the steady state—we may regard it as always established in this reaction system.

In order to isolate Reaction 2 it is necessary to choose experimental conditions under which the rates of Reaction 3 and of the reaction

$$I^- + H_2O_2 \xrightarrow{k_1 = 0.69} IO^- + H_2O \qquad (6)$$

are negligible. Simple calculations employing all the above specific rate and equilibrium constants show that in a saturated iodine solution [$(I_2) = 0.00132$],[3] buffered to maintain a_{H^+} at 10^{-6} M, and in which (I^-) is 10^{-3}, more than 99% of the peroxide should react with hypoiodite ion. As oxygen is evolved and iodide ion accumulates (*cf.* Reaction 1), the relative rates of Reactions 2 and 3 will decrease (*cf.* Eqs. 4, 5 and 6). The concentration of iodide ion will, however, always be governed by the equilibrium

$$I_3^- \rightleftharpoons I^- + I_2; \quad \frac{(I^-)(I_2)}{(I_3^-)} = 0.00140 \qquad (7)$$

and, since the tri-iodide ion formed does not react directly with hydrogen peroxide,[4] this decrease in the relative rates is correspondingly less than would be calculated from Reaction 1 alone.

A series of preliminary experiments indicated the feasibility of measuring k_2 by following the rate of oxygen evolution with the apparatus described in I, provided that (I_2) could be maintained near the saturation value by keeping finely divided iodine in contact with the reaction mixture. This experimental method was accordingly adopted. To maintain a_{H^+} at a (nearly) constant value, the potassium phosphate buffer studied by Cohn[5] was employed; total phosphate was always 0.2 M.

The rate to be expected for Reaction 2 in a saturated iodine solution may be written as[6]

$$+\frac{dx}{dt} = k_2' \frac{(I_2)}{(a_{H^+})^2 (I^-)} (a - x) = k_2\, 6(10^{-24}) \frac{1.32(10^{-3})}{\text{const.}\,(I^-)} (a - x) \qquad (8)$$

[3] Bray and McKay, THIS JOURNAL, **32**, 914 (1910); **33**, 1485 (1911).

[4] Abel's conclusion (Ref. 1a) that tri-iodide ion has no direct kinetic role in this reaction system is completely confirmed by the experiments in I.

[5] Cohn, THIS JOURNAL, **49**, 173 (1927). Values of a_{H^+} were calculated as in I, where this buffer was also used.

[6] Compare I, Eqs. 9 and 9a. Above, in Eq. 8, x denotes cc. of oxygen evolved at time t; a is the value of x when reaction is complete. So long as x and $(a-x)$ are expressed in the same units, the value of $k = dx/dt/(a-x)$ is independent of the particular unit employed.

In the first part of all experiments, readings of x were taken at ten-second intervals. If x_1, x_2 and x_3 are the values of x at $t-1/6$, t, and $t + 1/6$, then at t minutes k was computed to be $3(x_3-x_1)/(a-x_2)$. This *differential* method of evaluating $k(I^-)$ is naturally severe, the more so when x alone determines (I^-).

We may write

$$\frac{dx}{dt}\Big/(a - x) = k = \frac{\text{const.}}{(I^-)} \qquad (9)$$

k thus defined is an apparently first-order "constant" introduced wholly for convenience in obtaining k_2 from the experimental results. This was done in the following manner. A value of the product $k(I^-)$ was calculated for practically every reading of evolved oxygen taken during an experiment; k was calculated as previously explained,[6] and (I^-) at t minutes was obtained from oxygen evolved[7] to that time and the initial (I^-), if iodide had been initially added. These values of this product were plotted against the time as abscissa, and the average value for an experiment taken as the ordinate corresponding to the best horizontal line through the experimental points. From this mean value of $k(I^-)$, k_2 for the experiment is easily calculated (Eqs. 9 and 8).

A series of experiments for which the initial reaction mixture was merely the phosphate buffer solution, containing hydrogen peroxide, in equilibrium with solid iodine gave values of k_2 which were erratic and usually lower than the value $3(10^{11})$ obtained in I. In these experiments the first values of $k(I^-)$ were always much lower than the rest; this fact pointed toward depletion of the dissolved iodine as the most probable cause of the difficulty.[8] In subsequent experiments, therefore, iodide ion was added initially in order that the reaction mixture might be "buffered" with respect to (I_2) through Reaction 7. The initial (I^-) was never high enough, however, to cause reduction of as much as 10% of the peroxide (Reaction 6).

Detailed results of two such experiments, which could be conveniently plotted together, are given in Fig. 1, which is self-explanatory. Points are plotted for practically every reading taken during each run to the time when only 1 cc. of oxygen remained to be evolved, that is, to within 96% of completion. For the experiments with iodide added to the reaction mixture (Table I, No. 24 *et seq.*), these results are representative, but they are less erratic than are those from reaction mixtures without added iodide (the first four experiments in Table I).

[7] If a 500-cc. volume of reaction mixture is used (I^-) is changed by unity when $[500/1000 \times 1/2 \times 25{,}050 \times (1 + 0.00132)/0.00140] = 12{,}170$ cc. oxygen is evolved; in this calculation, the factor $1/2$ is introduced because 1 mole of oxygen represents 2 moles total iodide (*cf.* Reaction 1); 25,050 is the volume of 1 mole of oxygen under average experimental conditions; the last factor is necessary because part of the total iodide formed is tied up as tri-iodide ion (*cf.* Reaction 7 and Footnote 3).

By omission of the last factor, one calculates that the evolution of 6260 cc. of oxygen corresponds to formation of one mole of acid in a liter of reaction mixture. This figure may obviously be used to calculate the change which takes place in the $H_2PO_4^-$—$HPO_4^=$ buffer as Reaction 2 proceeds.

[8] Supersaturation was probably not very serious in these experiments as solid iodine was present and the rate of stirring was always high. (In this connection, *cf.* I.) Duplicate experiments with different rates of stirring gave similar results.

In this table the average $k(I^-)$ values are summarized. For each experiment, the values listed under a_{H^+} and (I^-) are those corresponding to the evolution of half the oxygen from the reaction mixture.[9] In the last column is entered, for the experiments in which it is appreciable, the percentage of peroxide which one calculates to have been reduced by iodide ion (Reaction 6). The k_2 values were calculated by the substitution of $(a_{H^+})^2$ and $k(I^-)$ in Equations 9 and 8. Only four (Nos. 1–4) of the experiments without added iodide ion have been given; these are entirely representative, and the inclusion of the others would in no wise affect the conclusions drawn below.

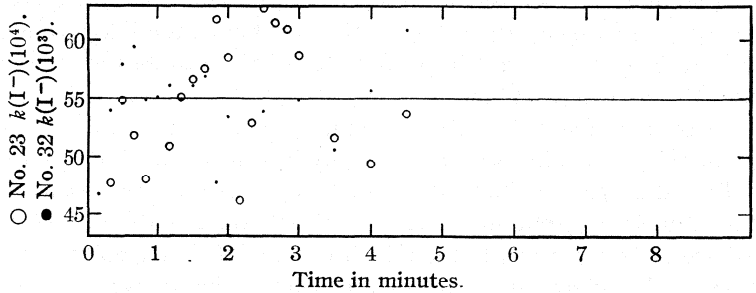

Fig. 1.—Detailed results of two experiments (see Table I).

In Table I the values of k_2 cover a two-fold range while the product $(a_{H^+})^2(I^-)$ which enters into their calculation varies 10^4-fold. As an average value, $k_2 = 2(10^{11})$ may be taken; and it is probably too low because (I_2) in some of the reaction mixtures fell below that of a saturated solution. Nevertheless, this average value is in satisfactory agreement with the value $3(10^{11})$ deduced in I from the steady state function, F;[10] the expectation that the rate of Reaction 2 at a distance from the steady state would be given by Equation 8 is thus completely confirmed. Further, the hydrolysis equilibrium of iodine (Reaction 4 or 5) may be regarded as always established in the iodine–iodide–hydrogen peroxide reaction system, and a previous conclusion,[2a,b] namely, that the specific rate of the reaction

$$I_2 + H_2O = HIO + I^- + H^+$$

is many times greater than the value 0.25 deduced by Abel, receives strong support from the data in Table I.

[9] The occurrence of Reaction 6 tends to increase the k_2 values if these are calculated on the assumption that (H_2O_2) is given directly by oxygen evolved. For this reason no measurements were carried out in which the percentage of peroxide reduced exceeded the experimental error in Table I; a correction for the occurrence of this reaction is scarcely necessary, and none was made.

[10] The value $k_2 = 2(10^{11})$ agrees exactly with what one would calculate from steady state experiments at low a_{H^+} in the acetate buffer solutions (I, Table Ia, Nos. 88 and 92); it is even higher than that corresponding to steady state measurements in Sørensen phosphate buffer solutions (*v*, I, footnote 10).

TABLE I

RATE MEASUREMENTS IN POTASSIUM PHOSPHATE BUFFER SOLUTIONS

Total phosphate, 0.2 *M*; temp., 25°; $(I_2) = 0.00132$; $(H_2O_2) = 0.002$, approximate initial value.

No.	$a_{H^+}(10^7)$[a]	(I^-)	$k(I^-)(10^4)$	$k_2(10^{-11})$	% reduction
1	16.8	0.001	6.4	2.3	.[b]
2	10.9	.001	10.6	1.6	.
3	10.9	.001	9.6	1.4	.
4	9.9	.001	14.6	1.8	.
21	6.93	.012	31.3	1.9	1
22	6.74	.006	29.6	1.7	.
23	5.33	.008	55	2.0	.
24	3.38	.019	143	2.1	2
25	4.17	.022	108	2.3	3
26	4.41	.025	89	2.2	5
27	2.24	.034	311	2.3	3
28	2.52	.037	269	2.1	4
29	2.81	.041	234	2.3	5
30	1.45	.066	588	1.6	5
31	1.65	.070	672	2.7	5
32	1.89	.074	550	2.5	7
33	9.2	.005	10.8	2.0	.
34	16.5	.009	12.9	2.7	.

[a] a_{H^+} are average, and (I^-) approximate average, values.

[b] . means that less than 0.5% of the peroxide is reduced.

We shall finally consider why Reaction 2, rather than the reaction

$$HO_2^- + HIO \longrightarrow O_2 + H_2O + I^- \qquad (10)$$

has been assumed as the compensating reaction in the catalysis of hydrogen peroxide by the iodine–iodide couple even though the experimental evidence does not at first sight seem to warrant the assumption of one reaction to the exclusion of the other. (Under the experimental conditions chosen, Reaction 10 would obviously have a rate law identical in form with Equation 8; the numerical value of the equilibrium constant involved would, of course, be different.) In the first place, hydrogen peroxide is at least ten-fold weaker as an acid than is HIO.[11] Second, it has not been necessary in many kinetic investigations involving hydrogen peroxide to assume HO_2^- as reactant. Finally, it seems logical to assume IO^-, a product of Reaction 6, as reactant in the compensating reaction in which hydrogen peroxide is oxidized. Bray and Livingston found such a role for hypobromous acid in their investigation of the bromine–bromide catalysis,[12] in which no similar ambiguity involving hydrogen ion exists.

[11] The value $(HO_2^-)(H^+)/(H_2O_2) = 2.4(10^{-12})$ [Joyner, *Z. anorg. Chem.*, **77**, 103 (1912)] is almost exactly one-tenth the value $(H^+)(IO^-)/(HIO) = 2\text{–}3(10^{-11})$ [Fürth, *Z. Elektrochem.*, **28**, 57 (1922)]. According to Luther and Sammet [*Z. Elektrochem.*, **11**, 293 (1905)] HIO is an even stronger acid.

[12] Bray and Livingston, THIS JOURNAL, (a) **45**, 1251 (1923); (b) **50**, 1654 (1928).

III. THE RATE OF OXIDATION, IN ACID SOLUTION, OF HYDROGEN PEROXIDE BY IODINE

Two attempts to deduce the specific rate of the reaction[13]

$$HIO + H_2O_2 \xrightarrow{\kappa_2} H^+ + I^- + H_2O + O_2 \qquad (3)$$

from steady state measurements have yielded the results[1a] $\kappa_2 = 3.3(10^5)$ and $\kappa_2 < 2(10^4)$ (*cf.* I). The disparity of these values indicates the necessity of isolating Reaction 3 in order that κ_2 may be directly measured. Because of the relative magnitudes of k_2, the specific rate of Reaction 2, and κ_2, this isolation can be accomplished only if the reaction mixture is at least moderately acid. Under these conditions it is necessary to minimize the rates not only of Reactions 2 and 6, but of the reactions[14]

$$H^+ + I^- + H_2O_2 \longrightarrow HIO + H_2O \qquad (11)$$

$$3I_2 + 3H_2O = IO_3^- + 5I^- + 6H^+ \qquad (12)$$

and

$$I_2 + 5H_2O_2 = 2IO_3^- + 4H_2O + 2H^+ \qquad (13)^{2b}$$

as well.

Calculation and preliminary experiments proved that this could successfully be accomplished in perchloric acid solutions if (I^-) was maintained at a low and (nearly) constant value through the "buffer" action of solid thallous iodide.[15] The rate of Reaction 3 was accordingly measured by

[13] Even though the specific rate of Reaction 3 is much smaller than that of Reaction 2, its value cannot be obtained directly because hypoiodous acid decomposes too rapidly into iodic and hydriodic acids.

[14] (a) Bray, *Z. physik. Chem.*, **54,** 463 (1906); (b) Noyes, *ibid.*, **18,** 118 (1895).

[15] To show that no appreciable conversion of iodine to iodate ion is to be expected in our reaction system, we employ the following data, valid for 25°

(a) $(Tl^+)(I^-) = 5.52(10^{-8})$, based on the measurements of Jones and Schumb, *Proc. Am. Acad. Arts Sci.*, **56,** 199 (1921).

(b) Solubility of $TlNO_3$ is 0.433 *M*, Berkeley, *Trans. Roy. Soc.* (London), **A203,** 211 (1904).

(c) The equilibrium constant for Reaction 12

$$\frac{(H^+)^6(IO_3^-)(I^-)^5}{(I_2)^3} = 2.8(10^{-47})$$, Luther and Sammet, *Z. Elektrochem.*, **11,** 293 (1905).

In a solution saturated with respect to TlI, $TlNO_3$ and I_2, and in which $(H^+) = 10^{-2}$, the equilibrium (IO_3^-) is approximately 10^{-9}. Iodate formation through hydrolysis alone (Reaction 12) is therefore negligible; in fact, such a reaction mixture might be used to study the induction period preceding Reaction 13 when no iodate is initially added. A set of experiments of this type (Ref. 2b, Table V) has shown that a delay of at least several hours' duration is to be expected before appreciable oxidation of iodine takes place; in this interval the rate of Reaction 3 can be measured.

Unless solid thallous iodide is in equilibrium with the reaction mixture, (I^-) may fall to a value much below 10^{-7}; then appreciable iodate formation may occur through Reaction 12, or Reaction 13, or both. From a reaction mixture to which no thallous iodide had been added, oxygen was evolved at a rate approximately two hundred times that expected for Reaction 3, and solid $TlIO_3$ was formed. No such oxidation of iodine was ever encountered when TlI(s) was known to be present.

following oxygen evolution from reaction mixtures containing thallous nitrate and perchloric acid, and in equilibrium[16] with the solids, iodine and thallous iodide; as in II, the apparatus described in I was employed. It was found that Reaction 3 proceeded so slowly that an accurate value of dO_2/dt could be secured before any great change had occurred in either (Tl^+) or (H^+) or (H_2O_2); values of κ_2 were therefore calculated from the rates of oxygen evolution by employing for these concentrations their values in the reaction mixture at the mid-point of the time interval over which dO_2/dt was measured.

Evidence obtained in steady state experiments (Ref. la and I) warrants the prediction of[17]

$$+\frac{dO_2}{dt} = \kappa_2\left[K\frac{(I_2)}{(H^+)(I^-)}\right](H_2O_2) = \kappa_2\left[3(10^{-13})\frac{0.00132}{(\text{const.})(\text{const.})}\right](H_2O_2) \qquad (14)$$

as the rate law followed by Reaction 3 at a distance from the steady state in a reaction mixture for which average values of a_{H^+} and (I^-) may be assumed, and which is in equilibrium with solid iodine. Equation 14 may be recast into the more convenient form

$$k = +\frac{dx}{dt}\Big/(a-x) = \left[\frac{3.96(10^{-16})}{(\text{const.})(\text{const.})}\right]\kappa_2 = [\text{const.}]\,\kappa_2 \qquad (15)$$

where a and x are defined as in II, Equation 9. The k there defined was a variable, for (I^-) always changed appreciably in the course of an experiment. Here, however, (I^-) is (practically) constant since no great displacement of the equilibrium

$$Tl^+ + I^- \rightleftharpoons TlI(s) \qquad (16)$$

occurs during a run; the k of Equation 15 thus maintains its value for an appreciable time.[18] If k is thus measured for an experiment, the corresponding value of κ_2 may be easily calculated by the substitution of average concentrations in Eq. 15; if the κ_2 values from experiments at 25° over sufficiently large concentration ranges are practically constant, their average may be taken as the value of κ_2 for this temperature.

[16] Blank experiments showed no appreciable oxidation of Tl^+ by H_2O_2.

[17] Compare with I, Eq. 20 and with II, Eq. 8. The quantities bracketed in the above Eqs. 14 and 15 are numerically equal for any one experiment.

[18] Average concentrations may be obtained for an experiment if the net reaction occurring is

$$I_2(s) + 2Tl^+ + H_2O_2 = 2TlI(s) + 2H^+ + O_2$$

From this definite relation between (H^+) and (Tl^+) and oxygen, and the known initial concentrations, the values of (H^+) and (Tl^+) for the reaction mixture at the mid-point of an experiment are obtained (*cf.* II, Footnote 7); (IIIO) corresponding to these average concentrations is the equilibrium concentration in Reaction 4 for $(I_2) = 0.00132$, while (I^-) is calculated from the relation $(Tl^+)(I^-) = 5.52(10^{-8})$. Obviously no correction for I_3^- formation is necessary in these calculations. Whether or not k as defined in Eq. 15 changes measurably in the course of an experiment may be used to test the validity of substituting average concentrations, as in Eq. 14: if no such change in k occurs, this procedure is valid. All experiments in Table II meet this test.

The experimental results and average concentrations are summarized in Table II; the lowest value of (I^-) in the table is that of a saturated thallous nitrate solution.[15b] The values given under $\kappa_{2\,exp.}$ were calculated directly from the k's; for experiments at low (H^+) these were corrected for the occurrence of Reaction 2, with the results given in the last column. This correction was made on the assumption that the part of k due to this reaction could be calculated from I, Equation 9; the value $k_2 = 4(10^{11})$ was used. From the remainder of k, which is due only to Reaction 3, the κ_2 values were calculated with the aid of Eq. 15. A comparison of the last two columns in Table II will show that the correction is always small, and negligible at the higher acid concentrations.

TABLE II

RATE MEASUREMENTS IN THALLOUS NITRATE–PERCHLORIC ACID SOLUTIONS

$(Tl^+) = 5.52(10^{-8})/(I^-)$; $(I_2) = 0.00132$; temp., 25°

No.	$(H^+)^a$	$(I^-)(10^6)$	$(HIO)(10^8)$	(H_2O_2)	$k(10^5)$	$\kappa_{2\,exp.}(10^{-8})$	$\kappa_2(10^{-8})$
16	0.0219	2.40	0.75	0.821	2.04	2.8	2.4
17	.0231	1.87	0.92	.821	2.78	3.0	2.6
18	.0245	1.16	1.39	.820	3.49	2.5	2.2
19	.0262	0.744	2.03	.820	4.66	2.3	2.0
20	.0287	0.457	2.91	.819	6.60	2.3	2.0
24	.0114	2.55	1.33	.404	2.23	1.7	1.3
25	.0127	1.66	1.88	.403	3.80	2.0	1.5
26	.0139	0.96	2.97	.401	7.16	2.4	1.9
27	.0158	.507	4.94	.400	12.4	2.5	2.0
28	.0183	.204	10.6	.398	26.9	2.5	2.0
46	.0116	.128	26.9	2.05	73	2	2.0
47	.0292	.128	10.7	2.05	32.6	3.0	2.5
48	.0500	.128	6.24	2.05	19.7	3.2	3.0
49	.0800	.128	3.90	2.05	12.3	3.2	3.1
50	.108	.128	2.89	2.05	8.3	2.9	2.8
51	.135	.128	2.31	2.05	5.95	2.6	2.5
52	.161	.128	1.94	2.05	4.53	2.3	2.2
53	.187	.128	1.67	2.05	3.61	2.2	2.2
54	.237	.128	1.32	2.05	2.49	1.9	1.9
55	.309	.128	1.01	2.05	1.76	1.8	1.8

[a] All concentrations are average.

The results in Table II require little additional comment. For an average value, we may take $\kappa_2 = 2.2(10^3)$ in complete agreement with the conclusion from I that this specific rate constant must be smaller than $2(10^4)$: Eq. 14 therefore governs the rate of Reaction 3 both at a distance from and at the steady state. The accuracy with which κ_2 is determined is all that could reasonably be expected; indeed, much of the variation in the κ_2 values of Table II is probably due to a salt effect on the equilibrium, Reaction 4. (The kinetic salt effect in Reaction 3 is likely to be very small, since neither of the reacting species is ionic.)

Conclusion

With the completion of the investigations which constitute the first three members of this series, the essential simplicity of the iodine–iodide catalysis of hydrogen peroxide seems well established. Why Abel encountered complications in studying the oxidation of hydrogen peroxide (Reaction 1) at a distance from the steady state is not yet clear; new evidence seems conclusive enough, however, to warrant the statement that in this reaction system there are possible (from $a_{H^+} = 10^{-8}$ to $a_{H^+} = 10^{-3}$) only three rate-determining steps, of which all are compensating reactions in the catalysis. The rate laws which they follow (I, Eq. 6; II, Eq. 9a; III, Eq. 14a) have been deduced at the steady state and verified at a distance from it. The numerical agreement[19] between the specific rate constants obtained under the two conditions is not always as good for our case as for that of Bray and Livingston;[12] this is probably due to several causes, among which may be mentioned that no explicit corrections have been made for salt effect, that this catalysis was investigated over a larger concentration range, and that in this system hydrogen peroxide is oxidized not in one reaction, but in two.

While the rate laws for the reaction system are thus definitely established, the mechanisms of the corresponding reactions are subject to an uncertainty of a type encountered in many kinetic investigations; for we have isolated neither hypoiodous acid nor its anion. Other mechanisms for the compensating reactions are conceivable; thus the mechanism

$$H_2O_2 + I_2 \cdot H_2O \rightleftharpoons X + H^+ + I^- \quad (17)$$

$$X \longrightarrow H^+ + I^- + H_2O^{20} \quad (18)$$

would formally satisfy the rate law for Reaction 3. A rate law so complex as this can often be interpreted in terms of several mechanisms, of which none can be considered as absolutely established until every intermediate compound it assumes has been isolated and found to react as it prescribes. Unfortunately, both hypoiodous acid and its anion are so unstable that for reactions involving them such proof cannot be obtained. When the absolute establishment of a mechanism is, beyond a certain point, impossible, the most reasonable of the possible mechanisms may be selected as that which best explains the empirically determined rate law; in this choice, the results of analogous kinetic investigations will serve as valuable guides. Further work may then confirm the mechanism selected, or demand its revision. Reactions 2, 3 and 6 have been thus assigned to the three definitely established rate laws for the reaction system comprising hydrogen peroxide, iodine, and iodide ion.

[19] Reaction 6 has been studied at a distance from the steady state by Noyes,[14b] among others. At higher concentrations of acid, the closely related Reaction 11 is a fourth possible rate-determining step.[14a]

[20] The rate law (Eq. 14) would be formally satisfied had H_2O been placed on the right-hand side of Equation 17, or had it been omitted from both equations.

Summary

1. One of the rate-determining steps in the oxidation of hydrogen peroxide by iodine has been isolated; for its rate law the differential equation

$$-\frac{d(H_2O_2)}{dt} = 12(10^{-13})\frac{(I_2)}{(a_{H^+})^2(I^-)}(H_2O_2) \text{ at } 25° \qquad (8a)$$

has been found valid over a large concentration range.

The most probable mechanism of this rate-determining step involves hypoiodite ion as the oxidizing agent

$$IO^- + H_2O_2 \xrightarrow{k_2} H_2O + I^- + O_2 \qquad (2)$$

At 25°, $k_2 = 2(10^{11})$. The agreement of this value with the value $3(10^{11})$ previously deduced from steady state measurements seems sufficiently good to warrant the conclusion that the hydrolysis equilibrium of iodine (Reaction 4 or 5) is always established in the iodine–iodide–peroxide reaction system.

2. An alternative mechanism involving hydroperoxide ion has been briefly discussed.

3. A second rate-determining step in the oxidation of hydrogen peroxide by iodine has been isolated; over a large concentration range its rate is given by the differential equation

$$-\frac{d(H_2O_2)}{dt} = 6.6(10^{-10})\frac{(I_2)}{(H^+)(I^-)}(H_2O_2), \text{ at } 25° \qquad (14a)$$

The most probable mechanism of this step is

$$HIO + H_2O_2 \longrightarrow H_2O + H^+ + I^- + O_2 \qquad (3)$$

At 25°, $\kappa_2 = 2.2(10^3)$, in complete agreement with evidence from steady state measurements.

It has been concluded that the reaction system comprising hydrogen peroxide, iodine and iodide ion can be interpreted in terms of the three compensating reactions within the wide range of experimental conditions over which the corresponding rate laws have been definitely established.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

LIQUID AMMONIA AS A SOLVENT. I. THE SOLUBILITY OF INORGANIC SALTS AT 25°

BY HERSCHEL HUNT

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The tremendous importance of liquid ammonia as a solvent has been pointed out by E. C. Franklin and his students and has prompted the determination of physical data in this fundamental field of chemistry. The object of this paper is to present solubility data at the same temperature as similar data available for other solvents so that comparisons may be made in the chemistry of various solutions. This basic work on solubilities will be followed by data on vapor pressures, rates of reactions and other constants.

Gore, Franklin and Kraus[1] have determined qualitatively the solubilities of about seven hundred organic and inorganic substances in liquid ammonia at −33°. This large mass of information has enabled Franklin and Kraus to group the substances according to their relative solubilities. Their work has been augmented by the researches of Divers, Cady, Kuriloff, Moissan, Abegg and Riesenfeld, de Carli, Fredenhagen and Scherer.[2]

Experimental

Thermostat.—The temperature of the bath was kept at 25.00 + 0.025°. The thermometer was calibrated against a U. S. Bureau of Standards thermometer.

Salts.—The salts were Baker's C. P. chemicals, which were recrystallized and carefully dried.

Ammonia.—The ammonia was the anhydrous ammonia of commerce. It was transferred from the storage tank to small three-liter cylinders of the type described by Fernelius and Johnson and allowed to stand in these cylinders with metallic sodium for several weeks before use.

Two methods were used for determining the amount of salt present in a given amount of solvent. The methods were found to check within 0.5% of each other. Method I was more satisfactory for the less soluble salts while Method II was necessary in the case of some salts whose solutions attack cotton.

Method I.—The measurements were made in 25 mm. Pyrex tubes. The tubes were filled by placing part A in a carbon dioxide–alcohol bath at −60° and distilling the ammonia from the cylinder into it. The B end of the tube was fitted with a two-holed rubber stopper and the exit tube was guarded with calcium chloride to prevent moisture from condensing in the cold tube. From ten to twenty-five grams of ammonia was used in each experiment. When this volume of ammonia was condensed the carefully

[1] G. Gore, *Proc. Roy. Soc.* (London), **21,** 140 (1873); E. C. Franklin and C. A. Kraus, *Am. Chem. J.*, **20,** 820 (1898).

[2] E. Divers, *Phil. Trans.*, **163,** 359 (1873); H. P. Cady, *J. Phys. Chem.*, **1,** 707 (1897); Kuriloff, *Z. physik. Chem.*, **25,** 109 (1898); H. Moissan, *Compt. rend.*, **133,** 713 (1901); Abegg and Riesenfeld, *Z. physik Chem.*, **40,** 84 (1902); T. de Carli, *Gazz. chim. ital.*, **57,** 347 (1927); K. Fredenhagen, *Z. anorg. allgem. Chem.*, **186,** 1 (1930); P. C. Scherer, Jr., THIS JOURNAL, **53,** 3694 (1931).

dried salt was quickly introduced into A, the bulbs C and D dropped in place and B was drawn down to a tip and sealed off.

The tube was then kept in position II, Fig. 1, in the thermostat, from one to three weeks with occasional shaking, being inverted during the shaking so that the solution in C filtered into A. The amount of salt placed in direct contact with the solvent was previously roughly determined so that it was never quite enough to saturate the solution. The end of C was closed with a very closely woven cotton cloth. This permitted salt to dissolve in the ammonia which enters C, and the solution to flow out, the undissolved salt being held back.

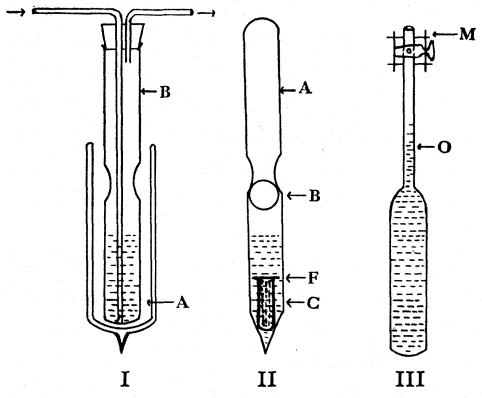

Fig. 1.—The solution and density tubes: F, filter cloth; M, clamp; O, calibration.

When the solution had been given ample time to reach equilibrium the tube was inverted in the bath and all of the solution drained into A. The tube was then removed to a freezing bath and sealed off at the neck between A and B. The tubes were so well drained that the volume change in A on chilling was only the change due to the vapor condensing. Since the tubes were uniformly about 80 cc. in volume and had about 30 cc. of free space the amount of vapor condensed was reduced to a minimum. The vapor pressures will vary from the most dilute to the most concentrated solutions in a manner which will tend to remove error from the final result. Because of this unavoidable error the results reported cannot have a precision greater than 0.5%. When A reached room temperature, it was rubbed dry and weighed on an analytical balance. The ammonia was boiled off, the tube and salt were warmed until all odor of ammonia was gone, and the salt deposited from the solution was weighed. This method gave the solubility in grams per grams of solvent. It has the advantage of being simple and of giving results which are reproducible, as shown in Table I.

TABLE I

REPRODUCIBILITY OF DETERMINATIONS

Salt	Experiment I G./100 g. NH_3	Experiment II G./100 g. NH_3	Experiment III G./100 g. NH_3
$NaNO_3$	97.65	97.60	97.55
NH_4NO_3	390.0	390.0	390.0
NH_4CNS	311.9	312.4	311.6
KBr	13.50	13.55	13.45
KNO_3	10.35	10.45	10.40
NaI	161.9	162.0	161.9

Method II.—A tube such as III, shown in Fig. 1, was used. Ammonia in excess was condensed upon the salt. The solution was brought to 25° in the thermostat and the ammonia was allowed to escape very slowly until a single crystal of the salt remained undissolved after long shaking. This method is quicker and gives results which are equally as reproducible as in the case of the highly soluble salts. The results given are the averages of three determinations which agree within 0.5%.

The solubilities expressed per 100 ml. of solvent were calculated using 0.604 as the density of ammonia at 25°.

TABLE II

THE SOLUBILITY OF INORGANIC SALTS IN LIQUID AMMONIA AT 25°

Salt	G./100 g. NH_3	G./100 ml. NH_3	Moles/10 moles NH_3	Moles/10 moles[a] H_2O
NaF	0.35	0.21	0.0142	0.21
NaCl	3.02	1.82	.088	1.11
NaBr	137.95	83.32	2.28	0.848
NaI	161.90	97.78	1.835	2.214
$NaNO_3$	97.60	58.95	1.95	1.927
NaCNS	205.50	124.12	4.313	...
Na_2SO_3	0.17	0.102	0.0023	0.447
Na_2SO_3	.088	.053	.001	.355
NH_4Cl	102.5	61.91	3.257	1.32
NH_4Br	237.9	143.69	4.13	1.45
NH_4NO_3	390.0	235.56	8.2875	4.82
NH_4CNS	312.0	188.45	6.969	1.55
$(NH_4)_2C_2O_3$	0.00−	0.00−	0.0	0.0696
$(NH_4)_2SO_3$	.00−	.00−	.0	1.045
KCl	.04	.024	.0009	0.96
KBr	13.50	8.15	.192	1.025
KI	182.0	109.92	1.86	1.608
K_2CO_3	0.00−	0.00−	0.0	1.458
K_2SO_4	.00−	.00−	.0	0.1245
KNO_3	10.4	6.28	.174	.664
KCNO	1.70	1.02	.0356	1.665

[a] Taken largely from Seidell, "Solubilities of Inorganic and Organic Compounds," 1919.

The density of a saturated solution of ammonium nitrate in ammonia was found to be 1.212 g. per ml. at 25°. The volume of tube III, Fig. 1, was calibrated. The ammonium nitrate solutions were weighed in it and their densities were calculated from the weight–volume ratio.

TABLE III

SOLUBILITY OF NH_4NO_3 IN MIXTURES OF NH_3 AND H_2O AT 25°

G. H_2O per 100 g. mixture	G. NH_4NO_3 per 100 g. solvent	G. H_2O per 100 g. mixture	G. NH_4NO_3 per 100 g. solvent
0.00	390.0	13.2	351.9
1.78	383.7	15.9	337.4
2.80	381.0	18.6	331.8
3.40	378.6	21.8	316.8
4.82	372.8	47.5	247.0
6.86	368.6	68.0	220.0
10.1	354.7	100.0	214.2
12.7	352.1		

Discussion of Results

In general the solubility of the halides increases as the atomic weight of the halogen increases. The salts of ammonia are the most soluble, and salts of sodium are more soluble than salts of potassium. The sulfates,

carbonates and oxalates examined were insoluble. The sulfites and cyanates were only sparingly soluble. This is in agreement with Franklin and Kraus' work at low temperatures.

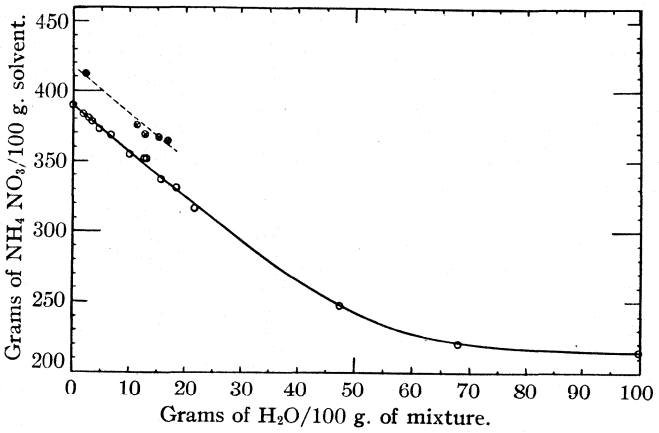

Fig. 2.—The solubility of ammonium nitrate in mixtures of ammonia and water: ○, β-ammonium nitrate; ⊕, α-ammonium nitrate.

The order of solubility in water and ammonia is not regular. A calculation of the solubilities in ammonia based on the physical properties of the solvents cannot be made from the solubilities in water. The solubility must be coördinately determined by properties of the salts as well as of the solvents. If the solution of ammonium nitrate is raised above 33° the α-form will crystallize on slowly cooling to 25° and, since it is more soluble than the β-form, points were obtained which lie above the curve.

Summary

1. The solubilities of seventeen inorganic salts in liquid ammonia have been determined quantitatively at 25°.

2. The solubilities in ammonia and water are not always concordant with the physical properties of the solvents.

3. The progressive addition of water decreases the solubility of ammonium nitrate in liquid ammonia.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

NEW HYDRATES OF MAGNESIUM PERCHLORATE. THEIR STRUCTURAL RELATION TO KNOWN FORMS OF THE HYDRATED PERCHLORIC ACIDS AND PROPERTIES AS INTENSIVE DEHYDRATING REAGENTS

BY G. FREDERICK SMITH, O. W. REES[1] AND V. R. HARDY

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Introduction

The oxonium structure of the crystalline form of perchloric acid having the melting point 49.90°[2] has been previously shown by Volmer.[3] The oxonium structure of all known hydrates of perchloric acid was indicated by the studies of Smith and Goehler.[4] Previously known hydrates of magnesium perchlorate are the hexahydrate and trihydrate. The latter material (trade name, Dehydrite) and anhydrous magnesium perchlorate (trade name, Anhydrone) are widely employed in the intensive drying of gases. The object of the present paper is to report new hydrates of magnesium perchlorate, to show their direct analogy to known forms of hydrated perchloric acid and to extend conclusions concerning the structural relations brought out by the perchloric acids and analogous magnesium salts.

Known Forms of Perchloric Acid and Analogous Magnesium Salts.—The data of Table I are used to show the analogy existing between various known forms of perchloric acid and the entire list of hydrated magnesium perchlorates. The diaquo- and tetraquo-magnesium perchlorates are prepared and described for the first time in connection with the work reported in this paper.

Discussion of Data in Table I.—In a previous paper[4] the oxonium structure of the hydrated perchloric acids resulted in a somewhat different formulation being applied to the hydrous perchloric acids. For example, considering the perchloric acid associated with two molecules of water, the formulas assigned to this modification were the following: $OH_3ClO_4 \cdot H_2O$ (oxonium perchlorate monohydrate) for the stable form, m. p. $-17.8°$, and $HClO_4 \cdot 2H_2O$ (perchloric acid dihydrate) for the less stable form, m. p. less than $-19.0°$. While this former interpretation is somewhat at variance with the data of Table I, it is based upon the assumption that the anion in the one case is more extensively hydrated than in the other. The newly modified interpretation seems to be somewhat preferable from

[1] Presented by O. W. Rees in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

[2] Smith and Goehler, *Ind. Eng. Chem., Anal. Ed.*, **3**, 8-61 (1931).

[3] Volmer, *Ann.*, **440**, 200 (1924).

[4] Ref. 2, p. 58.

TABLE I

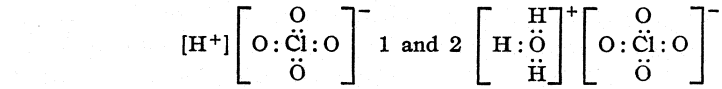
	Perchloric acid hydrate	Mg salt—Werner formulation[a]
1	$HClO_4$ (m. p. app. −112°) anhydrous perchloric acid[5]	$[Mg](ClO_4)_2$ anhydrous magnesium perchlorate[6]
2	OH_3ClO_4 (m. p. 49.90°) oxonium perchlorate[4]	$[Mg(H_2O)_2](ClO_4)_2$ diaquo-magnesium perchlorate[7]
3	$O_2H_5ClO_4$ (m. p. −17.8°) dioxonium perchlorate[4,5]	$[Mg(H_2O)_4](ClO_4)_2$ tetraquo-magnesium perchlorate[7]
4	$OH_3ClO_4 \cdot H_2O$ (m. p. < −19°) oxonium perchlorate monohydrate[4]	
5	$\left.\begin{matrix}O_2H_5ClO_4\\O_2H_5ClO_4\end{matrix}\right\rangle H_2O$ (m. p. −29.8°)[5]	
6	$O_2H_7ClO_4$ (m. p. −37°)[5] trioxonium perchlorate	$[Mg(H_2O)_6](ClO_4)_2$ hexaquo-magnesium perchlorate[6,8]
7	$O_2H_5ClO_4 \cdot H_2O$ (m. p. −43.2°)[5] dioxonium perchlorate monohydrate	
8	$\left.\begin{matrix}O_2H_7ClO_4\\O_2H_7ClO_4\end{matrix}\right\rangle H_2O$ (m. p. −41.4°)[5]	

[a] Triaquo-magnesium perchlorate[6,9] may be considered as the salt formed by the action of oxonium perchlorate and dioxonium perchlorate, thus:

$$MgO + \begin{matrix}OH_3ClO_4\\O_2H_5ClO_4\end{matrix} \longrightarrow [Mg(H_2O)_3](ClO_4)_2 + H_2O.$$

an extended study of new hydrated magnesium salt analogs of the acids under discussion predicted by a study of Table I. The two new hydrated magnesium perchlorates $[Mg(H_2O)_2]$ $(ClO_4)_2$ and $[Mg(H_2O)_4]$ $(ClO_4)_2$ were, as a result, studied for the first time. The present interpretation was also suggested by the paper of Latimer and Rodebush,[10] in which they present a plausible explanation for the association of water molecules to form dihydrol and trihydrol or more extensively associated water molecules. The present interpretation is also made more plausible by the study of the perchlorate amines of the alkaline earth metals and magnesium to be reported at a later date. Finally, the new interpretation as applied to the structure of the hydrated perchloric acids naturally follows from a study of the physical constants of the magnesium perchlorate hydrates following the rules of coördination in their Werner formulations.

The Structure of the Hydrated Perchloric Acids.—The electronic structure of the hydrated perchloric acids numbering 1–8 in Table I are given as follows, each individual form identified by number



Structure 1 is readily accepted. Structure 2, oxonium perchlorate, is the only one possible in accordance with the findings of Volmer follow-

[5] Van Wyk, *Z. anorg. Chem.*, **48**, 1 (1906).

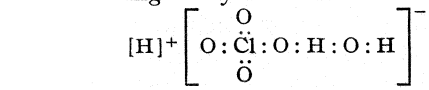
[6] Willard and Smith, THIS JOURNAL, **44**, 2254 (1922).

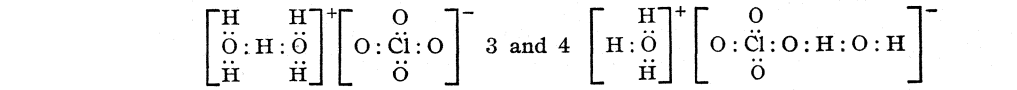
[7] Smith, Rees and Hardy, this paper.

[8] Weinland and Ensgraber, *Z. anorg. Chem.*, **84**, 372 (1914).

[9] Smith, Brown and Ross, *Ind. Eng. Chem.*, **16**, 20 (1924).

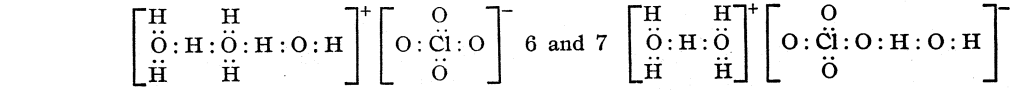
[10] Latimer and Rodebush, THIS JOURNAL, **42**, 1419 (1920).

ing x-ray studies. The hydration of the anion resulting in the structure  is not possible since two crystalline forms of this acid are not known as shown by Smith and Goehler.[2] The structure shown in the above hydrated anion is excluded because of the well-known great increase in stability of oxonium perchlorate as compared to anhydrous perchloric acid. This is not observed in the comparison of higher hydrates in which hydration of the anion is postulated. The melting point of oxonium perchlorate is comparatively high (49.90°), which is associated with hydration of the cation. Therefore for the pairs of known modifications of the higher hydrated perchloric acids, that having the higher melting point must be considered to have the total hydration associated with the cation.



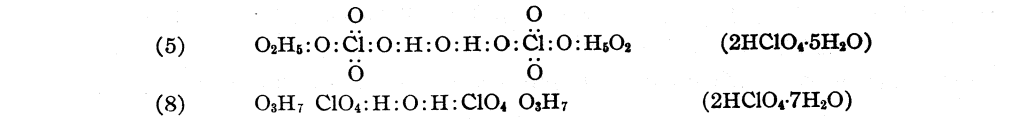
In the case of structure 3 and structure 4, two forms of this acid were shown to exist by Smith and Goehler.[4] The unstable form, 4, having the lower melting point, is so readily transformed to form 3 that the existence of this modification was not indicated by van Wyk,[5] although two forms of the next higher hydrate were shown in the same investigation, probably because of an increased difference in melting points in the latter case. That the stable form is that indicated in formula 3 is proved by the previously demonstrated dissociation of the material to form successively oxonium perchlorate, formula 2, and finally anhydrous perchloric acid.[11] These dissociations would not be possible were the stable forms to correspond to those having hydrated anions.

Similarly two forms of the next higher hydrate of perchloric acid are known as follows



Here again the form 6 having the higher melting point is given the structure in which the cation is most highly hydrated.

As the ratio of acid to water molecules decreases, even before reaching the ratio $HClO_4:3H_2O$, there appears a tendency for polymerization through the medium of the ClO_4 anion. Thus



(5) $(2HClO_4\cdot 5H_2O)$

(8) $(2HClO_4\cdot 7H_2O)$

[11] Ref. 2, p. 55.

Here, an implied polymerization through the union of the two molecules of forms 3 and 6 due to a bonding of both anions in each case by one water molecule might be explained by a similar union linking the two cations. The latter alternative is not plausible for a number of reasons. Corresponding hydrated magnesium perchlorates are not known. Two forms of the acids, 5 and 8, are not known. The rate of change in viscosity for solutions of perchloric acid in water with increase in acid concentration is greatest[5] over the range corresponding to formulas 5 to 8, inclusive. More extensively hydrated forms of perchloric acid than that of formula 8 are not probable since a dilute solution of perchloric acid in water, when concentrated by boiling, begins to develop acid in the vapor phase at a concentration approximately represented by formula 8 for the liquid phase.

Acids of formulas 5 to 8 inclusive are easily dissociated to form dioxonium perchlorate (formula 3). Constant boiling perchloric acid (b. p. 203° at 1 atmosphere) corresponds most closely to the latter form (72.5% $HClO_4$). By distillation at reduced pressure it is impossible to exceed the concentration (73.60%) indicated by formula 3. Repeated and continuous distillation at pressures much less than one millimeter do not result in more than a minute increase in acid concentration (less than 0.3%) which must be attributed to the phenomena of superheating.[12] At the same time modifications 1, 2, 3, 4, 6 and 7 were shown to exist in the vapor phase upon distillation at reduced pressures from 7 to 18 millimeters and their separation in the vapor phase accomplished. The dissociations were then made possible by the effect of 50–60° of superheating. Dioxonium perchlorate is dehydrated to oxonium perchlorate by the use of concentrated sulfuric acid. Oxonium perchlorate is dehydrated to form anhydrous perchloric acid by contact with phosphorus pentoxide, which finally forms Cl_2O_7.[13]

Conclusions relative to the precise structure of the hydrated perchloric acids necessarily are associated with intuitive speculation in a great measure. Following such lines of speculation it is interesting to express the relationship existing between values for the ratio of acid to water at which the hydrated perchloric acids exist and the melting point of the numbered forms previously discussed in connection with Table I. This is done graphically in Fig. 1. Here melting points are plotted on the vertical and acid–water molecular ratios on the horizontal axis. The stable forms 1, 2, 3 and 6 are shown on the solid black line AAA. The forms 4 and 7 which convert readily to forms 3 and 6, respectively, fall on the branch AC (dashed line). The polymerized forms 5 and 8 fall between these values on the part of AAA indicated by AB.

New Hydrates of Magnesium Perchlorate.—Since the more stable

[12] Smith and Koch, *Ind. Eng. Chem., Anal. Ed.*, **3**, 52 (1931).

[13] Michael and Conn, *Am. Chem. J.*, **23**, 444 (1900).

forms of perchloric acid show increasing melting points with decreasing hydration of the cation, and hydrated magnesium perchlorates other than the tri- and hexahydrated forms have not been previously shown, the di- and tetrahydrated magnesium perchlorates would be predicted from the existence of oxonium and dioxonium perchlorates. The two new forms of hydrated magnesium perchlorate are indicated by the principles governing the formation of complex structures of the Werner type, namely: (a) oxygen shows a greater tendency to coördinate than does hydrogen. (b) The tendency of an ion to form a covalent link is greater the larger the charge, the less its size if a cation, and the greater its size if an anion. (c) The cation has a tendency to act as acceptor and the anion as donor. (d) Magnesium shows coördination numbers of 2, 3, 4 or 6 (its maximum). (Elements of the periodic table from sodium to bromine show a maximum coördination number of 6.) (e) Crystalline substances in which the two ions have different charges or where there is a great difference in their size are likely to show hydration.

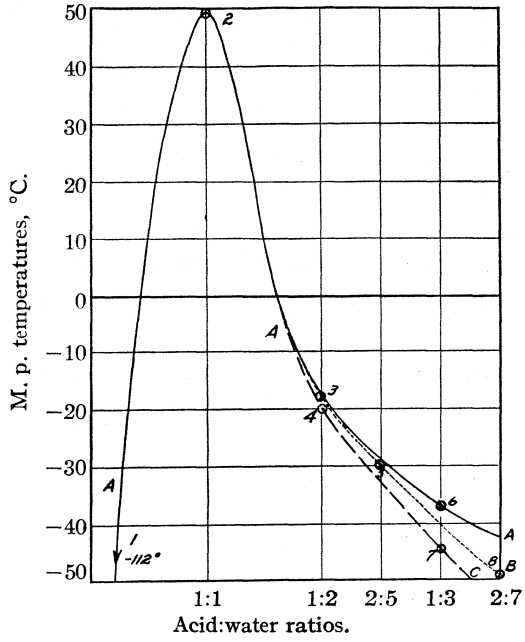


Fig. 1.

All the structures shown in Table I conform to these rules. With the possible exception of beryllium, magnesium represents the metal of lowest atomic weight suitable for study of the bivalent group. The already extended application of magnesium perchlorate as an intensive dehydrating agent increases the interest in this problem.

From an examination of Table II it will be seen that the vapor pressure of tetraquo-magnesium perchlorate lies between 3 and 10 millimeters at 50°. The vapor pressure of diaquo-magnesium perchlorate is less than 10 millimeters at 125°. (By separate determination it was easily shown that the vapor pressure of diaquo-magnesium perchlorate is zero at temperatures up to 135°.) The vapor pressure of diaquo-magnesium perchlorate becomes appreciable at 150° but its dissociation is very slow at this temperature. (Even at 200° the dissociation is slow and temperatures up to 250°

TABLE II

DEHYDRATION OF HEXAQUO-MAGNESIUM PERCHLORATE AT VARIOUS TEMPERATURES (PRESSURE, 10–15 MM.)

Sample weights $[Mg(H_2O)_6](ClO_4)_2$ from 2.5 to 3.75 g.

Temp., °C.	Percentage loss in weight — Time in days — 1	2	3	4	5	14	21	Mg. salt hydrate formed	Theoretical loss, %
50[a]	0.20	0.50	...	3.79	...	10.79	10.70	$[Mg(H_2O)_4](ClO_4)_2$	10.81
75	13.57	20.96	21.60	..	...	...	...	$[Mg(H_2O)_2](ClO_4)_2$	21.62
100	21.66	21.66	...	..	...	...	...	$[Mg(H_2O)_2](ClO_4)_2$	21.62
125	21.66	21.69	...	..	...	...	...	$[Mg(H_2O)_2](ClO_4)_2$	21.62
150	20.98	...	28.49	..	31.89	...	...	$Mg(ClO_4)_2$	32.42

[a] When the pressure was reduced to a value of 3–4 mm. after 29 additional days this sample was dissociated to form diaquo-magnesium perchlorate (loss found, 22.60%).

are preferable.) The preparation of diaquo-magnesium and anhydrous magnesium perchlorates on a large scale for commercial use has been described by Smith and Rees.[14]

TABLE III

DEHYDRATION OF HEXAQUO-MAGNESIUM PERCHLORATE IN CONTACT WITH VARIOUS DEHYDRATING REAGENTS AT 125–175°

Desiccant	Temp., °C.	Percentage loss in weight — Time in hours — 12	16	20	24	Fraction of water removed, %
Silica gel	125	...	...	1.81	2.57	7.9
"Hydralo"	150	9.06	9.27	..	...	28.6
"Hydralo"	175	10.71	10.38	..	...	32.0
P_2O_5	150	13.85	14.83	..	...	45.74
Anhydrone	150	21.01	...	..	21.66	66.81

By examination of Table III it will be seen that over the temperature range 125–175° "Anhydrone" (anhydrous magnesium perchlorate) is the most efficient dehydrating agent of all commercially available desiccants whose efficiency is known to be such as to exert zero vapor pressure at ordinary temperature (barium oxide[15] was not used in the comparisons). Even at 125° the dehydrating value of silica gel is negligible. "Hydralo" (dehydrated aluminum hydroxide) at 175° is capable of dehydrating hexaquo-magnesium perchlorate only to the formation of tetraquo-magnesium perchlorate. Phosphorus pentoxide at 150° is not nearly as rapid in its dehydration as Anhydrone at the same temperature. In the case of the use of Anhydrone, the lowest known hydrate of magnesium perchlorate (diaquo-magnesium perchlorate) was formed giving the theoretical loss in weight of 21.7%. The use of phosphorus pentoxide at 150° is not recommended since the vapor pressure of its water addition products is appreciable and results in the contamination of the sample dehydrated, vitiating results.

[14] Smith and Rees, *Ind. Eng. Chem.*, **23**, 1328 (1931).

[15] Booth and McIntyre, *Ind. Eng. Chem., Anal. Ed.*, **2**, 12 (1930).

For the experiments given in Table III, a vacuum metal desiccator was used which is to be described in a subsequent paper. It is to be noted that for these experiments in the comparison of the dehydrating efficiency of the various desiccants, hydrated magnesium perchlorate represents the most stable known hydrate for use in such work. Hydrated copper sulfate is ordinarily used but has a higher vapor pressure at comparable temperatures.

Finally, to show experimentally conditions under which the complete list of known hydrates of magnesium perchlorate can be formed, a stock of hexaquo-magnesium perchlorate was stored in a vacuum desiccator without dehydrating agent and kept at 50° with continuous evacuation. A pressure of 10–15 mm. was used for twenty-one days until the loss in weight was constant and tetraquo-magnesium perchlorate formed. The pressure was then reduced to 3–4 mm. and the dehydration completed at the same temperature. The results are shown in Fig. 3. The flat portions of the dehydration curve correspond to the successive dehydrations represented as

$$[Mg(H_2O)_6](ClO_4)_2 \longrightarrow [Mg(H_2O)_4](ClO_4)_2 \longrightarrow [Mg(H_2O)_3](ClO_4)_2 \longrightarrow [Mg(H_2O)_2](ClO_4)_2$$

The stability of the triaquo derivative is seen to be less marked than of the remaining forms as indicated by slight break in the curve at the point corresponding to this composition. To carry the dehydration to completion a temperature of 150° or above to 250° must be employed.

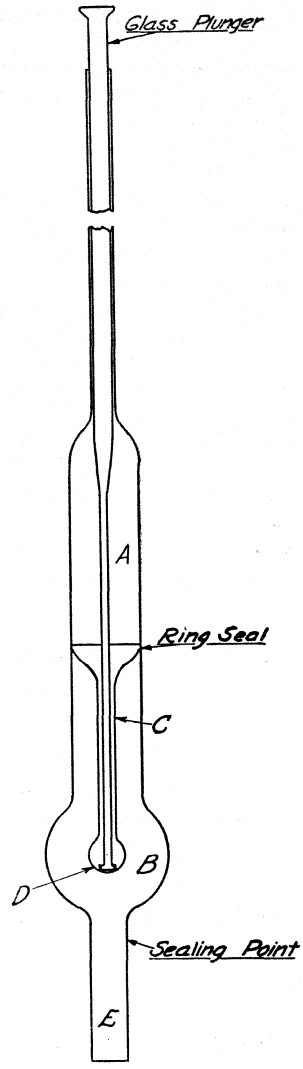


Fig. 2.

Heat of Hydration of Various Forms of Hydrated Magnesium Perchlorate.—To show the increase in stability of magnesium perchlorate having various degrees of its coördination valences satisfied, the experimental determination of the heats of hydration and solution of the various forms was undertaken. For this purpose the glass reaction vessel shown in Fig. 2 was employed. The two partition cell of 150–200 cc. capacity is divided by use of the ring seal into a portion A, to contain the water used, separated from the reaction chamber B, which contains the particular form of magnesium perchlorate being examined, by the delivery tube C, which extends compartment B into C. The connection between B and C is made by perforating the thin bulb D using the glass plunger indicated. The method used in charging the sample into the reaction vessel consisted in preparing the particular hydrate of magnesium perchlorate to be used in a reaction tube terminating in a narrow neck which could be

inserted within the reaction vessel through tube E. A weighed portion of hexaquomagnesium perchlorate was dehydrated under the proper conditions to prepare the salt hydrate in question. The dehydration was carried out until, by noting that the loss in weight was the theoretical amount, the reaction was complete. Finally the narrow neck of the sample preparation tube was inserted within E and the apparatus turned upside down to deliver the sample to the calorimeter tube. This was then sealed off under vacuum at the point shown. Excess of water was then added at A and the glass plunger inserted, provided with a small rubber bulb at its upper extremity to provide manual circulation of the solution formed after the partition between sections A and B was broken.

The calorimeter tube (Fig. 2) was provided with two copper bands around sections A and B having copper fins soldered to them bent at such an angle as to give circulation to the water of the calorimeter when a vertical movement of the calorimeter reaction chamber was employed. The calorimeter tube was a large cylindrical Dewar flask inserted within a still larger cylindrical Dewar flask and the latter placed in a can from which it was separated by infusorial earth and the outside of the can encased in felt. The calorimeter tube was mounted in a support which was provided with a mechanism to impart a vertical movement with an amplitude of 5 cm. The plunging mechanism was operated by use of a motor and pulley and the speed was 30–40 vertical displacements per minute. A weighed portion of water was placed in the inside Dewar flask and a Beckmann thermometer within the same flask. The movement of the calorimeter tube with its stirring mechanism attached stirred the bath water and when the condition of temperature equilibrium of the whole system was obtained the partition between the water chamber A (of the reaction vessel) and the reaction chamber B was broken by a gentle downward thrust on the plunger, the time noted, and the temperature rise plotted. The results of the various determinations are given in Table IV.

TABLE IV

HEAT OF SOLUTION OF ANHYDROUS MAGNESIUM PERCHLORATE AND ITS HYDRATES

Calorimeter water used in each case, 830 g.

Material	Dehydration analysis Loss in weight in %, Calcd.	Found	Sample, g.	Rise in temp., °C.	Molecular heat of solution, calories	$Mg(ClO_4)_2$ heat of hydration, calories per gram mole
$[Mg(H_2O)_6](ClO_4)_2$	...	...	7.4560	−0.02	−738	...
			7.8013	− .025	−881	...
					Av. −809	
$[Mg(H_2O)_4](ClO_4)_2$	10.86	10.3	9.2558	+0.29	7678	8487
			9.5981	+ .28	7149	7958
			8.0483	+ .22	6698	7507
						Av. 7984
$[Mg(H_2O)_2](ClO_4)_2$	21.73	21.77	6.0588	+0.52	18466	19275
			7.0998	+ .60	18182	18991
			7.3193	+ .63	18521	19330
						Av. 19199
$Mg(ClO_4)_2$	32.60	32.70	7.3531	+1.24	31247	32056
			7.9880	+1.355	31430	32239
			7.6863	+1.37	33021	33830
						Av. 32708

From an examination of Table IV it is noted that heat of hydration of anhydrous magnesium perchlorate ("Anhydrone") is practically the same as the heat of reaction[16] between the ordinary amorphous form of phosphorus pentoxide and water (33,000 calories per gram mole). Since the heat of reaction evolved in the saturation of the coördinate covalences of the magnesium ion of magnesium perchlorate is approximately equal to the heat of solution of phosphorus pentoxide in water, which is a covalence reaction phenomenon, the equality between these two dehydrating agents (Anhydrone and phosphorus pentoxide) in drying intensity would be predicted and has been established. The heat of reaction involved in the saturation of the first two coördination covalences of the magnesium ion is much greater than that for the saturation of the second pair and the saturation of the last pair results in still less heat evolved. The increase in heat

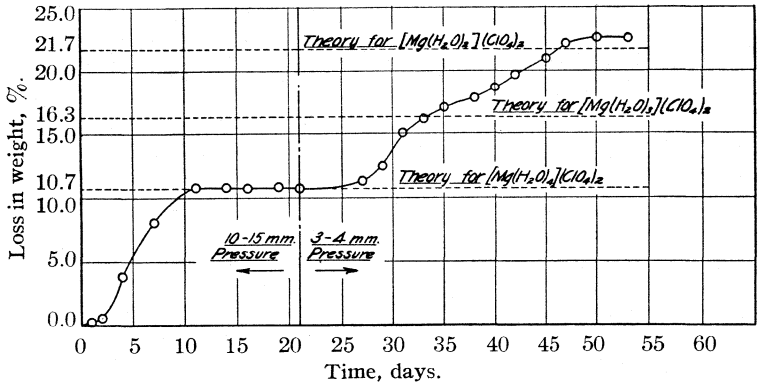


Fig. 3.—Vacuum dehydration of $[Mg(H_2O)_6](ClO_4)_2$, no desiccant, pressures 10–15 and 3–4 mm.

evolved upon hydration of the successively lower forms would be predicted from the increase in temperature required to show a measurable vapor pressure for the same forms. Thus, tetraquo-magnesium perchlorate shows its first appreciable vapor pressure at 50°. The diaquo form shows its first appreciable vapor pressure at 135°. If the heat of hydration of the former is taken as 8000 calories per gram mole, the heat of hydration of the latter would be estimated at 21,500 calories as compared with the value found of 19,200 calories. Conversely, if the heat of hydration of the anhydrous form is 33,000 calories, it would not be expected that the diaquo form would show an appreciable vapor pressure under 200°, which is found to be experimentally justified.

It is to be noted that since the temperature of dehydration of diaquo-magnesium perchlorate must be greater than 135°, anhydrous magnesium

[16] Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1928, Vol. VIII, p. 943.

perchlorate is a perfect drying agent up to this temperature. The use of the latter drying agent at temperatures between 50 and 135° therefore prevents the formation of higher hydrates than the diaquo form and facilitates regeneration of the spent desiccant.

x-Ray Powder Diffraction Patterns of Hydrated Magnesium Perchlorates.—For this study a polychromatic molybdenum radiation produced by a standard outfit together with a Hull Quadrant Cassette with a filter of zirconium dioxide was employed. The method of charging the capillary tubes with the samples in question was a problem because of their extreme deliquescence. The process employed was as follows.

A piece of 15-mm. Pyrex tubing about 7 or 10 cm. in length was drawn out on one end to a capillary of about 6.3 cm. length and a half to one mm. bore. A sample of magnesium perchlorate hexahydrate, which had been thoroughly ground, together with five or six $^3/_{16}$-inch steel ball bearings, was placed in the large part of the tube. The large end of the tube was then drawn down in the flame and a long piece of 6-mm. glass tubing sealed on. The whole thing was then placed in an electric oven at the desired temperature with the long glass tube extending out through the top of the oven. This tube was connected to a vacuum pump with a weighed anhydrone tube in the line. By regulating the temperature of the oven the desired dehydration of the hexahydrated material could be brought about and this could be followed by the increased weight of the drying tube. When the theoretical loss for the production of the desired hydrate had occurred, the system was removed from the oven, rolled and shaken in order to effect grinding, and the capillary packed by tapping the material gently down into it. When this was completed the capillary was fused off near the large tube. Later a sample was removed from the large tube and analyzed. This gave a double check on the constitution of the material in the capillary tube.

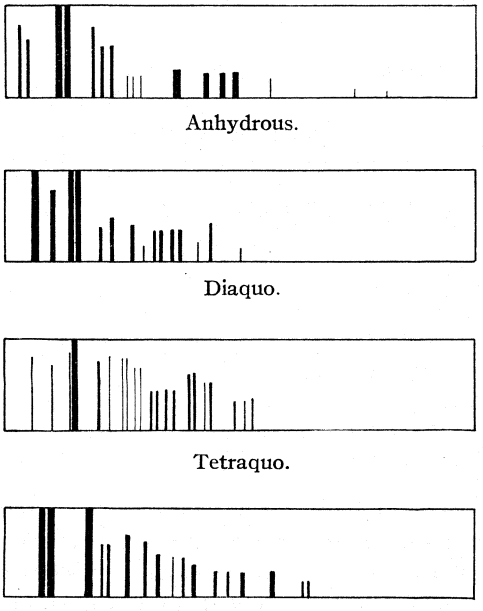


Fig. 4.

The results from the x-ray powder diffraction photographs are shown by reference to Fig. 4. It will be seen from an examination of the results from the various samples that separate and distinct patterns are shown for each form and the deviation is least pronounced in the comparison of the hexaquo and tetraquo forms. The x-ray examination of the various hydrates of magnesium perchlorate cannot be extended to include Laue

diffraction patterns until a process is developed for the preparation of individual crystals of the various types for examination. This problem is complicated by the fact that the lower hydrates cannot be prepared in aqueous solution by ordinary processes because of the high temperature required. The x-ray powder patterns indicate the existence of the various forms associated with marked distinctions in structural relationships.

Assistance on the part of Professor G. L. Clark in the x-ray studies is gratefully acknowledged.

Summary

1. The structural relationships existing between the numerous forms of the hydrated perchloric acids have been discussed and the experimental justification for the conclusions drawn has been indicated.

2. Two new forms of hydrated magnesium perchlorates, diaquo- and tetraquo-magnesium perchlorate, were predicted from a study of the various hydrates of perchloric acid and the conditions for their preparation described.

3. Vapor pressure studies involving the use of the various forms of hydrated magnesium perchlorates have been made and the dehydrating efficiency of the anhydrous form compared to that of other highly intensive desiccants.

4. x-Ray powder diffraction patterns of the various hydrates of magnesium perchlorate have been prepared.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 316]

THE ENTROPIES OF SOME SIMPLE POLYATOMIC GASES CALCULATED FROM SPECTRAL DATA

BY RICHARD M. BADGER AND SHO-CHOW WOO

RECEIVED APRIL 25, 1932 PUBLISHED SEPTEMBER 5, 1932

Introduction

Knowledge of the nature of the energy levels of diatomic molecules has now advanced to such a state that when appropriate data are available it is possible to calculate specific heats and entropies with great accuracy and with results in which we may be entirely confident, as has been shown by comparisons between calculated values and those obtained from specific heat data.

The polyatomic molecule in most cases offers considerably greater difficulties, and for those of the most general type there is as yet probably no case in which data are available for making any exact calculation. However, in two special cases the computation becomes very much sim-

plified, namely, the symmetrical rotator type of molecule, and the molecule having a linear configuration in the normal state; for several, examples of these data are available. Two of the symmetrical rotator molecules, ammonia and methane, have been treated by Villars,[1] but unfortunately the spectra of these gases have not been fully interpreted as yet, and one of the moments of inertia of ammonia may be in some doubt.

It is the purpose of this paper to treat four of the linear polyatomic molecules for which accurate spectroscopic data have recently been published, and which appear to be understood in sufficient detail so that we may be quite confident in the results of our calculations. After our calculations were completed our attention was called to a letter from W. H. Rodebush in the *Physical Review*[2] in which calculated values for the entropies of carbon dioxide and nitrous oxide were given. The former agrees approximately with our results but the value for nitrous oxide seems to be too low by about 0.2 entropy unit, apparently due to the use of the incorrect moment of inertia for this gas which is given in the paper of Plyler and Barker.[3] In view of this fact, and since none of the details of the calculations were given in the letter of Rhodebush, we believe it may be of value to give our results as originally planned.

The methods of calculating entropies from spectral data have been the subject of so many papers[4] that it seems unnecessary to discuss our computations in any detail, except in regard to some points which are more or less special for the particular molecules involved.

The Linear Triatomic Molecules Carbon Dioxide, Nitric Oxide and Hydrogen Cyanide

Vibrational Energy Levels.—The infra-red and Raman spectra of gaseous carbon dioxide,[5] nitrous oxide[3,5c] and hydrogen cyanide[5a,6] have been investigated and we have conclusive evidence that the molecules are linear in the normal state, that carbon dioxide is symmetrical and that nitrous oxide is unsymmetrical. Molecules of the general type of which these are examples have three normal modes of vibration which we shall designate by the symbols ν_1^{δ}, ν_2 and ν_3.[7] The second and third are

[1] Villars, *Phys. Rev.*, **38**, 1552 (1931).

[2] Rodebush, *ibid.*, **40**, 113 (1932).

[3] Plyler and Barker, *ibid.*, **38**, 1828 (1931), and see below.

[4] For example: Giauque, THIS JOURNAL, **52**, 4808 (1930); Rodebush, *Chem. Rev.*, **9**, 319 (1931).

[5] (a) See Schaefer and Matossi, "Das Ultrarote Spektrum," Julius Springer, Berlin, 1930, for references; (b) Sleator, *Phys. Rev.*, **38**, 147 (1931); (c) Dickinson, Dillon and Rasetti, *ibid.*, **34**, 582 (1929); (d) Houston and Lewis, *Proc. Natl. Acad. Sci.*, **17**, 229 (1931).

[6] Badger and Binder, *Phys. Rev.*, **37**, 800 (1931).

[7] We shall use the convention that the fundamental modes of oscillation are designated by subscripts in order of increasing frequency. The type of motion is designated

longitudinal or "valence" vibrations of relatively high frequency. In carbon dioxide ν_2 is "inactive" since it produces no changes in electric moment in the symmetrical molecule, but in the other two molecules it is weakly active. The other type of oscillation ν_1^δ is the one with which we shall be chiefly concerned since it is of relatively low frequency. It is a motion in which the two molecular bonds are bent with respect to each other, and the molecule is periodically deformed from its linear condition. In the case of a strictly harmonic oscillator the excited levels of the ν_1^δ vibration are degenerate with a weight of $v_1^\delta + 1$, where v_1^δ is the vibrational quantum number of the state.[8] In the actual molecules the degeneracy is partly removed by the non-harmonic nature of the oscillation, and is probably completely removed when the molecule is rotating.

Unfortunately some of the $v_1^\delta + 1$ levels do not combine with the ground level in absorption, but their energy may be determined indirectly if absorptions from a known excited level to these states are observed. One simply adds the energy of the observed transition to the energy of the initial level.

In the case of carbon dioxide the situation is further complicated by the fact that the energy of the states $v_1^\delta = 2$, $v_2 = 0$, and of the state $v_1^\delta = 0$, $v_2 = 1$ are very nearly equal. This case has been discussed by Fermi[9] on the assumption that in the unperturbed case these energies would be exactly equal, so that there would be a single degenerate state of weight 4. He shows that in the case of coupling between the two types of oscillation concerned, a resonance effect causes the degenerate state to split into three, one of which is still degenerate with a weight of 2, and he calculates the separation of the new levels with the aid of an estimated coupling energy. His discussion is obviously too simplified to take account of the situation in carbon dioxide in an exact way, and the agreement between calculation and the Raman spectrum must to some extent be fortuitous, but it is very important in calling attention to an effect which may be rather common in polyatomic molecules where the chance is great that vibrational levels of different types of oscillation may nearly coincide.

Fortunately, with the assistance of the infra-red and Raman spectra together we are able to find the energies of most of the states which are important for our purposes, and for a few others we may make a sufficiently accurate estimate. At this point we should like to correct an impression which seems to be fairly general to the effect that the Raman spectrum alone yields sufficient information for making the type of calculations

by the superscript; δ indicates a deformation oscillation, that is, one in which the motion is principally a bending of a molecular bond, and its absence a longitudinal or valence oscillation. An inactive vibration is indicated by i in the superscript.

[8] The problems with which we are here concerned are discussed by Dennison, *Rev. Mod. Phys.*, **3**, 280 (1931).

[9] Fermi, *Z. Physik*, **71**, 250 (1931).

with which we are here concerned. Usually about two-thirds of the necessary data has to be obtained from infra-red investigations.

Rotational Energy.—It is found that for the linear polyatomic molecules the energies in the lower oscillational states are quite accurately given by a formula of the same type as that applicable to the diatomic molecules.

$$E = E_{\text{vib.}} + j(j+1)\frac{h^2}{8\pi^2 I}$$

The stretching of the molecule due to rotation seems to be negligible, that is, I may be taken constant for a given vibrational state. But for nitrous oxide and hydrogen cyanide the data are sufficiently accurate to show that it is different for different oscillational levels. The difference is so small, however, and the higher levels contribute so little to the entropy at ordinary temperature, that we are perfectly justified in taking I constant and in calculating the rotational and vibrational entropies separately, just as is frequently done for diatomic molecules.

The moment of inertia of nitrous oxide given in the paper of Plyler and Barker[3] is a misprint, and we have calculated our value from the constants given for the bands at 17μ and 8μ. For the moment of inertia of carbon dioxide we have taken the mean of the value given by Houston[5d] and one given in a private communication to one of us by E. F. Barker (70.6×10^{-40} from infra-red data).

Due to the large moment of inertia the partition function sum may be very accurately replaced by the integral and we obtain, in the case of nitrous oxide or hydrogen cyamide

$$Q_{\text{rot.}} = \sum_0^\infty (2j+1)\, e^{-j(j+1)\sigma} = \int_0^\infty (2j+1)\, e^{-j(j+1)\sigma}\, dj = \frac{1}{\sigma} = \frac{8\pi^2 IkT}{h^2}$$

Since carbon dioxide is symmetrical and the oxygen nuclei have no spin, only half the rotational levels are permitted in any given oscillational state. Due to the symmetry properties of the oscillations, in some cases the even levels will be permitted and others the odd ones. We must consequently write for the total partition function

$$Q = \sum_0^\infty (4j+1)\, e^{-2j(2j+1)\sigma} \sum_{\text{ev.}} p e^{-E_{\text{vib.}}/kT} + \sum_0^\infty (4j+3)\, e^{-(2j+1)(2j+2)\sigma} \sum_{\text{odd}} p e^{-E_{\text{vib.}}/kT}$$

The first part of the expression takes care of the vibrational states in which the even rotational levels are permitted, and the second part of the remainder. But as σ becomes small, the sums taken over the rotational levels will approach the same value whether the even or the odd levels are summed. Consequently we may, to a very good degree of approximation, write

$$Q \backsimeq {}^1/_2 \sum_0^\infty (2j+1)\, e^{-j(j+1)\sigma} \sum e^{-E_{vib.}/kT}$$

and

$$Q_{rot.} \backsimeq {}^1/_2 \int_0^\infty (2j+1)\, e^{-j(j+1)\sigma}\, dj = \frac{1}{2\sigma} = \frac{4\pi^2 IkT}{h^2}$$

The data employed in our calculations and some of the steps are given in Table I. It should be noted that the entropies calculated as above described do not contain the part due to spin and are the values which may be compared with the results of specific heat measurements. We may call them the "virtual" entropies and shall designate them by the symbol S^*. To obtain the absolute entropies we should presumably add, in the case of nitrous oxide, $R \ln 9$, and in the case of hydrogen cyanide $R \ln 6$.

TABLE I

CALCULATION OF THE ENTROPIES OF CARBON DIOXIDE, NITROUS OXIDE AND HYDROGEN CYANIDE AT 298.2°A.

The symbol p indicates the weight of a degenerate state or the number of states having the same or nearly the same energy.

	State			CO_2		N_2O		HCN	
	v_1^δ	v_2	v_3	$E_{vib.}$ (cm.$^{-1}$)	p	$E_{vib.}$ (cm.$^{-1}$)	p	$E_{vib.}$ (cm.$^{-1}$)	p
Vibrational	0	0	0	0	1	0	1	0	1
States	1	0	0	669	2	589.0	2	710	2
	2	0	0	1285	1	1167.3	1	~1411	3
				1316[a]	1	1179.6[c]	2		
				~1340[b]	1				
	0	1	0	1388	1	1285.4	1	~2090	1
	3	0	0	~2000	6	~1750	4	~2112	4
	1	1	0			~1868	2		
$Q_{vib.}$				1.088		1.133		1.068	
$T(d \ln Q_{vib.}/dT)$				0.281		0.372		0.232	
$I \times 10^{40}$				70.4		65.95		18.79	
$Q_{rot.}$				265.1		496.6		141.5	
$S_{vib.}$				0.726		0.987		0.592	
$S_{rot.}$				13.071		14.318		11.823	
${}^3/_2 R \ln M$				11.275		11.276		9.818	
${}^5/_2 R \ln 298.2 + S_0$				25.996		25.996		25.996	
$S^*_{298.2}$				51.07		52.58		48.23	
						$R \ln 9 =$		4.365 $R \ln 6 =$	3.559
$S_{298.2}$ (absolute)				51.07		56.94		51.79	

[a] 1316 = 669 + 647. [b] 1340 ≃ 2 × 669. [c] 1179.6 = 589.0 + 590.6

The only gas of the above three for which accurate data are available for comparison seems to be carbon dioxide. Using the calorimetrically determined entropy of carbon, the entropy of oxygen calculated by Giauque and Johnston[10] and the free energy and heat of formation of carbon dioxide as given in the "International Critical Tables," we find for the entropy of

[10] Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

this gas 50.0 entropy units at 298.2°A. The heat of formation may be a little uncertain, and if we use the value accepted by Lewis and Randall we obtain 50.5, a somewhat better check.

There are some data on hydrogen cyanide but when they are considered together with the calculated entropies they are found to be inconsistent. We shall reserve a discussion of the situation until somewhat later as we expect to redetermine the heat of combustion of hydrogen cyanide, in this Laboratory.

Acetylene.—Acetylene has been the subject of careful spectroscopic investigations[11] which show it to be a linear molecule. Unfortunately there is a slight uncertainty in regard to some of the vibrational states. An interpretation of the spectrum given by Mecke[12] seems to be not quite correct in some details since his designation of several bands is not in agreement with transition rules which seem to be on a good theoretical basis. Acetylene has in all five normal modes of oscillation, but only three of these and some of their combinations are of sufficiently low frequency to contribute appreciably to the entropy at ordinary temperatures. The lowest frequency $\nu^{\delta i}$ is not known directly but may be estimated from some combination bands to be about 620 ± 20 cm.$^{-1}$. This uncertainty introduces a possible error of about 0.04 entropy units in the calculation, and consequently is not serious.

The moment of inertia has been determined for several vibrational states but may be considered constant for the levels with which we are concerned. Due to the spins of the hydrogen nuclei and the absence of any in the carbon nuclei we have a situation similar to that found in the hydrogen

TABLE II

THE ENTROPY OF ACETYLENE AT 298.2°A.

Vibrational states State $\nu_1^{\delta i}$	ν_2^{δ}	ν_3^{i}	$E_{\text{vib.}}$ (cm.$^{-1}$)	p		
0	0	0	0	1	$I = 23.509 \times 10^{-40}$	
1	0	0	~ 620	2	$Q_{\text{rot.}} = \frac{1}{2\sigma}$	= 88.51
0	1	0	729.3	2		
2	0	0	~1240	3	$Q_{\text{vib.}}$	= 1.181
1	1	0	1328.5	4	$T\,(d \ln Q_{\text{vib.}}/dT)$	= 0.5390
0	2	0	~1460	3	$S_{\text{rot.}}$	= 10.892
3	0	0	~1860	4	$S_{\text{vib.}}$	= 1.401
2	1	0	~1970	6	$^3/_2\,R \ln M$	= 9.710
0	0	1	1975	1	$^5/_2\,R \ln 298.2 + S_0$	= 25.996
1	2	0	~2070	6	$S^*_{298.2}$	= 48.00
0	3	0	~2190	4	$R \ln 4$	= 2.754
					$S_{298.2}$ (abs.)	= 50.75

[11] Levin and Meyer, *J. Opt. Soc. Am.*, **16**, 137 (1928); Hedfield and Mecke, *Z. Physik*, **64**, 151 (1930).

[12] Mecke, *ibid.*, **64**, 173 (1930).

molecule. Alternate rotational levels have a weight of one, and the remainder a weight of three, but whether it is the odd or even levels which have the greater weight depends on the symmetry of the oscillational state. It is easily shown, however, that at temperatures high enough so that the rotational sum may be replaced by integrals the expression for Q reduces to the following

$$Q = Q_{\text{rot.}} \cdot Q_{\text{vib.}} \backsimeq {}^4/_2 \int_0^\infty (2j + 1)\, e^{-j(j+1)\sigma}\, dj \times Q_{\text{vib.}}$$

$$= \frac{4}{2\sigma} Q_{\text{vib.}}$$

The use of this expression gives us the absolute entropy, including the part due to spin. If the factor 4 is omitted we obtain the "virtual" entropy.

Summary

1. The calculation of the entropies of linear polyatomic molecules from spectroscopic data is shown to be similar to and only slightly more complicated than similar calculations for diatomic molecules.

2. The entropies of carbon dioxide, nitrous oxide, hydrogen cyanide and acetylene at 298.2°A. have been calculated from spectral data. The "virtual" entropies (those to be compared with calorimetric data) are found to be 51.07, 52.58, 48.23 and 48.00 entropy units, respectively. The absolute entropies are 51.07, 56.94, 51.79 and 50.75, respectively.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS FROM THE STANDPOINT OF FREE RADICALS. II. EXPERIMENTAL EVIDENCE OF THE DECOMPOSITION OF ORGANIC COMPOUNDS INTO FREE RADICALS

BY F. O. RICE, W. R. JOHNSTON[1] AND B. L. EVERING

RECEIVED MAY 6, 1932 PUBLISHED SEPTEMBER 5, 1932

In a recent paper[2] there was proposed an explanation for the decomposition of paraffin hydrocarbons based on the assumption that the unimolecular decomposition consists of the primary rupture of a C–C bond, with the formation of free radicals,[3] followed by the decomposition of those

[1] State Fellow, Washington.

[2] Rice, THIS JOURNAL, **53**, 1959 (1931).

[3] The following is a bibliography of some of the more recent work in which the thermal production and reactions of free radicals are studied: (a) Taylor, *Am. Phil. Soc.*, **65**, 90 (1926); (b) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); (c) Schultze and Müller, *Z. physik. Chem.*, [B] **6**, 267 (1929); (d) Paneth, *ibid.*, [B] **7**, 155 (1930); (e) Paneth and Lautsch, *Nature*, **125**, 564 (1930); (f) Taylor and Jones, THIS JOURNAL, **52**, 1111 (1930); (g) Paneth and Herzfeld, *Z. Elektrochem.*, **8**, 9 (1931); (h) Paneth and Lautsch, *Ber.*, **64**, 2702 (1931); (i) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).

radicals larger than ethyl into olefins and smaller free radicals, which then react with the surrounding hydrocarbon molecules forming a saturated hydrocarbon and regenerating free radicals. In this way a chain mechanism can be set up which explains in a satisfactory manner the different products formed in the pyrogenic decomposition of hydrocarbons. We have found this scheme highly satisfactory as a means of representing the thermal decomposition of a wide variety of compounds; we have applied it to the thermal decomposition of unsaturated hydrocarbons, ketones, aldehydes, acids and ethers, and it leads to a semi-quantitative prediction of the products formed which is in good agreement with the results of experiment. However, before publishing an account of these formal schemes it seemed desirable to attempt to obtain some evidence that the decomposition of organic compounds really proceeds through a mechanism of free radicals. While we have not been successful in proving beyond doubt that the ordinary thermal decomposition of hydrocarbons proceeds through such a mechanism, we have obtained a sufficient number of interesting experimental results bearing on this question that it seems desirable to publish an account of the work.

The outstanding difficulty in connection with any attempt to establish mechanisms based on free radical formation lies in the recent estimates of the strength of the C–C and C–H bonds; thus Mecke[4] calculates the energy of a C–H bond in methane to be 115 Cal. and that of C–C bonds in different hydrocarbons to be 110–115 Cal., as compared with the old values of 90 Cal. and 65 Cal., respectively. Since hydrocarbons decompose unimolecularly with an energy of activation of approximately 65 Cal., it is obvious that either hydrocarbons do not decompose through the mechanism of free radical formation, or else that the high values obtained from spectral data are incorrect. If the decomposition of organic compounds proceeds through a mechanism involving the primary rupture of a C–C bond, the strength of this bond cannot be greater than about 80 Cal.[5] A preliminary account of some experiments designed to demonstrate directly that free radicals are formed when hydrocarbons and other organic compounds are heated, was presented last year.[6]

[4] Mecke, *Nature*, **125**, 526 (1931). Since this paper was submitted, the authors have had an opportunity of discussing this matter with Profesor Mecke. He states that the thermal dissociation of organic compounds into *normal* fragments may certainly be in the range 70–80 Cal., since the high values given in his previous papers are for the adiabatic dissociation into fragments, one or more of which are *excited*. The primary process which actually takes place determines the experimentally found energy of activation. See Mecke, *Z. physik. Chem.*, **B18**, 53 (1932).

[5] This figure was obtained by taking the sum of the activation energy and the average vibrational energy; Professor D. H. Andrews finds from calculations based on Raman spectra that this latter figure for butane is 16.1 Cal. at 900°K.

[6] "The Preparation of Free Radicals," F. O. Rice and W. R. Johnston; "The Strength of the C–C Bond," F. O. Rice and B. L. Evering. Papers presented at the Buffalo Meeting of the American Chemical Society, September, 1931.

At that time we used an extremely simple method similar in principle to that of Paneth and Hofeditz;[3b] we found that when hydrocarbon vapors at pressures of a few mm. were passed through a quartz tube heated in the range of 800–1000°, the gases leaving the furnace rapidly removed mirrors of many different metals, such as lead, zinc and antimony, even at distances of 30 to 40 cm. from the furnace.

The first question which we may consider is whether this high temperature decomposition (in the range 800–1000°) is the same as the ordinary decomposition that occurs in the range 550–650°; a preliminary calculation supports the assumption that the two reactions are the same. Thus, from the results of Pease and Durgan[7] we find that butane must be heated for 5.2 seconds at 625° to undergo a 10% decomposition; in our own experiments the velocity of flow was of the order of 10^4 cm. per sec. and since the furnace was 10 cm. long the time of heating was of the order of 10^{-3} sec. By making a simple approximate calculation, using the Arrhenius equation and assuming the energy of activation to be 65,000 Cal., we find that we must heat butane to 900° for 10^{-3} sec. in order to decompose it to the extent of 10%. While we were able to remove mirrors at 800° or even lower, the hydrocarbon was obviously undergoing only a trace of decomposition; when, however, the temperature was in the neighborhood of 900°, a substantial fraction decomposed, as was shown by the amount of gas evolved and the amount of hydrocarbon recovered in the liquid-air trap.

The second question which we must consider is whether the agent that removes the mirrors really consists of free radicals formed by the rupture of a C–C bond, or whether it is perhaps composed of "hot" molecules, as suggested by Burk,[8] or of alkylidene radicals formed when two hydrogen atoms attached to the same carbon atom split off and form a hydrogen molecule, as suggested by Kassel.[9] There is also the possibility that in the high temperature decomposition the free radicals are produced at the silica surface; according to this suggestion a hydrogen atom of, for example, a butane molecule would stick to the silica surface, and the butyl radical would fly off and decompose into smaller radicals which are swept out of the furnace. On the basis of this mechanism, the free radicals are produced at the hot walls in the furnace and recombine on the cold walls outside.

One can best decide between these various hypotheses by a chemical analysis of the products formed by the combination of the metal and the active agent. We did not find it convenient to use metals such as lead, antimony or zinc for identification purposes, partly because the alkyl derivatives of these metals are liquids and the small quantities formed

[7] Pease and Durgan, THIS JOURNAL, **52**, 1262 (1930).

[8] Burk, *J. Phys. Chem.*, **35**, 2446 (1931).

[9] Kassel, *Chem. Rev.*, **10**, 18 (1932); Kassel, "Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., 1932, p. 233.

cannot readily be separated from the excess of hydrocarbon or other organic compound employed, and partly because if two or more radicals were present a large number of different compounds would result, owing to the polyvalent character of these elements. We found that by bringing the active material in contact with a cold surface on which metallic mercury continually condensed, it was possible to obtain mercury dialkyls which react readily and quantitatively with mercuric bromide to form alkyl mercuric bromides. These latter compounds are well-defined crystalline solids with definite melting points. Using this technique we have been able to show that when acetone is decomposed in our apparatus it gives only methyl groups, whereas propane and butane give a mixture of methyl and ethyl groups, the former predominating. It seems reasonably certain from such experiments that the agent that removes the mirror really consists of free alkyl radicals. Further work is necessary in order to determine whether the radicals are produced by a rupture of a C–C bond in the homogeneous gas phase or by the rupture of a C–H bond at a hot silica surface.

We have made some measurements of the life time of the free radicals by following Paneth's plan of noting the time of removal of standard mirrors placed at different distances from the furnace. We found that the rate of disappearance of the radicals at the concentrations produced in our experiment was of about the same order as that obtained by Paneth, namely, a half-life period of 0.006 sec. However, our unimolecular "constants" showed considerable drift and the bimolecular "constants" showed the same effect although not to quite the same extent. Possibly under the conditions of our experiments combination occurs to an appreciable extent both on the wall and in the gas phase. The rate of disappearance of the radicals seemed to be approximately independent of the compound used to produce them.

This method of production of free radicals from organic compounds suggests several ways for measuring directly the strength of the C–C bond. The first method permits us to make a direct measurement of the decomposition into free radicals. The time intervals required for the removal of a standard mirror at different distances from the furnace give us an arbitrary measure of the concentration of the radicals at these points, and by extrapolating we can obtain the concentration of the radicals as they leave the furnace. If we do this for two temperatures, both in the range in which the fractional decomposition is small, the ratio of the two concentrations so obtained is the ratio of the two velocity constants, and a simple calculation gives us at once the energy of activation of the decomposition into free radicals. If this energy of activation should be about 65,000 Cal. we would have strong evidence that the ordinary thermal decomposition of hydrocarbons consists of a primary dissociation into

radicals. Some preliminary experiments with acetone have indicated a value of 67,000 Cal. for the activation energy of the dissociation into free radicals, as compared with the accepted value of 68,500 Cal. for the ordinary thermal decomposition.[10]

The second method consists of an analysis of the products of the decomposition; thus if all the C–C bonds in butane have the same strength, the ratio of methyl and propyl to ethyl groups should be 2:1. It appears, however, that under the conditions of our experiment, in which there was considerable decomposition of the butane, the propyl groups are unstable and decompose, probably into ethylene and methyl groups. Under these conditions we should expect the decomposition to yield methyl and ethyl groups in the ratio of 2:1. Actually an experiment yielded a mixture of methyl mercuric bromide and ethyl mercuric bromide in the ratio of approximately 2.3:1. This method is subject to serious limitations because the decomposition in the furnace may not consist of a homogeneous dissociation through rupture of a C–C bond, and because the ethyl groups probably decompose to some extent into ethylene and hydrogen atoms or into methyl and methylene groups. The third way consists of a direct measurement of the heat of combination of two methyl groups, by passing the gases from the furnace into a calorimeter and noting the rise in temperature and the amount of ethane formed. We have not as yet made any measurements along these lines.

Experimental

Original Paneth Experiment.—We first built an apparatus in all respects practically identical with that of Paneth and Hofeditz,[3b] using hydrogen as the gas for carrying the lead tetramethyl. Our results completely confirmed those obtained in the original experiment. Following this we carried out a few simple experiments with the free methyl groups which were formed, according to the original method, in a current of hydrogen.

A platinum–rhodium thermocouple, sensitive to 0.5°, showed no rise in temperature when placed in the current of hydrogen containing the free methyl groups; that these were present in abundance could easily be shown by the fact that a lead mirror was readily removed after the gas had passed over the thermocouple.

In our next experiment we inserted a coil of copper wire consisting of about twenty turns of wire of 0.2 mm. diameter between the furnace and the mirror. A qualitative test showed that this had no effect on the methyl groups, since lead mirrors were removed apparently just as easily whether the coil was there or not. Heating the copper wire up to about 300° was also without effect. This experiment was repeated, using both iron and nickel in place of the copper, in each case with identical results. None of these metals, either hot or cold, had any perceptible effect on the methyl groups.

In another experiment a heavy lead mirror was formed for about 3 cm. along the tube; free methyl groups could not pass through this in the cold, since they combine

[10] Hinshelwood and Hutchinson, *Proc. Roy. Soc.* (London), **A111**, 245 (1926).

with it to form lead tetramethyl, but on heating the mirror to about 200° the free methyl groups apparently passed through unchanged, since they readily removed cold lead mirrors further down the tube.

Use of Condensable Gases.—In order to detect the free methyl radicals formed in the decomposition of lead tetramethyl, it is necessary to have a very rapid stream of gas in order to sweep the radicals away quickly from the heated zone in which they are formed. The use of a permanent gas such as hydrogen or nitrogen necessitates an elaborate pumping system, since all of the gas must be pumped out of the apparatus. If, however, one could use a substance which is frozen out by liquid air and which is not attacked by the free radicals, the experiment would be very much simplified, since an ordinary oil pump could then be used to maintain a vacuum in the apparatus. It occurred to us that water vapor had all of the characteristics that we required since it can be completely frozen out, is very stable and is easily purified. Our experiments with water vapor were successful and we found that metallic mirrors could be readily removed by the simple apparatus shown in Fig. 1.

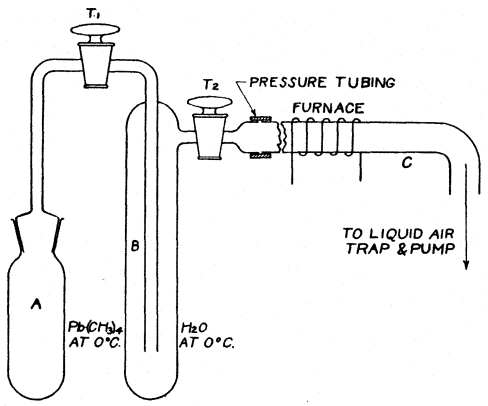


Fig. 1.—Apparatus for preparing free methyl groups using lead tetramethyl in a current of water vapor.

The quartz tube C can conveniently be about 50 cm. long and 0.4 cm. internal diameter, and contains a small piece of metal at the low pressure end which can be used to form mirrors. We have found that thick-walled rubber tubing is quite satisfactory for joining the ends of this quartz tube to the rest of the apparatus. The pressure in B is kept at about 4 mm.; by opening the stopcock T_1 the lead tetramethyl vapor bubbles through the water, and the rate can be easily regulated. When stopcock T_1 is shut, and T_2 is open, so that only water vapor passes over the metallic mirror, even the strongest heating of the quartz tube has no effect on either a lead or antimony mirror.

Carbon dioxide may also be used to carry the lead tetramethyl, but in this case the latter is kept in the trap B, in which a temperature about −80° is maintained and solid carbon dioxide is kept in trap A which is also maintained at −80°. The tubing joining A and B should have 50–100 cm. of 1 mm. capillary for convenience in regulating the flow of the carbon dioxide.

We have also found that the apparatus may be simplified still further by making a solution of lead tetramethyl in an organic solvent such as heptane or acetone. In this case no other transport gas is needed and only reservoir B is required; the temperature of this is adjusted so that the vapor pressure of the organic compound is 1 to 2 mm. as it enters the furnace. By using capillary tubing between trap B and the quartz tube the vapor pressure of the organic compound in B may be comparatively high. We found that a 1% solution of lead tetramethyl in heptane or acetone is quite satisfactory.

In removing mirrors by any of the methods described in this section, the first step is to open stopcocks T_1 and T_2 and evacuate the apparatus. This automatically removes all dissolved oxygen and makes unnecessary the elaborate purification train in the original Paneth experiment. The furnace is then heated to 500–600° and a metal-

lic mirror is formed by heating the piece of metal in the quartz tube. The mirror is then cooled with water, the stopcocks T_1 and T_2 are opened, and the current of gas containing the free methyl groups is allowed to pass over the mirror. Frequently the first mirror is either not removed or removed with difficulty because of surface impurities, and it is best to heat this while the current of gas is flowing and drive it down the tube. The stopcocks may then be turned off and a new clean mirror formed.

Life of Free Methyl Groups.—We next attempted to determine the life time of the free methyl groups produced by heating lead tetramethyl in a current of acetone. We followed the method developed by Paneth and his co-workers exactly, using a standard metallic mirror, which is distilled onto a quartz tube, and measuring the time of removal by the free radicals. The reciprocal of this time is assumed to be proportional to the concentration of the radicals. By taking measurements of the times of removal of standard mirrors at different distances from the furnace we found that the concentration of free methyl groups diminished rapidly as they passed down the tube. We measured the acetone pressures at the inlet and outlet of the quartz tube and also measured the weight of acetone passing through the apparatus in a known time interval. From this we could determine the time taken for the free methyl groups to pass from the end of the furnace to the standard mirror.

Paneth and his co-workers have investigated very completely the kinetics of the disappearance of the free methyl and free ethyl groups produced by the decomposition of the corresponding lead tetra-alkyl, using hydrogen, nitrogen and neon–helium mixtures as transport gases. They found that the rate of disappearance was approximately independent of the nature and pressure (over a range of a few mm.) of these gases, that the radicals disappeared according to a unimolecular law, and that the half-life was approximately 0.006 sec. in a tube of about 0.4 cm. diameter. Paneth and Herzfeld showed that the radicals combine mainly on the wall and only a small proportion combine in the homogeneous gas phase.

We present in Table I the results of some preliminary measurements in a quartz tube 0.4 cm. diameter, the acetone pressure at the standard mirror being 0.22 mm. mercury; the standard mirror was kept at one point and the furnace was moved along the tube to different distances from the mirror. The fall in pressure down the tube was 0.007 mm. per cm. length.

TABLE I

RATE OF DISAPPEARANCE OF FREE METHYL GROUPS FROM LEAD TETRAMETHYL

Using acetone as transport gas. 1% lead tetramethyl in acetone.

d, cm.	34	32	30	28	26	24	22	20
$\Delta t \times 10^4$, sec.	74.6	68.5	63.0	57.3	52.0	47.0	42.2	37.6
t_m, sec.	183	163	132	88	86	68	47	32

d is distance from furnace to standard mirror; Δt, time taken to travel from furnace to standard mirror; t_m, time required to remove standard mirror.

The constants calculated according to a first order equation show considerable drift so that the half-life varies from $1–2 \times 10^{-3}$ sec. as compared with 6×10^{-3} sec. obtained by Paneth and Hofeditz. There is somewhat better, but still not very good, agreement with a second order equation.

Free Radicals from Organic Compounds.—It seemed from the fore-

going experiments that it should be possible to decompose organic compounds, such as hydrocarbons or ketones, according to these methods but using the vapor of the material itself as transport gas. The apparatus shown in Fig. 2 was made for this purpose. It consists of a conical Pyrex flask A of about 50 cc. capacity, fitted with a well ground joint connected with 10–15 cm. of Pyrex tubing about 1 mm. internal diameter; this tube is fitted with the stopcock T_1 and is connected by pressure tubing to the quartz tube B, which is about 0.4 cm. in diameter and 50 cm. long. This tube in turn is connected by pressure tubing with a liquid-air trap and the pumping system. Tube B is also fitted with an electric furnace capable of sliding along the tube and has a groove at C for holding small pieces of different metals.

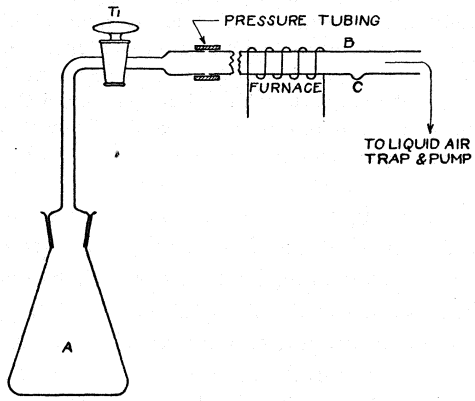


Fig. 2.—Apparatus for preparing free radicals from organic compounds.

When using this apparatus, about 20 cc. of an organic compound is placed in A and the apparatus is evacuated for a few minutes with stopcock T_1 open and flask A kept at a temperature about 50–100° below the boiling point of the organic compound. Any good oil pump capable of giving a vacuum of 0.05 mm. will do, although we found it practical to use an auxiliary mercury vapor pump on account of the greater speed of evacuation. When all the dissolved air has been displaced from the liquid and swept out of the apparatus, stopcock T_1 is closed and the apparatus is ready for use.

We found that a great variety of organic compounds, such as hydrocarbons, alcohols, ketones, acids, ethers and aldehydes, when passed through the furnace at 800–1000°, readily removed mirrors of many different metals, such as lead, antimony or zinc. The metal alkyls formed were caught in the liquid-air trap, together with the excess of the organic compound. Thus, when the fragments from acetone were used to remove antimony mirrors, the trap contained a colorless antimony compound, presumably antimony trimethyl, and a yellow oil insoluble in acetone, which on cooling in liquid air changed to a deep red solid. This oxidizes spontaneously in the air and is presumably the same compound that has been described by Paneth and Hofeditz.[3b]

It is very inconvenient to attempt to identify the free radicals in these compounds directly partly because of the difficulty of separating the small quantity formed from the excess of the original organic compound used as

the source of the free radicals and partly because of the large number of different compounds formed when we have a polyvalent metal and two or more free radicals present. We shall describe our final method of identification in a succeeding section.

It is particularly important in connection with this work not to permit any trace of oxygen to come in contact with the metallic mirror, since this prevents attack by the free radicals, presumably by coating the surface with a film of oxide.[11] However, after the furnace has been heated and the stream of organic compound is passing through, it is perfectly possible to admit oxygen on the side of the furnace away from the mirror; in fact we have removed lead and antimony mirrors by bubbling oxygen through the heptane in flask A. The limit to the amount of oxygen that can be used is fixed by the capacity of the furnace to bring about complete removal of free oxygen so that none reaches the mirror.

Surface impurities also may prevent attack by the free radicals. Preliminary heating in a current of pure hydrogen or other reducing gas frequently cleans up the metal so that the first mirror is readily removed.

Life of Free Radicals from Organic Compounds.—This can be determined, using the apparatus shown in Fig. 2, in a manner exactly similar to that described in the previous section, in which the life of free methyl groups obtained from lead tetramethyl was measured. The results, using acetone and heptane, are given in Table II. As before, the unimolecular velocity constants show a considerable drift and the half-life for the methyl groups from acetone varies from 0.55×10^{-3} to 2.8×10^{-3} sec. and the half-

TABLE II

RATE OF DISAPPEARANCE OF FREE RADICALS FROM HEPTANE AND ACETONE

Heptane			Acetone		
d, cm.	$\Delta t \times 10^4$, sec.	t_m, sec.	d, cm.	$\Delta t \times 10^4$, sec.	t_m, sec.
20	39.2	48	20	37.6	95
10	17.2	11	20	37.6	80
30	66.0	64	13	22.4	58
15	27.6	25	10	16.5	21
21	41.5	47	16	28.5	77
14	25.5	18	20	37.6	100
28	60.1	64	15	26.4	56
24	49.4	48	10	16.5	24
16	29.8	35			
12	22.3	19			

d is distance from furnace to standard mirror; Δt, time taken to travel from furnace to standard mirror; t_m, time required to remove standard mirror. Cross section of tube 0.4 cm. Pressure of heptane at mirror 0.24 mm.; fall in pressure, 0.0077 mm. per cm. length. Pressure of acetone at mirror 0.24 mm.; fall in pressure of acetone 0.007 mm. per cm. length.

[11] Paneth and Lautsch have recently reported[3h] that mirrors of tellurium are not subject to this inactivation.

life of the fragments from heptane varies from 0.84×10^{-3} to 2.2×10^{-3} sec. The observations do not give a very satisfactory constant when substituted in a second order equation.

Identification of Free Radicals.—We have found mercury alkyls most convenient for identification purposes, since they react quickly and quantitatively at ordinary temperatures with mercuric halides to give alkyl mercuric halides,[12] which are well-defined crystalline compounds. The apparatus shown in Fig. 3 was used for preparing the mercury alkyls from the free radicals.

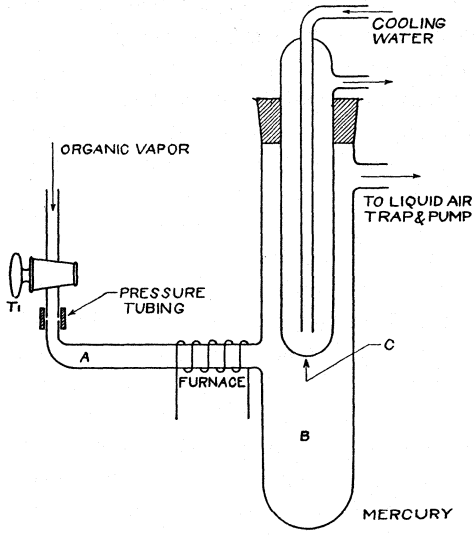


Fig. 3.—Apparatus for the preparation of organo-metallic compounds.

The organic compound is kept in a conical flask (not shown in the sketch) which is connected with the quartz sidearm A by means of pressure tubing. The temperature of the conical flask and the tubing from it are so arranged that a pressure of about 1 mm. is maintained at the entrance to sidearm A, which can be heated by means of an electric furnace to 800–1000°. The quartz tube B contains a few cc. of mercury; this is heated and distils and condenses on the water-cooled Pyrex tube C. The outer walls of B may be cooled either by air or water so that an additional pumping action is obtained.[13] Before starting a run a few cc. of saturated alcoholic mercuric bromide is placed in the liquid-air trap. This apparatus can be run continuously for several hours and requires no attention beyond renewing the liquid air occasionally. In one experiment we obtained almost a gram of alkyl mercuric bromides in a three-hour run, and it seems probable that by using a larger apparatus we could obtain 10-g. lots in a day's run. At the end of a run the contents of the liquid-air trap were allowed to warm up to room temperature[14] and filtered from the suspended mercury. A few

[12] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., New York, 1921, p. 65.

[13] See Newman, "Production and Measurement of Low Pressures," D. Van Nostrand Co., New York, 1925, p. 75.

[14] Organic solvents containing mercuric bromides or finely suspended mercury were never allowed to warm to higher than room temperature since there is the possibility of formation of organometallic compounds. Frequent tests showed that mercuric bromide does not react with organic substances under the conditions of our experiment.

cc. of hot alcohol was poured over the residue to dissolve any precipitated alkyl mercuric bromides, since these are not very soluble in cold ethyl alcohol. The filtrate containing the alkyl mercuric bromides was then evaporated to dryness at room temperature in a vacuum, and the solid residue sublimed by heating below 50° for an hour or two. In this way all the alkyl mercuric bromide can be separated from the excess of mercuric bromide, since the latter does not start to sublime at an appreciable rate below 70°.

In an experiment (No. 105) using acetone as the source of the free radicals and mercuric chloride[15] in the liquid-air trap, we obtained 0.5 g. of material from the first sublimation (carried out at 90°). This material melted at 140°, and a test with ammonium sulfide showed the presence of a large proportion of mercuric chloride. A second sublimation at 55° gave 0.22 g. of material which melted at 170°; this is the melting point given in the literature for methyl mercuric chloride.[16] A test with ammonium sulfide proved the second sublimate to be entirely free from mercuric chloride. A few grams of methyl mercuric chloride were prepared through the Grignard reaction[16] and a small quantity of this product was mixed with an approximately equal quantity of our material obtained from free radicals. The mixture melted at 170° and on cooling and solidifying it again melted at 170°. A mixture of equal parts of methyl mercuric chloride and mercuric chloride was ground up together in a mortar and the mixture was found to melt at 140–145°.

A similar experiment (No. 111) was performed using butane[17] as the source of the free radicals and having mercuric bromide in the liquid-air trap. The results of the sublimation are given in Table III.

TABLE III

FREE RADICALS FROM BUTANE

M. p. of CH_3HgBr, 160°; m. p. of C_2H_5HgBr, 193.5°

Fraction	Time of sublimation, hours	Temp. of sublimation, °C.	Yield, g.	M. p., °C.
1	1.0	40	0.217	157
2	1.0	50	.161	160.5
3	1.5	50	.110	172
4	1.5	50	.048	181.5
5	1.0	60	Trace	...

We have carried out a number of experiments in which we examined the alkyl mercuric bromides obtained from butane without finding any indication of the presence of propyl mercuric bromide. The product appears to

[15] Mercuric bromide is preferable to mercuric chloride because there is a greater difference in volatility between it and its alkyl derivatives than in the case of the chloride.

[16] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[17] 99% butane supplied by the Ohio Chemical and Manufacturing Co.

consist entirely of a mixture of methyl and ethyl mercuric bromides, although we were not able to isolate pure ethyl mercuric bromide and obtain a mixed melting point owing to the small quantities available.[18] By comparing the melting points of the fractions obtained in the butane decomposition with the melting points of known mixtures, we obtained a rough estimate of the composition of the four fractions, which contained approximately 10, 20, 62 and 80% of the ethyl compound, respectively. This estimate was further checked by measuring the lowering of the melting point of the pure substances caused by measured small additions of the different fractions. From these estimates we can conclude that under the conditions of our experiment, butane decomposes to give methyl and ethyl radicals in the proportion 7:3.

Propane[19] was also decomposed in the same apparatus (Experiment No. 112) using mercuric bromide in the liquid-air trap; a total of 0.906 g. of alkyl mercuric bromides was obtained from a preliminary sublimation at 60°. The results of a further sublimation into fractions are given in Table IV.

TABLE IV

FREE RADICALS FROM PROPANE

Fraction	Time of sublimation, hours	Temp. of sublimation, °C.	Yield	M. p., °C.
1	0.25	20	Trace	154.5
2	1	30	0.03	157
3	1	40	.03	157.5
4	1	50	.07	157
5	1	55	.18	157
6	2	55	.37	159.5
7	1	60	.04	175–177

We estimate, using the same method as described above for butane, that propane gives methyl and ethyl groups in the proportion 4:1.

Temperature Coefficient of Dissociation into Free Radicals.—An approximate estimate was obtained for acetone by using the apparatus shown in Fig. 2. A standard mirror of antimony was formed at a measured distance from the end of the furnace and the time of removal was noted with the temperature of the furnace at 746°; the experiment was then repeated with the furnace at 820°. Measurements were made with mirrors at different distances from the furnace and a series of ratios of the times of disappearance of such standard mirrors was thus obtained. The following are some of the measurements for acetone

[18] Further confirmation of these views has been obtained by comparing the x-ray spectra of methyl, ethyl and propyl mercuric bromides with the spectra of our fractions. This study was made by Dr. F. R. Whaley and will be described in a separate communication.

[19] We wish to thank the Carbide and Carbon Chemical Co. for supplying us with a cylinder of pure propane.

Distance from end of furnace, cm.	3.6	1.9	1.6
Time of disappearance, 746 °C., sec.	235.5	186	168
Time of disappearance, 820 °C., sec.	40	26.5	22
Ratio, t_{820}/t_{746}	5.9	7.0	7.6

We then deposited a series of standard mirrors perhaps 1–2 mm. beyond the edge of the furnace and kept them cool by a jet of air; we obtained the value 9.1 for the ratio, t_{820}/t_{746}. The values of the energy of activation Q for different ratios are

Q	60,000	65,000	70,000	75,000	80,000
k_{820}/k_{746}	7.43	8.79	10.41	12.3	14.52

Although our measurements are very crude, we have convinced ourselves that the ratio of the velocity constants at the two temperatures is less than 10.4 at the end of the furnace and therefore the energy of activation for the reaction producing the free radicals must be about 67,000 cal. per mole as compared with 68,500 obtained by Hinshelwood and Hutchinson for the ordinary thermal decomposition. This very close agreement is somewhat fortuitous because our measurements are probably in error to the extent of ±5000 cal.

Experiments at Higher Pressures.—It seemed desirable to see whether we could obtain any evidence of the existence of free radicals when a hydrocarbon was heated at higher pressures (40–70 mm.) in the temperature range 550–650°; to this end we constructed the apparatus shown in Fig. 4. It consists of a quartz tube A connected with a butane reservoir through a quartz to Pyrex seal and stopcock T_1. A mercury pressure gage P enables us to determine the pressure in A, which can be allowed to come to any desired point by regulating stopcock T_2 which is connected with the pumping system. Tube A is fitted with an inner tube D through which a stream of cooling water circulates; tube A also contains a small piece of antimony with an iron core which can be moved from point B to point C and back by means of a magnet.

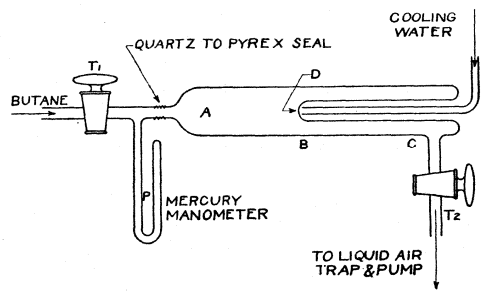


Fig. 4.—Apparatus for testing for the presence of free radicals at higher pressures.

In a preliminary experiment, stopcock T_2 was kept fully open so that there was a pressure of only 1–2 mm. of butane in tube A. The piece of antimony was drawn to point B and an antimony mirror distilled onto the inner tube at point D. The piece of antimony was then drawn down to point C and the tube A heated in the range 800–1000° with the oxyhydrogen flame; mirrors formed in this way were very readily removed.

A second experiment was then performed; after forming a mirror at D and removing the piece of antimony to C, stopcock T_2 was partly closed, so that the pressure in A rose to 70 mm. The part of the tube at B was then heated strongly by means of an ordinary Bunsen burner for several minutes. A large flame was used and the tube was heated strongly for several cm. on each side of the point B; the temperature was probably in the range 550–650°. However, we did not notice the slightest effect on the mirror. On opening stopcock T_2 and reducing the pressure to 1–2 mm., continued heating with the Bunsen flame likewise had no effect; however, on heating with the oxyhydrogen flame the mirror was rapidly removed. We then repeated this experiment but heated the tube B, which contained the butane at 70 mm., with the oxyhydrogen flame instead of the Bunsen burner. Several minutes heating had no effect whatsoever on the mirror as long as the pressure was in the neighborhood of 70 mm.; however, as soon as we opened the stopcock T_2 and reduced the pressure to 1 to 2 mm., the mirror was rapidly and completely removed. It seems therefore that free radicals must have been produced in this experiment but had all recombined before they could diffuse across the 2 or 3 mm. of gas at 70 mm. to the mirror; presumably recombination of free radicals, probably through primary collisions, occurs very rapidly at higher pressures since several experiments in the range 40–70 mm. gave identical results.

Discussion

It seems well at this point to consider the bearing of these results on the theory proposed in the first paper of this series.[2] In order to do this we must consider separately the several different possible reactions which may bring about the production of free radicals.

In the first place, the high temperature decomposition may consist of a homogeneous dissociation into free radicals through the rupture of a C–C bond; the radicals thus formed may be swept out of the furnace without undergoing any reaction with the surrounding molecules. On this basis, propane should yield a 1:1 mixture of methyl and ethyl groups, and butane should yield a mixture of methyl and ethyl groups in the ratio of 2:1, assuming that the propyl radicals largely decompose into ethylene and methyl groups and that the three C–C bonds are approximately equal in strength. Acetone, on this basis, might be expected to decompose into methyl groups since the acetyl group formed in the primary decomposition probably goes to pieces at once, forming CO and CH_3. This scheme is not in very good agreement with our experiments because it calls for a ratio of methyl to ethyl of 1:1 in propane and 2:1 in butane, whereas the experimental results are 4:1 and 2.3:1, respectively. However, we must remember that the free radicals are produced by heating the hydrocarbon vapor to 800–900° and undoubtedly they must undergo many collisions with the surrounding hydrocarbon molecules before leaving the furnace; consequently we may expect a chain mechanism such as was described in the first paper of the series; the free radicals which combine with the metallic mirrors should be the same as the carriers postulated in the previous paper. According to this view ethane should not give metal alkyls because the hydrogen atom is the only carrier, propane should give only methyl groups, and butane should give methyl and ethyl groups in the ratio of 3:2, assuming no decomposition of the ethyl

groups. Our results so far are more in accord with this scheme than with that discussed in the previous paragraph.

Finally it is possible that the hydrocarbon may lose a hydrogen atom at the heated quartz surface of the furnace. This would yield the same products as the suggested chain mechanism since in this case a hydrogen atom is given up to the surface instead of to a free radical.

The experimental work that we have done so far is in very good accord with the views expressed in the first paper of this series, and we believe that further work along these lines will enable us to decide definitely as to whether free radicals play an important part in the decomposition of organic compounds in the range 550–650°.

The authors wish to thank Dr. K. F. Herzfeld and Dr. J. E. Mayer for many suggestions and help during the course of this work. We also wish to thank Mr. C. E. Schildknecht for help in preparing some of the organometallic compounds from free radicals.

Conclusions

1. A condensable gas such as water vapor or carbon dioxide can be substituted for the permanent gas used in the experiment of Paneth and Hofeditz for the production of free radicals from lead alkyls. A very simple apparatus can therefore be used for preparing the free radicals.

2. A great variety of organic compounds when heated in the range 800–1000° decompose into free radicals; by removing the products rapidly from the furnace, the free radicals formed can be combined with many different metals.

3. When acetone is decomposed in this way it gives only methyl groups, propane gives 80% methyl and 20% ethyl and butane gives 70% methyl and 30% ethyl.

4. The half-life of the free radicals obtained under these conditions is about $1–2 \times 10^{-3}$ sec. as compared with 6×10^{-3} sec. obtained by Paneth and his co-workers. The rate of disappearance does not follow either a first order or second order equation very well.

5. The temperature coefficient of the decomposition into free radicals has been measured for acetone and has been found to be approximately identical with the temperature coefficient of the ordinary thermal decomposition of acetone.

6. A qualitative experiment proved that free radicals in butane at 40–70 mm. pressure did not show the Paneth effect on a metallic mirror a few mm. away from the point of origin of the free radicals.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE PHYSICAL LABORATORY, THE STATE UNIVERSITY OF IOWA]

THE VAPOR PRESSURES OF AQUEOUS SOLUTIONS OF LITHIUM NITRATE AND THE ACTIVITY COEFFICIENTS OF SOME ALKALI SALTS IN SOLUTIONS OF HIGH CONCENTRATION AT 25°

BY J. N. PEARCE AND A. F. NELSON

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Of all the colligative properties of solutions none are more accessible to thermodynamic treatment than the lowering of the vapor pressure of the solvent. Further, the advantages offered by this method are that it can be employed isothermally, that the vapor pressure can be measured over the entire range of concentration from pure solvent to the saturated solution in contact with the solid salt, and that the activity of the solvent can be obtained directly from vapor pressure measurements. An accurate knowledge of the vapor pressures of solutions permits us to calculate the free energy of dilution and the activities of both the solute and the solvent. It affords also a very valuable method for testing the theories of concentrated solutions.

The best obtainable chemically pure lithium nitrate was repeatedly recrystallized from pure distilled water. The purified salt was then dissolved at room temperature to form a stock solution just short of saturation and stored in a tight glass-stoppered bottle. The exact concentration of this solution was determined by a series of determinations in which accurately weighed portions were converted to the sulfate and heated to constant weight. All of the solutions were first prepared on a molar basis by diluting accurately weighed portions of the mother solution to one liter at 25°. The various solutions were made up with conductivity water which had been distilled from an alkaline solution of potassium permanganate.

The density of each solution at 25° was accurately determined, at least in duplicate, by means of large 35-cc. Ostwald pycnometers, using a similar pycnometer for counterpoise. An accurately calibrated set of precision brass weights was used. All weighings were made on a large precision balance by the oscillation method and were corrected for the buoyancy of the air. The weights of the solution taken in these density measurements are accurate to one part in 300,000.

The apparatus and experimental procedure employed in this research were those devised by Pearce and Snow.[1] The vapor pressure apparatus, exclusive of the generators, preheater and absorber, was immersed in a large Freas water thermostat maintained at 25 ± 0.005°.

The actual calculation of the vapor pressure of the solvent over the solution requires the knowledge of three values only: the corrected barometric pressure, P, and the weight of water vapor, W_W, taken up by the phos-

[1] Pearce and Snow, *J Phys. Chem.*, **31**, 231 (1927).

phorus pentoxide absorber while W_S grams of silver are being deposited in the coulometer. The number of moles of water vapor, n_1, and the total number of moles of hydrogen and oxygen, n_2, electrolytically generated are calculated from W_W and W_S, respectively. The vapor pressure of the solvent, p, is calculated directly from these data by means of the simple relation

$$P = \frac{n_1}{n_1 + n_2} P$$

The essential vapor pressure data for solutions of lithium nitrate are collected in Table I. Here m is the molality of the solution, d is the density and p is the vapor pressure. Each vapor pressure recorded is the mean of at least three independently determined values. Only in one case did the pressure differ from the mean by more than 0.003 mm. We are including also data previously obtained for solutions of potassium chloride,[1] potassium iodide,[2] sodium chloride,[3] sodium bromide[2] and lithium chloride.[4] The data for these are collected in Tables II to VI. The vapor pressure data for all of the salts are graphically represented in Figs. 1 and 2. For all of these salts (Fig. 1) the vapor pressure of the solvent diminishes rapidly with increasing concentration and finally attains the value characteristic of the saturated solution at 25°. It will be observed that the vapor pressure of the lithium chloride solution at saturation (m = 19.2)

TABLE I

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF LITHIUM NITRATE AT 25°

m	d	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^{0,1}$, cal.
0.00000	0.99707	23.752	1.000	1.000	...	..
.10058	1.00116	23.676	0.997	0.766	1.92	12
.20179	1.00494	23.593	.993	.726	3.98	772
.40594	1.01295	23.431	.986	.697	8.07	1548
.61264	1.02074	23.256	.979	.688	12.51	2026
.82194	1.02847	23.071	.971	.696	17.24	2388
1.0339	1.03616	22.882	.963	.718	22.12	2704
2.1115	1.07507	21.823	.919	.969	50.11	3899
3.3106	1.11303	20.518	.864	1.275	86.76	4757
4.5706	1.15094	19.028	.801	1.600	131.45	5396
5.9276	1.18825	17.481	.736	1.938	181.71	5924
7.3940	1.22515	15.843	.667	2.239	240.0	6378
8.9836	1.26183	14.128	.597	2.546	306.2	6776
10.7055	1.29886	12.403	.541	2.891	364.2	7100
11.8331	1.32024	11.359	.478	3.174	437.6	7353
12.8639[a]	1.33885	10.456	.442	3.415	484.1	7532

[a] Saturated.

[2] Pearce, Taylor and Bartlett, THIS JOURNAL, 50, 2951 (1928).

[3] Fred Fordemwalt, Master's thesis, Iowa.

[4] Donald Tilden, Master's thesis, Iowa.

is only a little more than one-half of the vapor pressure of pure water at 0°. The relative positions of the vapor pressure curves and the relative magni-

TABLE II

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE at 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^{0\cdot1}$, cal.
0.0	23.752	1.000	1.000	...	..
.2	23.597	0.993	0.708	3.88	733
.4	23.448	.988	.655	7.63	1463
.6	23.296	.981	.627	11.49	1892
.8	23.155	.975	.607	15.09	2195
1.0	23.017	.969	.595	18.63	2436
1.5	22.620	.952	.576	28.94	2878
2.0	22.243	.936	.536	38.90	3192
2.5	21.877	.921	.557	48.74	3444
3.0	21.497	.905	.557	59.13	3660
3.5	21.089	.888	.557	70.62	3843
4.0	20.696	.871	.564	81.64	4016
4.81[a]	20.021	.843	.576	101.29	4260

[a] Saturated.

TABLE III

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF POTASSIUM IODIDE AT 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^{0\cdot1}$, cal.
0.0	23.752	1.000	1.000	...	..
.1	23.686	0.997	0.734	1.65	0
.2	23.620	.994	.666	3.30	707
.4	23.486	.988	.597	6.68	1399
.6	23.384	.983	.558	10.17	1799
.8	23.211	.976	.535	14.31	2091
1.0	23.072	.971	.519	17.22	2319
1.5	22.702	.957	.496	26.21	2746
2.0	22.316	.940	.483	36.97	3062
2.5	21.922	.923	.479	47.52	3311
3.0	21.516	.906	.480	59.60	3526
3.5	21.100	.888	.486	70.17	3727
4.0	20.681	.871	.492	82.07	3900
4.5	20.253	.853	.498	94.52	4054
5.0	19.822	.834	.511	107.2	4209
5.5	19.392	.816	.546	120.0	4401
6.0	18.966	.799	.577	133.4	4569
6.5	18.529	.780	.608	147.2	4726
7.0	18.082	.761	.644	161.7	4883
7.5	17.635	.742	.680	176.5	5029
8.0	17.190	.724	.709	191.6	5155
8.5	16.750	.705	.748	207.1	5290
8.938[a]	16.370	.689	.783	220.6	5404

[a] Saturated.

TABLE IV

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF SODIUM CHLORIDE AT 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^{0.1}$, cal.
0.0	23.752	1.000	1.000	...	..
.2	23.594	0.992	0.732	4.74	782
.4	23.444	.987	.659	7.74	1480
.6	23.286	.980	.641	11.77	1928
.8	23.127	.974	.633	15.70	2254
1.0	22.969	.969	.630	18.74	2513
1.5	22.560	.949	.638	31.28	3009
2.0	22.134	.930	.657	43.11	3385
2.5	21.692	.914	.721	53.04	3759
3.0	21.227	.894	.788	66.71	4081
3.5	20.733	.868	.862	83.81	4370
4.0	20.210	.850	.944	96.38	4636
4.5	19.677	.828	1.087	111.6	4943
5.0	19.135	.803	1.136	129.9	5120
5.5	18.576	.782	1.182	145.7	5281
6.0	17.990	.758	1.238	164.7	5439
6.138[a]	17.825	.704	1.372	208.2	5587

[a] Saturated.

tudes of the vapor pressures at any given concentration are characteristic of the individual salts, as will be discussed later.

The plots of the fractional lowering of the vapor pressure against the molal concentrations of these uni-univalent salts are shown in Fig. 2. Theoretically, the fractional lowering of the vapor pressure of the solvent of an ideal solution is equal to the mole fraction of the solute. For non-electrolytes

$$\frac{p_0 - p}{p_0} = \frac{n_2}{n_1 + n_2}$$

If we assume complete dissociation of these binary salts, and if the ions behave as perfect solutes, the fractional lowering should be given by

$$\frac{p_0 - p}{p_0} = \frac{2n_2}{n_1 + 2n_2}$$

Here n_1 is the number of moles of water and $2n_2$ is the number of moles of ions from n_2 moles of the binary salt. If then, to repeat, we assume that the salts are completely dissociated and that their ions form perfect solutes, the curves representing the fractional lowering of the vapor pressure with the concentration of the salts should coincide exactly with the mole fraction–molality curve. While it is already a well-known fact, it is also very evident from Fig. 2 that solutions of these salts are far from ideal. While other causes may be effective, the position and slopes of these curves, especially in the more concentrated solutions, show, perhaps more than anything else, the rate of change in the apparent mole fraction of the water actually present as solvent.

TABLE V

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF SODIUM BROMIDE AT 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^{0,1}$, cal.
0.0	23.752	1.000	1.000	...	..
.1	23.675	0.997	0.739	1.92	0
.2	23.608	.994	.693	3.60	746
.4	23.448	.987	.643	7.63	1479
.6	23.292	.981	.628	11.59	1932
.8	23.136	.974	.611	15.58	2240
1.0	22.973	.967	.607	19.77	2499
1.5	22.556	.950	.598	30.56	2960
2.0	22.128	.932	.633	41.98	3369
2.5	21.670	.912	.715	54.38	3778
3.0	21.181	.892	.812	67.90	4145
3.5	20.655	.870	.924	82.81	4481
4.0	20.094	.848	1.036	99.14	4775
4.5	19.501	.821	1.203	116.9	5092
5.0	18.876	.795	1.374	136.2	5374
5.5	18.242	.768	1.565	156.5	5641
6.0	17.603	.741	1.762	177.6	5885
6.5	16.934	.713	2.010	200.6	6136
7.0	16.234	.682	2.291	225.6	6379
7.5	15.570	.656	2.594	250.3	6607
8.0	14.888	.627	2.951	276.9	6838
8.5	14.231	.599	3.348	303.6	7059
9.0	13.582	.572	3.784	331.3	7277
9.131[a]	13.409	.565	3.895	338.9	7324

[a] Saturated.

It has been shown[5] long ago that the hydrating power of a salt in solution is primarily a function of the cation, that the hydration of an ion is an inverse function of its volume, and that the magnitude of hydration of the ions is a periodic function of the atomic weights. It is interesting to note, Fig. 2, that the curves for the fractional lowering of the vapor pressure produced by the two potassium salts are practically superimposed, the one on the other. Just above them lie the curves for the two sodium salts; the fractional lowering produced by the sodium bromide is at all concentrations greater than that for the corresponding solutions of sodium chloride. Of the two, sodium bromide exhibits the greater hydrating power. Still higher on the plot lie the curves for the lithium salts with the most highly hydrated lithium chloride on top.

The order of increasing fractional lowering of the vapor pressure of water produced by the different salts at any one concentration is exactly that to be predicted on the basis of the hydrate theory. In the hydration of the ions part of the water molecules are removed from the field of action as solvent.

[5] Jones and Pearce, *Am. Chem. J.*, **38**, 683 (1907); see also Washburn and Millard THIS JOURNAL, **37**, 694 (1915).

TABLE VI

THE VAPOR PRESSURE, ACTIVITY COEFFICIENT AND FREE ENERGY DATA FOR AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE AT 25°

m	p, mm.	a_1	$\gamma_\pm$	$-\Delta\bar{F}_1$, cal.	$-\Delta\bar{F}_2^0$, cal.
0.0	23.752	1.000	1.000	....	....
.1004	23.724	0.999	0.755	0.70	3
.2185	23.633	.995	.710	2.98	853
.4040	23.492	.989	.678	6.53	1527
.6082	23.349	.983	.678	10.14	2012
.8142	23.166	.975	.689	14.80	2377
1.0216	22.992	.968	.711	19.28	2683
1.5471	22.399	.943	.895	34.76	3448
2.0845	21.751	.916	1.155	52.17	3583
2.6327	21.110	.889	1.457	69.90	4656
3.1940	20.370	.858	1.827	91.05	5154
3.7687	19.594	.825	2.284	114.1	5615
4.3576	18.787	.791	2.849	139.0	6049
4.9582	17.687	.745	3.550	174.8	6450
5.5749	16.574	.697	4.467	213.3	6875
6.2074	15.592	.657	5.472	249.4	7243
6.8567	14.562	.613	6.713	290.0	7603
7.5199	13.337	.562	8.180	342.1	7947
8.2002	12.274	.517	9.986	391.3	8286
9.6109	10.260	.432	14.545	497.5	8920
11.0955	8.046	.339	19.972	641.7	9467
12.6577	6.388	.269		778.6	
14.3221	5.054	.214		915.0	
16.0508	4.003	.168		1055.7	
17.8635	3.203	.135		1187.8	
19.2186[a]	2.770	.117		1273.8	

[a] Saturated.

According to the Mass Law, the hydration per single ion should be greatest in the most dilute solutions and it should decrease in magnitude as the concentration of the ions is increased. In spite of this decrease in the magnitude of ionic hydration with increase in concentration, the total amount of water removed from the field of solvent by hydration should be greatest in the most concentrated solution. The greater the number of molecules taken up as hydrate water, the greater will be the decrease in the effective value of n_1, and, correspondingly, the greater will be the mole fraction of the solute. It follows, therefore, that if the value of the mole fraction of the solute is thus abnormally increased by the formation of hydrates in the solution, the fractional lowering of the vapor pressure will be increased correspondingly. This is fully borne out by the relative positions and slopes of the curves in Fig. 2.

There is still another way of explaining the abnormally high fractional lowering of the vapor pressure produced by these salts. According to the present views, strong electrolytes in aqueous solution are completely, or

practically completely, dissociated at all concentrations. All deviations of the colligative properties of these solutions from the behavior demanded by the classical theory are considered to be due to the influence of interionic attraction.[6] Because of the electrical attraction between the positive and negative ions, there are on an average in the neighborhood of any given ion more ions of unlike than of like sign. Consequently, with increase in concentration of the ions accompanying the addition of the salt the attraction between the ions will increase and will attain a maximum value at

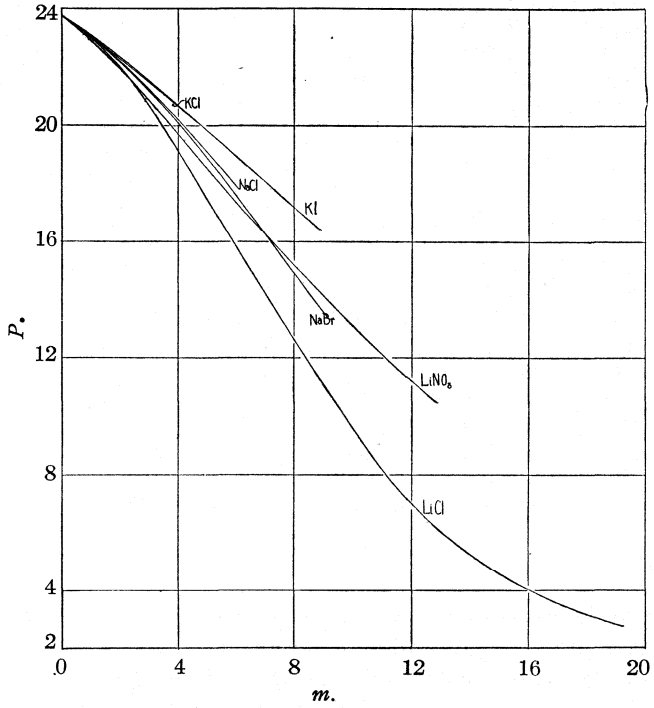

Fig. 1.

saturation. At saturation when the ions are at their closest approach they will assume, doubtless, within the solvent a more or less mobile, lattice-like structure. Further, the molecules of the polar solvents possess a dipole structure. Hence, if we consider the ions in solution as point charges, the molecules of the solvent will not be unaffected by the presence of the strong electric fields of the ions. Some of the dipole water molecules will be attracted to and oriented by the electrically charged ions. Because of this attraction and orientation these molecules will lose a part, if not all, of their characteristic fugacity. Hence, the vapor pressure of the solution will be less than it would be if no such attraction existed. It is obvious, therefore,

[6] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

that with increasing concentration of the ions the number of water dipoles thus affected and removed from the field of solvent as such will be increased. At saturation the concentration of the ions, and hence the attractive influence of their charges, is fixed. The system becomes invariant and the vapor pressure is constant for a given temperature. The ultimate effect will be the same as that which would be produced by ionic hydration in the ordinary sense.

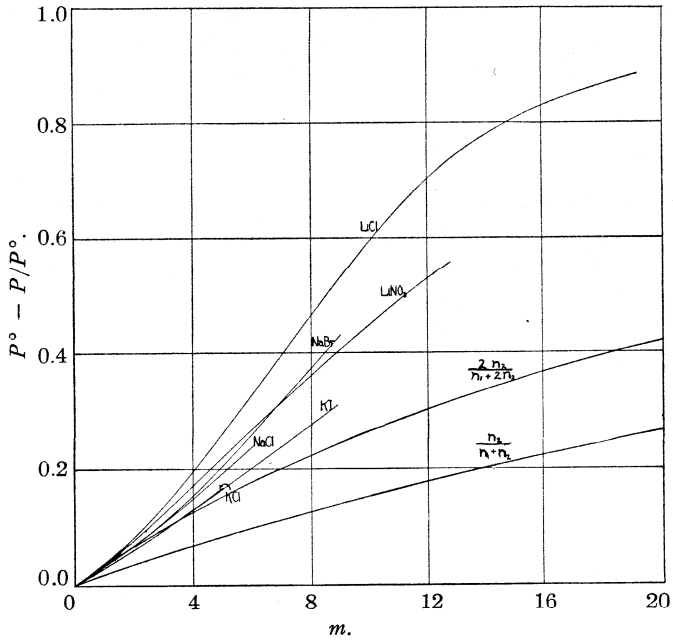

Fig. 2.

In this discussion we have assumed that the univalent ions of smaller ionic volume will have the greater charge densities. For this reason they will attract and orient a greater number of water dipoles than will the univalent ions of large ionic volume. The relative positions of the mole fraction–molality curves for these salts must, therefore, be the same as those described above.

The above considerations apply equally well in explaining the positions of the vapor pressure curves of the various solutions, Fig. 1. As we might expect, the positions of the vapor pressure–molality curves assume an order exactly the reverse of that taken by those for the fractional lowering. Briefly stated, the greater the degree of hydration of the ions of a salt at a given concentration, the smaller will be the amount of water present as solvent and, hence, the lower will be the vapor pressure of the solution. It would seem to follow, therefore, that any theory of interionic attraction

must take into account the influence of the solvent dipoles which, in their attraction by the charged ions, must modify to some degree the attraction between the ions themselves.

At all concentrations above 4 m the fractional lowering of the vapor pressure produced by these salts is greater than that calculated for the completely dissociated salt. At the lower concentrations, however, the fractional lowering curves appear to lie slightly below the theoretical curve. The concentrations at which the two intersect extend to higher concentrations as the hydrating power of the ions increases.

The activity of the solvent has been calculated by means of the series relation[7]

$$\ln a_1 = -\left(\frac{p_0 - p}{p_0}\right) - \frac{1}{2}\left(\frac{p_0 - p}{p_0}\right)^2 - \frac{1}{3}\left(\frac{p_0 - p}{p_0}\right)^3 \cdots$$

In very dilute solutions only the first term is of any significance, but more terms must be added as the concentration is increased. In our calculations of ln a_1 terms have been added until the effect of an additional term becomes negligible.

The activity coefficients of the ions, $\gamma_{\pm}$, were calculated by means of the relation of Randall and White[8]

$$\ln \gamma_{\pm} = -\frac{h}{2.303} - \frac{2}{2.303}\int_0^{m^{1/2}} \frac{h}{m^{1/2}}\, dm^{1/2}$$

where $h = 1 + 55.51 \ln a_1/\nu m$, and ν is the number of ions formed from one molecule.

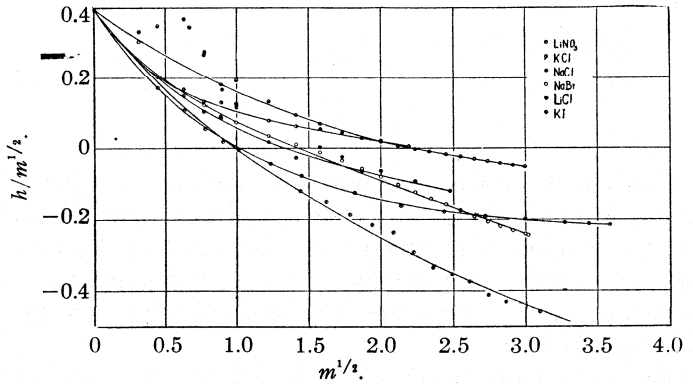

Fig. 3.

The value of h was calculated for each concentration and the values of $h/m^{1/2}$ were then plotted against the square roots of the corresponding molalities. A smooth curve, Fig. 3, was then drawn through the points to

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 274.

[8] Randall and White, THIS JOURNAL, **48**, 2514 (1926).

the limiting value[9] of $h/m^{1/2}$ (0.394) for $m = 0$ at 25°. The integral in the equation is the area under the curve. This was measured by means of a polar planimeter.

The activity coefficients calculated in this manner have been plotted against the square roots of the corresponding concentrations, Fig. 4. For the sake of convenience in plotting, five of the curves have been displaced upward successively by increments of 0.025. For each salt the values of the activity coefficients pass through a minimum value and then rise more or less rapidly with increase in concentration of the salt. Here again we observe that the increase in the value of the activity coefficients at the

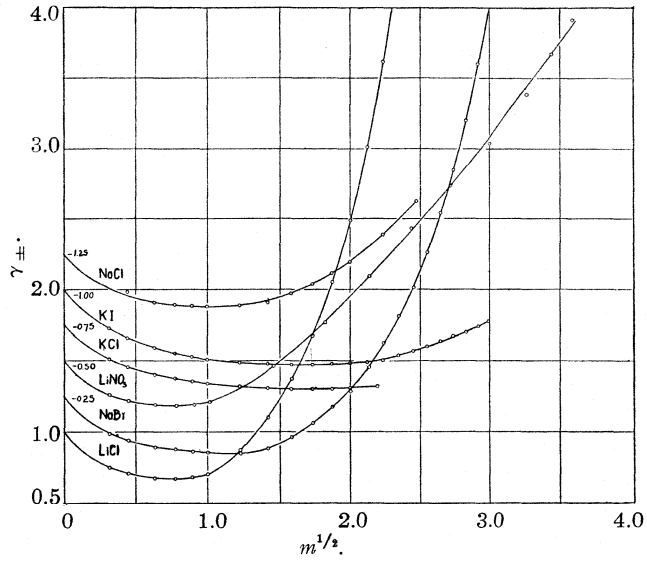

Fig. 4.

higher concentrations is the most rapid for those salts which are the most highly hydrated in solution. The curves for the slightly hydrated potassium salts are practically superimposed the one on the other. Owing to the sensitivity of the h function to slight errors, the values of the activity coefficients of lithium chloride above 11.0 m have not been included. It is needless to say that they are very high.

Alluring as it might be, any attempt to apply the Debye-Hückel equation,[6] or any of its subsequent modifications, to solutions of the concentrations here used would be futile indeed.

The accuracy attainable by our vapor pressure method is to be seen by a comparison of the activity coefficients of potassium chloride determined by different methods, Table VII. The values given by Randall and White[8]

[9] Randall, THIS JOURNAL, **48**, 2512 (1926).

TABLE VII

A COMPARISON OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE OBTAINED BY DIFFERENT METHODS

m	V. p. (R.-W.)[10]	F. p. (Harned)[11]	E. m. f. (Harned)[12]	V. p. (*P.-S.*)[1]
0.001		0.965	0.965	0.965
.005		.926	.926	.926
.010		.899	.899	.900
.050		.809	.815	.813
.100	0.772	.762	.764	.763
.200	.715		.712	.708
.500	.651		.644	.638
1.000	.651		.597	.595
1.500			.576	.576
2.000	.570		.569	.563
2.500			.568	.557
3.000			.571	.557
3.500			.571	.557
4.000			.581	.564
4.810				.574

are calculated from the vapor pressure data of Frazer, Lovelace and Sease[10] at 20°. The data for freezing point[11] and electromotive[12] force methods are taken from compilations by Harned. For comparable concentrations the agreement is excellent indeed.

The free energy change involved in the transfer of one mole of water from the pure solvent to a solution of any molality m is given by $-\Delta F_1 = RT \ln 1/a_1$. These values have been calculated for each series of salt solutions and are to be found in the next to the last column of Tables I to VI. The values given in the last column in each table represent the change in free energy accompanying the transfer of one mole of solute from a solution of molality m to one which is exactly 0.1 m. Here again we find that for any given concentration the values of $-\Delta F_1$ and $-\Delta \overline{F}_2^{0.1}$ are always greater, the greater the hydrating power of the dissolved salt.

Summary

The vapor pressures of aqueous solutions of lithium nitrate and five alkali halides have been determined at 25° for concentrations ranging from 0.1 m up to saturation.

From these data there have been calculated the activity of the solvent, the geometric mean activity coefficients of the ions, and the free energy changes accompanying the transfer of solute and solvent.

[10] Frazer, Lovelace and Sease, THIS JOURNAL, **43**, 102 (1921).

[11] Harned, in Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931, p. 769.

[12] Harned, *ibid.*, p. 772.

A theoretical discussion of the vapor pressure relations of the various salts has been given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ALDEHYDE BISULFITE COMPOUNDS. II. THE EFFECT OF VARYING HYDROGEN ION AND OF VARYING TEMPERATURE UPON THE EQUILIBRIUM BETWEEN BENZALDEHYDE AND BISULFITE ION

BY T. D. STEWART AND L. H. DONNALLY

RECEIVED MAY 17, 1932 PUBLISHED SEPTEMBER 5, 1932

Elsewhere we have shown[1] that the specific rate of dissociation of benzaldehyde bisulfite

$$C_6H_5CH(OH)SO_3^- \longrightarrow C_6H_5CHO + HSO_3^- \qquad (1)$$

increases rapidly as the hydrogen-ion concentration is decreased from (H^+) 10^{-2} to 10^{-7}. Since the equilibrium at $(H^+) = 10^{-7}$ is still in favor of the bisulfite compound, the reverse of Reaction 1 is evidently even faster. Therefore it is not possible to use an ordinary titration method for the determination of the amounts of the substances in equilibrium. The method developed is as follows.

Experiment.—Benzaldehyde which had been distilled in an atmosphere of nitrogen was added mole per mole to C. P. sodium bisulfite. Distilled water which had been boiled and saturated with nitrogen was added and the reaction allowed to go to completion. All water used was boiled and saturated with nitrogen to expel both carbon dioxide and oxygen. The salt thus obtained was washed four times with water and finally dissolved in water to make an approximately 1 *M* solution of sodium benzaldehyde bisulfite; 5 cc. of this solution was diluted for each determination to one liter, making the initial concentration of benzaldehyde bisulfite about 0.005 *M*. These solutions were allowed to stand in the thermostat to reach equilibrium.

Except for determinations at *P*H 1 and 13 where solutions of 1 *N* hydrochloric acid and 0.1 *N* sodium hydroxide were used, buffer solutions of standard or measured *P*H values were employed for the dilution. In the range *P*H 1.5 to 3 and *P*H 6 to 7.5 a phosphate buffer, and *P*H 1.5 to 3 and *P*H 6, acetate buffer solutions were used, the acidities of which were determined against standard buffer solutions with a glass electrode. From *P*H 9 to 12 Sörensen standard borate buffer solutions were used. For the phosphate and acetate buffer solutions it was determined by means of a glass electrode that the bisulfite compound, benzaldehyde and bisulfite ion in equilibrium had a negligible effect on the *P*H values of the solution. With the borate buffer a hydrogen electrode was used for this purpose. In this case because of the doubtful effect of bisulfite on the electrode benzaldehyde alone of the constituents was used. A negligible effect was found.

Analysis.—Since the dissociation reaction is slow at *P*H 2, the determination of ionic sulfite in equilibrium in the buffer solutions was made by rapidly acidifying the solution and simultaneously adding iodine in slight excess of the ionic sulfite. For this purpose an amount of 1 *N* hydrochloric acid sufficient to acidify the particular buffer

[1] Stewart and Donnally, THIS JOURNAL, **54**, 2333 (1932).

to P_H 2 was placed in a two-liter beaker. Iodine solution was added, and to the mixture with vigorous stirring the buffered equilibrium mixture was rapidly added. The excess of iodine was then back titrated with thiosulfate and the time during which the solution was in contact with excess iodine was measured. In order to make a correction for this time (which never amounted to more than 0.2 cc. out of 90), 0.2 cc. of iodine was added and the time of disappearance of this iodine was measured. Bicarbonate was then added and the amount of bisulfite addition compound was determined by further titration with iodine. The P_H value of the borate buffer solution was, when necessary, corrected for the amount of acid added as bisulfite.

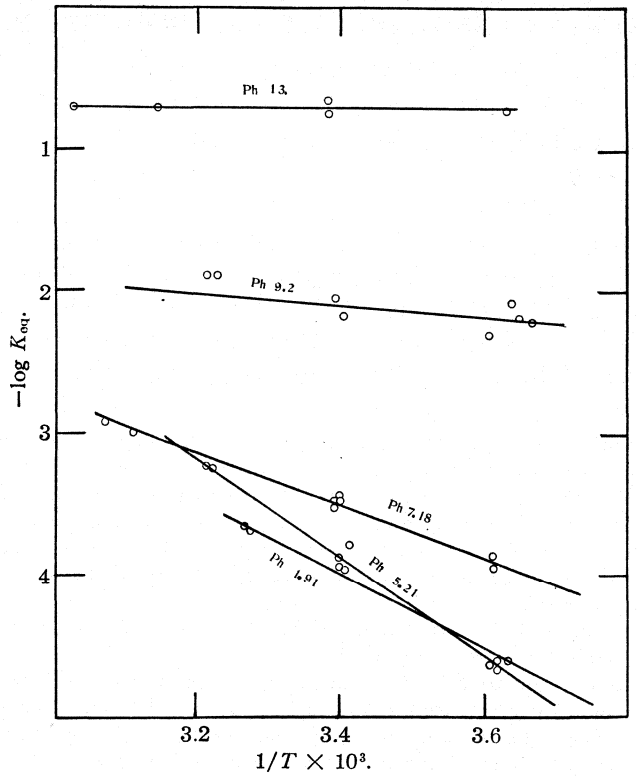

Fig. 1.—The change in equilibrium with the temperature.

It is evident that after addition to the 1 N acid solution the P_H can never be greater than 2, but that at the interface of the two solutions when mixed there is a time when the iodine is competing with the benzaldehyde for the sulfite ion. There is good reason to believe that the iodine–sulfite reaction is many times as fast as the benzaldehyde–sulfite reaction; nevertheless, it was decided to test the possibility of change in the equilibrium amount during this acidification. Two solutions were made up, one containing 0.0015 mole of benzaldehyde, 0.1 mole of hydrochloric acid and 0.004 mole of iodine in 300 cc., the other containing 0.0015 mole of sodium sulfite and 0.05 mole of sodium hydroxide, in 200 cc. of solution.

The second solution was added to the first and it was found that about 5×10^{-6} mole of benzaldehyde bisulfite had been formed, which is within experimental error.

Determinations were made at several values of P_H for various temperatures, the results being given in Table I, and plotted on Fig. 1. Table II gives results obtained for other values of P_H, at 21°. In Table III are average values of the equilibrium constant taken at 21° for all values of

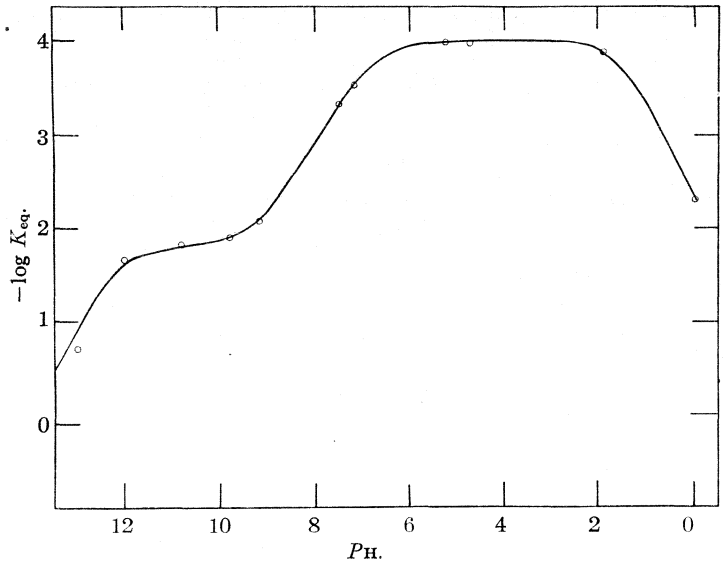

Fig. 2.—The change in the equilibrium with change in hydrogen-ion concentration at 21°.

P_H measured. On Fig. 2 we have plotted log K against P_H. The constant is defined by the equation

$$K_{eq.} = \frac{(\Sigma H_2SO_3)(\Sigma C_6H_5CHO)}{(\Sigma C_6H_5CH(OH)SO_3H)}$$

where the summation symbol implies, respectively, the total ionic sulfite, the free benzaldehyde and the total addition product in any form. The unit concentration is moles per liter.

TABLE I

EFFECT OF TEMPERATURE AND HYDROGEN-ION CONCENTRATION UPON THE EQUILIBRIUM

Phosphate buffer, P_H 1.91; phosphate buffer, P_H 7.18; acetate buffer, P_H 5.21

Temp., °C.	$K \times 10^5$	Temp., °C.	$K \times 10^4$	Temp., °C.	$K \times 10^4$
3.2	2.20	3.4	1.12	1.7	0.244
3.4	2.48	3.5	1.37	3.5	.240
19.6	15.8	20.9	3.40	20.3	1.07
20.3	13.1	20.9	3.29	20.4	1.10
34.6	57.4	21.5	2.91	20.9	1.13
37.3	60.8	21.5	3.22	32.3	2.10
		46.2	10.2	33.0	2.21
		53.1	12.5		

TABLE I (*Concluded*)

0.1 *N* NaOH, P_H 13		Borate buffer, P_H 9.2	
Temp., °C.	*K*	Temp., °C.	$K \times 10^2$
2.0	0.190	0.0	0.610
22.0	.237	.9	.648
22.0	.185	4.2	.472
45.0	.193	20.4	.664
58.0	.201	21.5	.889
		35.9	1.29
		38.9	1.31

TABLE II

THE EQUILIBRIUM AT 21° AT VARYING HYDROGEN-ION CONCENTRATIONS

Borate buffer		Borate buffer		Acetate buffer	
P_H	$K \times 10^2$	P_H	$K \times 10^2$	P_H	$K \times 10^4$
12.0	1.99	9.8	1.22	4.77	1.06
12.0	2.06	9.8	1.21	4.77	1.07
12.0	2.22	9.2	0.817		
12.0	1.92	9.2	0.848	1.0 *N* HCl	
12.0	2.05	Phosphate buffer		P_H	$K \times 10^3$
10.8	1.73	P_H	$K \times 10^4$	0.0	5.05
10.8	1.37	7.55	4.10	0.0	4.73
10.8	1.48	7.55	4.15		

TABLE III

AVERAGE VALUES OF *K* AT TEMPERATURE 21°

P_H	*K*	P_H	*K*
0.00	4.85×10^{-3}	9.20	8.32×10^{-3}
1.91	1.26×10^{-4}	9.80	1.21×10^{-2}
4.77	1.06×10^{-4}	10.8	1.53×10^{-2}
5.21	1.00×10^{-4}	12.0	2.05×10^{-2}
7.18	2.95×10^{-4}	13.0	2.0×10^{-1}
7.55	4.15×10^{-4}		

Summary

The equilibrium in dilute solution between benzaldehyde, sodium bisulfite and sodium benzaldehyde bisulfite has been measured in the range from 1.0 *N* acid to 0.1 *N* alkali.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ALDEHYDE BISULFITES. III. THE EFFECT OF CHANGING HYDROGEN-ION CONCENTRATION UPON THE SPECIFIC REACTION RATE OF THE ADDITION OF SODIUM BISULFITE TO BENZALDEHYDE. IV. DISCUSSION OF THE EQUILIBRIUM, RATES, AND TEMPERATURE COEFFICIENTS AS AFFECTED BY HYDROGEN-ION CONCENTRATION

BY T. D. STEWART AND L. H. DONNALLY

RECEIVED MAY 17, 1932 PUBLISHED SEPTEMBER 5, 1932

For the system benzaldehyde, sodium bisulfite and their addition product we have elsewhere[1] reported the apparent specific dissociation velocity constants from P_H 1 to 6.8 and the apparent equilibrium constants from P_H 1 to 13. From these data it is possible to calculate the apparent specific velocity constants for the addition reaction

$$\Sigma C_6H_5CHO + \Sigma HSO_3^- \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \Sigma C_6H_5CH(OH)SO_3^- \qquad (1)$$

over a range P_H 1 to 6.8 from the relation

$$\frac{k_1}{k_2} = K_{eq.} = \frac{(\Sigma C_6H_5CHO)(\Sigma HSO_3^-)}{(\Sigma C_6H_5CH(OH)SO_3^-)} \qquad (2)$$

$K_{eq.}$, k_2 and k_1 are, respectively, the equilibrium constant, the specific rate of addition and the specific rate of dissociation. These calculated values, a few of which are given in Table I, have been verified by three sets of experiments made at P_H 1.91, 5.2 and 7.5. The results of these are also given in Table I.

TABLE I

CALCULATED AND OBSERVED SPECIFIC REACTION RATES OF THE ADDITION REACTION AT 21°

P_H	k_2 (obs.)	k_2 (calcd.)	P_H	k_2 (obs.)	k_2 (calcd.)[a]
1.91	27	26.2	7.5	2×10^5	5×10^5
	26.8			4×10^5	
	28			6×10^5	
	30			4×10^5	
5.2	1.0×10^4	1.3×10^4			

[a] This calculated value was obtained by a method described in Part IV which permits the calculation of k_2 from P_H 3 to 13. Only the equilibrium could be directly measured at P_H 7.5 with accuracy.

The procedure was to add benzaldehyde solution quickly to a solution of sulfite in a buffer with very vigorous mechanical stirring. The solutions were deaerated and the reaction carried out in nitrogen. At the end of a measured time the reaction was stopped by the addition of excess iodine mixed with acid precisely as described in the measurements on equilibrium.[1]

[1] Stewart and Donnally, THIS JOURNAL, **54**, 2333 (1932).

The time intervals varied from three seconds to thirty minutes. By varying concentrations of benzaldehyde and sulfite it was determined that each of these substances came into the rate law to the first power.

The calculated values are probably more accurate than the observed, because of the greater precision of the measurements of rate and equilibrium. The agreement shows complete correlation between the experimentally determined quantities and justifies the use of Equation (2).

IV. Discussion of the Equilibria, Rates and Temperature Coefficients as Affected by the Hydrogen-Ion Concentration.—By making certain assumptions with regard to rate laws it is possible to deduce the apparent specific reaction rates for both the addition and dissociation reactions in the alkaline region (PH 7 to 13) where both reactions are too fast to measure. The change in the apparent specific rate constants, k_2 and k_1, and in the apparent equilibrium constant, $K_{eq.}$, with the change in PH, may be accounted for by assuming that each of the various ionic and molecular species present in a solution of sodium bisulfite, benzaldehyde and their addition product, is concerned in a specific reaction rate characteristic of it. Only those species whose concentrations are a function of hydrogen-ion concentration are of course considered. These molecular species may be detailed as follows: (1) the three derivatives of H_2SO_3, namely sulfite ion, bisulfite ion and sulfurous acid, which react with benzaldehyde at specific rates k_d, k_e and k_f, respectively; (2) the three derivatives of benzaldehyde bisulfite, namely

$$C_6H_5CH\begin{cases}O^- \\ SO_3^-\end{cases}, \quad C_6H_5CH(OH)(SO_3^-) \text{ and } C_6H_5CH(OH)SO_3H$$

which dissociate into bisulfite or sulfite and benzaldehyde at specific rates of k_a, k_b and k_c, respectively; (3) the two species of benzaldehyde

$$C_6H_5CHO \text{ and } C_6H_5CH\begin{cases}O^- \\ OH\end{cases}$$

the ion reacting with sulfite at a very slow rate and present in appreciable amount only in very alkaline solution.

The Addition Reaction.—The general rate law for the addition reaction may be written as

$$\frac{-d(\Sigma H_2SO_3)}{dt} = k_2(\Sigma H_2SO_3)(\Sigma C_6H_5CHO) = C_6H_5CHO\,[k_dSO_3^- + k_e(HSO_3^-) + k_f(H_2SO_3)] \quad (3)$$

The constant k_2 has been evaluated in Part III of this series as a function of PH, and log k_2 has been plotted against PH in Fig. 1. Simple rate laws corresponding to limited ranges of PH will be established, and through them the constants k_d, k_e and k_f may be evaluated.

For the region PH 3 to PH 6 in Fig. 1, it is seen that within experimental error log k_2 is directly proportional to PH and that the slope of the curve is

nearly unity, which means that k_2 is directly proportional to the first power of hydroxyl ion. Since the first and second dissociation constants, K'_A[2] and K''_A[3] of sulfurous acid are, respectively, 1.7×10^{-2} and 1.1×10^{-7}, the ratio of bisulfite ion to sulfite ion in the above P_H range is greater than

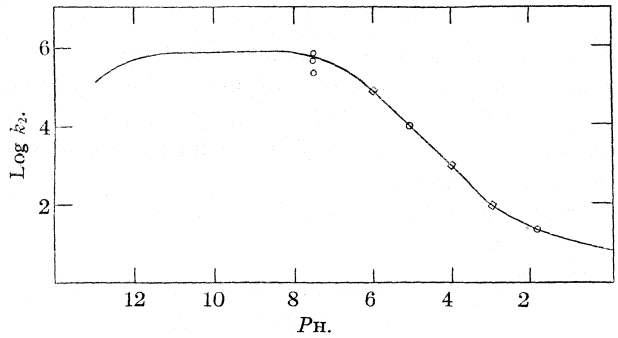

Fig. 1.—The change in the specific addition reaction rate with hydrogen-ion concentration at 21°: circles represent directly determined data; squares represent a calculation of k_2 from the ratio k_1/K_{eq}.

ten, and the concentration of sulfurous acid is negligible. The predominating molecular species present is therefore bisulfite ion and the empirical rate law becomes

$$\frac{-d(HSO_3^-)}{dt} = C(OH^-)(HSO_3^-)(C_6H_5CHO) = \frac{CK_W}{K''_A}(SO_3^=)(C_6H_5CHO) = k_d(SO_3^-)(C_6H_5HCO) \quad (4)$$

where C is a constant defined by the equation

$$k_2 = C(OH^-) \quad (5)$$

and K_W and K''_A are the dissociation constants of water and bisulfite ion, respectively. It is therefore evident that in the P_H region under discussion, the predominating rate-determining step may be considered as involving sulfite, not bisulfite, ion and that k_d is the specific reaction constant for that path. The equations are

$$C_6H_5CHO + SO_3^= \longrightarrow C_6H_5CH(OH^-)(SO_3^-) \xrightarrow[\text{fast}]{H^+} C_6H_5CH(OH)SO_3^- \quad (6)$$

The evolution of k_d from the observed k_2 is best made in the center of this P_H region, since at the acid end the path involving bisulfite ion cannot be neglected, and at the alkaline end the concentration of sulfite ion deviates widely from that given by the assumption of a linear relationship to the hydroxyl-ion concentration. At P_H 5.2, (H^+) is 6.3×10^{-6} and k_2 is 1.3×10^4 min.$^{-1}$, from which k_d is $7.45 = 10^5$ min.$^{-1}$.

[2] "International Critical Tables," Vol. VI, p. 260.

[3] Kolthoff, *Chem. Weekbl.*, **16**, 1154 (1918).

For the region P_H 6 to 11 it seems reasonable to assume that the rate-determining step involves sulfite ion also.

$$\frac{-d(\Sigma H_2SO_3)}{dt} = k_2(\Sigma H_2SO_3)(C_6H_5CHO) = k_d(SO_3^=)(C_6H_5CHO) \quad (7)$$

$$k_2 = k_d \frac{(SO_3^=)}{(\Sigma H_2SO_3)} \quad (8)$$

Using this equation it is possible to evaluate k_2 between P_H 6 to 11, in which range k_d is approached as a maximum. The measured value of k_2 at P_H 7.5, given in Table I, Part III, is of the correct order of magnitude, the agreement of observed and calculated values being better than the possible experimental error in k_2.

The Dissociation Reaction.—The general rate law for the reaction of dissociation may be written as

$$\frac{-d(\Sigma C_6H_5CH(OH)SO_3H)}{dt} = k_1(\Sigma C_6H_5CH(OH)SO_3H) = k_a(C_6H_5CH(O^-)(SO_3^-) + k_bC_6H_5CH(OH)(SO_3^-) + k_c(C_6H_5CH(OH)SO_3H) \quad (9)$$

The constant k_1 has been evaluated in Part I of this series as a function of P_H, and log k_1 has been plotted against P_H in Fig. 2.

For the region P_H 3 to 6.8 (Fig. 2), covered by the observed values of k_1, we observe the same sort of linear relationship between log k_1 and P_H, of unit slope, as has been discussed for the addition reaction. Since the acid, $C_6H_5CH(OH)SO_3H$, has a first dissociation constant K'_B of at least 3×10^{-2},[4] the concentration of the ion $C_6H_5CH(OH)SO_3^-$ does not change appreciably in this P_H range. The increase in k_1 must therefore be due either to hydroxyl-ion catalysis or a weak second dissociation of the hydroxysulfonic acid. Using the latter assumption the rate law becomes

$$\frac{-d(C_6H_5CH(OH)SO_3^-)}{dt} = k_a(C_6H_5CH(O^-)SO_3^-) \quad (10)$$

For the P_H range 3 to 6, an approximate relation holds where K''_B is the second dissociation constant of the hydroxysulfonic acid.

$$k_1 = \frac{k_aK''_B}{(H^+)} \quad (11)$$

Over the P_H range 3 to 11

$$k_1 = k_a \frac{(C_6H_5CH(O^-)SO_3^-)}{(\Sigma C_6H_5CH(OH)SO_3H)} \quad (12)$$

[4] The first dissociation constant of sulfurous acid K'_A is given in the "International Critical Tables," Vol. VI, p. 260, as 1.7×10^{-2}. To compare this with the first dissociation constant of the acid $C_6H_5CH(OH)SO_3H$, 500-cc. volumes of 0.1 M solution of the salts were titrated with 6.00 N hydrochloric acid using a glass electrode. The e. m. f. measurements were

6.0 N HCl, cc.	0.0	1.0	2.0	4.0	5.0	8.0
$NaHSO_3$ solution, cc.	0.3330	0.2190	0.0990	0.0790	0.0720	0.0606
$C_6H_5CH(OH)SO_3Na$ solution, cc.	0.1732	0.0897	0.0772	0.0644	0.0630	0.0546

From this it appears that the first dissociation constant of the α-hydroxysulfonic acid is about 3.7×10^{-2}.

With increasing alkalinity, k_1 approaches k_a as a maximum and so the latter can be evaluated, since the equilibrium constant, K_{eq}, is known over the P_H range 0–13 (see Part II) and the apparent specific addition rate constant, k_2, can be calculated in the alkaline range by the method given in the previous section. When k_1 is thus evaluated from the product $k_1K_{eq.}$ for different values of P_H, and log k_1 plotted against P_H, a plot similar to that of Fig. 2 is obtained, with a maximum value for k_1 reached at about P_H 11 of 1.1×10^4 min.$^{-1}$. Assuming this value for k_1, and taking the observed value of k_1 at P_H 5 as 7.65×10^{-1}, we find K''_B to be 6.95×10^{-10}.

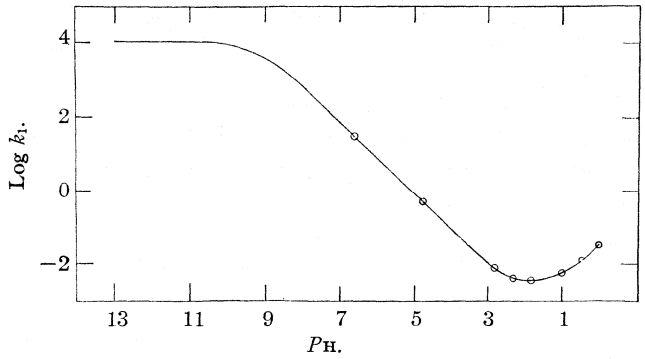

Fig. 2.—The change in the specific dissociation reaction rate with hydrogen-ion concentration at 21°.

The alternative explanation of the increased reaction rate based on catalysis by hydroxide ion seems to be unnecessary. If the calculation of the apparent specific rates of addition k_2 in the alkaline range is correct, then the calculated values of the dissociation reaction (k_1) in the alkaline range are also correct. But these indicate a marked deviation in the range P_H 9 to 11 from values directly proportional to hydroxide ion (see Fig. 2), which is hardly to be expected if the increase in rate in the P_H range 3 to 9 were due to catalysis by hydroxide ion.

In the region P_H 1 to 3, the rate of dissociation reaches a minimum. No simple rate law is applicable, so that this region is assumed to involve all three steps postulated in equation 9.

In the region P_H 1 to 0 a first order dependence of k_1 upon hydrogen ion is again observed (Fig. 2). We shall assume provisionally that this is due to the formation in small amount of the relatively reactive undissociated hydroxysulfonic acid, whose first dissociation constant K'_B we estimated above to be 3.7×10^{-2}. The first order dependence of k_1 upon hydrogen-ion concentration is obviously inconsistent, in this P_H range, with this value of the dissociation constant, so we shall use the above assumption and our measurements to evaluate the constant, bearing

in mind that for acids of this strength the constant has little real significance. Using the same development as before we find

$$\frac{-d(\Sigma C_6H_5CH(OH)SO_3H)}{dt} = k_1(\Sigma C_6H_5CH(OH)SO_3H) = k_c(C_6H_5CH(OH)SO_3H) \quad (13)$$

and for the limited P_H range, where log k_1 is proportional to P_H

$$k_1 = \frac{k_c(H^+)}{K'_B} \quad (14)$$

Using a method to be described in the next section, the best values of k_c and K'_B are of the order 30 × min.$^{-1}$ and 1 × 10^3, respectively. These values are consistent with the data involving rates and with the above assumed mechanism. The inconsistency with the measured value of K'_B may be taken as indicating the presence of a still larger number of reacting species or what amounts to the same thing, a hydrogen-ion catalysis of the reaction of the undissociated sulfonic acid. In this P_H region, then, the important rate-determining step involves hydrogen ion to the first power, and the simplest single explanation rests upon the assumption that the sulfonic acid is a very strong acid. In keeping with this, the main reaction in acid solution may be written

$$C_6H_5CHO + H_2SO_3 \rightleftharpoons C_6H_5CH(OH)SO_3^- + H^+ \quad (15)$$

Measurements of the equilibrium show the proper dependence upon the hydrogen-ion concentration and suggest a difference in the strengths of the two acids of far greater magnitude than is given by the electrode measurements.[5]

The Equilibrium.—The apparent equilibrium constant is conventionally defined by Equation 2, Part III, using the dissociation as the forward reaction. The main reaction for specific P_H regions, as deduced from the foregoing and from Fig. 2, Part II are

For the region P_H 0–1

$$C_6H_5CHO + H_2SO_3 \rightleftharpoons C_6H_5CH(OH)SO_3^- + H^+ \quad (16)$$

For the region P_H 3–7

$$C_6H_5CHO + HSO_3^- \rightleftharpoons C_6H_5CH(OH)SO_3^- \quad (17)$$

For the region P_H 10–12

$$C_6H_5CHO + SO_3^= \rightleftharpoons C_6H_5CH(O^-)SO_3^- \quad (18)$$

For the region P_H 12–13

$$C_6H_5CHO + OH^- \rightleftharpoons C_6H_5CH(O^-)(OH) \quad (19)$$

$$C_6H_5CH(O^-)(OH) + SO_3^= \rightleftharpoons C_6H_5CH(O^-)SO_3^- + OH^- \quad (20)$$

These equations describe the dependence or independence of the equilibrium with respect to P_H (Fig. 2, Part II). The intermediate regions involve a combination of these main reactions. The addition of hydroxide

[5] An alternative explanation of the shift of equilibrium with hydrogen ion would be the removal of benzaldehyde from the equilibrium in the form of an oxonium salt. It should also be mentioned that the ionic strength of the solution in the acid range varies considerably, but that previous measurements in buffers of different concentration showed a very slight dependence of the rates and equilibrium upon the ionic strength as compared to dependence upon the hydrogen-ion concentration.

ion to benzaldehyde is assumed to explain the increase in dissociation with increase in P_H in strongly alkaline solutions. There is abundant evidence of this type of reaction.

General Equations.—The apparent specific dissociation rate constant, k_1, may be expressed in terms of the hydrogen-ion concentration, (H^+), the two dissociation constants, K'_B and K''_B of the hydroxysulfonic acid, and the specific reaction rate constants k_a, k_b and k_c which have been previously defined. By using the relation

$$(\Sigma C_6H_5CH(OH)SO_3H) = (C_6H_5CH(O^-)SO_3^-) + (C_6H_5CH(OH)SO_3^-) + (C_6H_5CH(OH)SO_3H) \quad (21)$$

and substituting into Equation 9 expressions defining the above quantities we obtain

$$\frac{-d(\Sigma C_6H_5CH(OH)SO_3H)}{dt} = \left[\frac{\frac{K''_Bk_a}{(H^+)} + k_b + \frac{k_c(H^+)}{K'_B}}{\frac{K''_B}{(H^+)} + 1 + \frac{(H^+)}{K'_B}}\right] \Sigma C_6H_5CH(OH)SO_3H \quad (22)$$

The first quantity in brackets on the right-hand side of the equation is the apparent specific reaction rate constant, or the constant we have designated as k_1. We have already evaluated two of the constants in Equation 22, k_a and K''_B. The value of k_b may be found by setting up simultaneous equations, or from Fig. 2 by drawing two lines with slope plus one and minus one through the points at P_H 0 and 5, respectively. The intersection of these two lines gives the moles per minute of benzaldehyde bisulfite dissociating through each of the paths $C_6H_5CH(OH)SO_3H$ and $C_6H_5CH(O^-)SO_3^-$ at the minimum point. From the curve the actual minimum is found and the difference between it and the sum of the moles per minute through the other two paths may be taken equal to k_b since the value of $(\Sigma C_6H_5CH(OH)SO_3H)$ is essentially that of $(C_6H_5CH(OH)SO_3^-$ at P_H 2. Evaluating the remaining constants simultaneously from observed values of k_1, k_c is found to be about 30 and K'_B about 1×10^3. A summary of the values of the constants is given in Table II.

TABLE II

THE CONSTANTS OF EQUATION 22

Constant	Numerical value	Reactant
k_a	1.1×10^4	$C_6H_5CH\langle^{O^-}_{SO_3^-}$
k_b	2.23×10^{-3}	$C_6H_5CH(OH)(SO_3^-)$
k_c	*ca.* 30	$C_6H_5OH(OH)SO_3H$
K''_B	6.95×10^{-10}	$C_6H_5CH(OH)SO_3^-$
K'_B	*ca.* 1×10^3	$C_6H_5CH(OH)(SO_3H)$

Table IV gives a summary of calculated values of k_1 as calculated from Equation 22. The curve of Fig. 2 was drawn through these calculated

points; the circles on the curve are experimental points which were reported in Part I of this series.

Similarly, the apparent specific addition rate constant may be expressed in terms of the hydrogen-ion concentration, (H^+), the two dissociation constants of sulfurous acid, K'_A and K''_B, the first dissociation constant K'_C of benzaldehyde as an acid, and the specific rate constants k_d, k_e and k_f, which have already been defined. Since

$$(\Sigma H_2SO_3) = (H_2SO_3) + (HSO_3^-) + (SO_3^=) \quad (23)$$

and

$$(\Sigma C_6H_5CHO) = (C_6H_5CHO) + (C_6H_5CH(O^-)(OH)) \quad (24)$$

Equation 3 becomes

$$\frac{-d(\Sigma H_2SO_3)}{dt} = \left[\frac{k_e + \frac{k_d K''_A}{(H^+)} + \frac{k_f(H^+)}{K'_A}}{\left[\frac{(H^+)}{K'_A} + 1 + \frac{K''_A}{(H^+)}\right]\left[1 + \frac{K'_C}{(H^+)}\right]}\right](\Sigma C_6H_5CHO)(\Sigma H_2SO_3) \quad (25)$$

It is assumed for the purpose of the calculation that the ion $C_6H_5CH(O^-)OH$ reacts at a negligible rate with sulfite ion, if at all. This leaves the same number of rate-determining steps for the addition and dissociation reactions.

The first quantity in brackets on the right-hand side of the equation is the apparent specific reaction rate constant for the addition reaction k_2. Of the constants in this equation we have already evaluated three, namely, k_d, K'_A and K''_A. K'_C, k_e and k_f were obtained by setting up and solving simultaneous equations involving the experimental values of k_2 at different hydrogen-ion concentrations. A summary of the constants is given in Table III.

TABLE III

THE CONSTANTS OF EQUATION 25

Constant	Numerical value	Reactant
k_d	7.5×10^5	$SO_3^=$
k_e	26	HSO_3^-
k_f	5.8	$H_2SO_3^-$
K_A	1.1×10^{-7}	HSO_3^-
K'_A	1.7×10^{-2}	H_2SO_3
K'_C	5×10^{-13}	$C_6H_5CH(OH)_2$

In Table IV is a summary of values of k_2 as calculated from Equation 25. The curve of Fig. 1 is drawn through these calculated points; the circles represent the experimental data.

A general expression for the equilibrium constant $K_{eq.}$ in terms of the various specific reaction rates, dissociation constants and hydrogen-ion concentrations may be obtained by equating the right-hand members of Equations 22 and 25. The values of $K_{eq.}$ given in Table IV were calculated using this expression. The curve of Fig. 2, Part II is a plot of these calculated values, the circles being the experimental points.

TABLE IV

APPARENT VELOCITY CONSTANTS OF THE ADDITION AND DISSOCIATION REACTIONS, AND THE APPARENT EQUILIBRIUM CONSTANTS AT 21°

P_H	k_2 (min.$^{-1}$)	k_1 (min.$^{-1}$)	$K_{eq.}$
0.00	6.62	3.26×10^{-2}	4.88×10^{-3}
1.00	11.8	5.34×10^{-3}	4.53×10^{-4}
2.00	27.0	3.32×10^{-3}	1.23×10^{-4}
3.00	10.1×10	9.89×10^{-3}	9.78×10^{-5}
4.00	7.99×10^{2}	7.85×10^{-2}	9.85×10^{-5}
5.00	7.67×10^{3}	7.65×10^{-1}	1.00×10^{-4}
6.00	6.98×10^{4}	7.63	1.09×10^{-4}
7.00	3.76×10^{5}	7.63×10	2.02×10^{-4}
8.00	6.74×10^{5}	7.20×10^{2}	1.07×10^{-3}
9.00	7.30×10^{5}	4.50×10^{3}	6.16×10^{-3}
10.00	7.35×10^{5}	9.65×10^{3}	1.31×10^{-2}
11.0	7.15×10^{5}	1.09×10^{4}	1.52×10^{-2}
12.0	4.90×10^{5}	1.10×10^{4}	2.24×10^{-2}
13.0	1.22×10^{5}	1.10×10^{4}	9.05×10^{-2}

The Change in the Heat of Activation of the Dissociation Reaction with Change in P_H.—In Part I of this series we reported the measured heat of activation of the dissociation reaction as a function of the hydrogen-ion concentration. The total reaction can be represented as being composed of one or more of three steps as discussed above, each with a characteristic heat of activation. In the range covered by the measurements these three paths are

$$\text{Path A, } Q_A,\ C_6H_5CH(OH)SO_3^- \underset{}{\overset{OH^-}{\rightleftharpoons}} C_6H_5CH(O^-)SO_3^- \xrightarrow{k_a} C_6H_5CHO + SO_3^= \tag{26}$$

$$\text{Path B, } Q_B,\ C_6H_5CH(OH)SO_3^- \xrightarrow{k_b} C_6H_5CHO + HSO_3^- \tag{27}$$

$$\text{Path C, } Q_C,\ C_6H_5CH(OH)SO_3^- + H^+ \rightleftharpoons C_6H_5CH(OH)SO_3H \xrightarrow{k_c} C_6H_5CHO + H_2SO_3 \tag{28}$$

The part of the apparent heat of activation due to each path is equal to the heat of activation corresponding to that path multiplied by the fraction of molecules which react by that path. The apparent heat of activation is then the sum of three terms or

$$Q_{apparent} = \frac{k_a\left(C_6H_5CH\begin{matrix}O^-\\SO_3\end{matrix}\right)Q_A + k_b\left(C_6H_5CH\begin{matrix}OH\\SO_3\end{matrix}\right)Q_B + k_c\left(C_6H_5CH\begin{matrix}OH\\SO_3H\end{matrix}\right)Q_C}{k_a\left(C_6H_5CH\begin{matrix}O^-\\SO_3^-\end{matrix}\right) + k_b\left(C_6H_5CH\begin{matrix}OH\\SO_3^-\end{matrix}\right) + k_c\left(C_6H_5CH\begin{matrix}OH\\SO_3H\end{matrix}\right)} \tag{29}$$

Substituting in this equation the expression for the first and second dissociation constants of the hydroxysulfonic acid, we obtain

$$Q_{\text{apparent}} = \frac{\frac{k_a K''_B Q_A}{H^+} + k_b Q_b + \frac{(H^+)k_c Q_c}{K'_B}}{\frac{k_a K''_B}{H^+} + k_b + \frac{k_c(H^+)}{K'_B}} \qquad (30)$$

Using the previously calculated values of k_a, K'_B, K''_B, k_b and k_c we are able, by setting up simultaneous equations and using our experimental data, to calculate the heat of activation corresponding to each path.

Q_A = 19,000 cal. Q_B = 21,500 cal. Q_C = 24,000 cal.

Using these values we may now substitute values of (H^+) in Equation 30 and obtain Q apparent for any (H^+). We have plotted in Fig. 3 the results of this calculation, drawing the curve through the calculated points. The circles represent the experimental data.

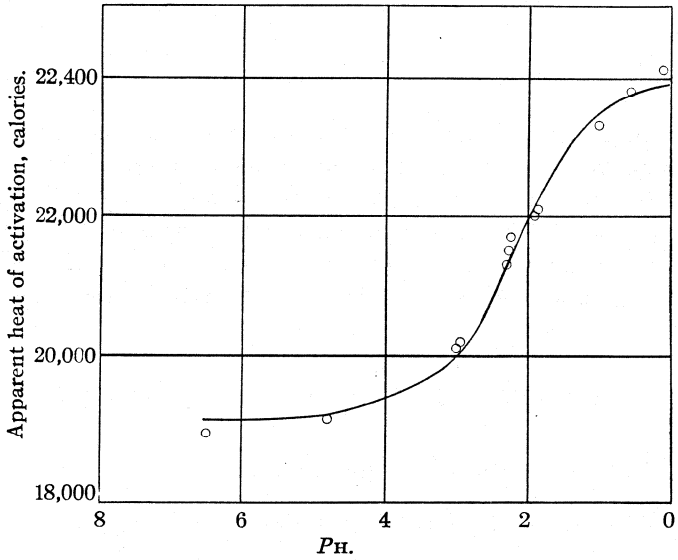

Fig. 3.—The change in activation energy with hydrogen-ion concentration at 21°.

The Heat of Dissociation of the Acid, $C_6H_5CH(OH)SO_3^-$.—The relation between heat of activation and specific reaction rate constant is expressed

$$k = Se^{-Q/RT}$$

where the symbols have their usual significance. If the factor S is the same for the rate paths A and B above, the heat of dissociation involved in path A may be calculated. S may be evaluated for path B, since Q_B is 21,500 calories and k_b is 2.23×10^{-3} at 21°. Using this value of S and the value of k_a at 21°, namely, 1.1×10^4, Q_A is found to be 12,600 calories. The measured value of Q_A, however, is 19,000 calories, and the difference,

−6400 calories, may be taken as the energy necessary to bring about the reversible dissociation involved in path A. This may be compared with −6025 calories for the heat of dissociation of phenol.[6] Since it is a reasonable value, the assumption of the constancy of the factor S may be considered supported for this case, which is interesting in view of the great difference (10^7-fold) in the specific reaction rates.

A similar calculation for the heat of dissociation involved in path C above is less valid, on account of the uncertainty of the value of k_c. Using the value 30 for k_c as given above, however, the heat of activation is calculated to be 16,000 calories or 8000 calories less than the measured value. This difference is the heat of formation of the neutral molecule, $C_6H_5CH(OH)SO_3H$, from its ions.

Summary

1. The apparent specific reaction rates of formation and dissociation of benzaldehyde bisulfite have been calculated for the P_H range 0 to 13.

2. The specific reaction rates at 21° of sulfite and bisulfite ions and of sulfurous acid, with benzaldehyde, are 7.35×10^5, 26 and 5.8 min.$^{-1}$, respectively.

3. In the P_H range 3 to 13, practically all of the addition reaction involves sulfite, not bisulfite, ion.

4. The specific reaction rates of dissociation at 21° for the bivalent and monovalent ions, and of the undissociated acid, α-hydroxybenzylsulfonic acid, are 1.1×10^4, 2.2×10^{-3} and about 30 min.$^{-1}$, respectively.

5. The hydroxysulfonic acid is a very strong monobasic acid; its second dissociation constant is 7.0×10^{-10}.

6. The first dissociation constant of benzaldehyde as an acid is 5×10^{-13}.

7. The heats of activation for each of the three paths involved in the dissociation have been calculated.

8. The heats of dissociation of the two acidic dissociations of α-hydroxylbenzylsulfonic acid have been calculated from the activation energies.

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[6] Landolt–Börnstein, "Physik.-Tabellen," 5 Auflage, Vol. II, p. 1577.

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 326]

THE NATURE OF THE CHEMICAL BOND. IV. THE ENERGY OF SINGLE BONDS AND THE RELATIVE ELECTRONEGATIVITY OF ATOMS

BY LINUS PAULING

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Recent developments in the application of the quantum mechanics to problems of molecular structure[1] have indicated that the properties of a bond between two atoms often are determined mainly by one single-electron orbital wave function for each atom, and are not strongly affected by the other atoms in the molecule; for when the wave function for a molecule containing single covalent bonds is set up with the use of single-electron orbital wave functions, it is found that each bond function tends to overlap to the maximum extent the other function involved in one bond, and to avoid overlapping all others, so that the resonance integrals other than those characteristic of the bonds are small. The empirical evidence of interatomic distances supports this view; it has been possible to formulate a set of covalent radii for use in purely covalent molecules (in which each atom forms covalent bonds to a number determined by its position in the periodic system) which accounts satisfactorily for observed distances in molecules to which a single Lewis electronic structure can be assigned.[2] It has also been found that changing the covalence of an atom, and hence the nature of the bond function, produces a change in the radius.[3]

Independence of the bonds in a molecule would require that the total energy of formation of the molecule from separate atoms be expressible as the sum of constant energy terms characteristic of the various bonds. This is found to be nearly true for molecules to which a single Lewis electronic structure can be assigned, the deviations from constancy of bond energy rarely exceeding 2 or 3%. Data on the heats of formation and heats of combustion of gaseous molecules may accordingly be used to evaluate the energies of various bonds. This procedure is adopted in the following pages. It is then shown that the energies of bonds, when discussed with the aid of the postulate of the additivity of the energies of normal covalent bonds, throw much light on their nature, in particular on the amount of ionic character possessed by them, and permit the localization of

[1] Linus Pauling, THIS JOURNAL, **53**, 1367, 3225 (1931); **54**, 988 (1932); J. C. Slater, *Phys. Rev.*, **37**, 481 (1931); **38**, 1109 (1931); F. Hund, *Z. Physik*, **73**, 1, 565 (1932).

[2] Linus Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932). Examples of molecules which resonate among several Lewis structures are given in this paper. Further discussion of the nitrous oxide molecule is given in a later note, Linus Pauling, *ibid.*, July, 1932.

[3] Linus Pauling and M. L. Huggins, *Z. Krist.*, to be published.

atoms on an "electronegativity map," with the aid of which their properties may be conveniently discussed. It is also found that bond energies provide evidence in regard to a number of questions relating to the structure of simple molecules, such as O_4, O_3, P_4, etc.

Extreme Ionic Bonds and Normal Covalent Bonds.—Before discussing the nature of actual bonds it is desirable to specify the sense in which the terms ionic and covalent will be used.

Early discussions of molecules such as the hydrogen halides treated them as consisting of ions which deformed each other to some extent. Now the wave functions corresponding to the normal and all excited states of F^-, for example, form a complete orthogonal set, so that any electronic structure of the HF molecule, even a normal covalent structure, could be accurately represented by a wave function built up from the wave functions for F^-, the contributions of excited states being considered to result from the deforming action of the proton. If, then, we are to distinguish at all between ionic bonds and bonds of other types, some arbitrary decision as to the extent to which excited ionic states are to be considered in constructing wave functions must be made. A number of phenomena formerly explained qualitatively as due to mutual polarization and deformation of ions have been quantitatively accounted for in other ways, and it has become evident that deformation of ions does not have the importance in determining the properties of molecules that it was formerly ascribed. Consequently I prefer, in an approximate treatment, to consider only states in which electrons occupy the most stable orbits in atoms or ions, and so to select for the wave function representing an extreme ionic molecule a function formed from those for normal undeformed ions.

A bond between two identical atoms, as H:H, Cl:Cl, C:C, etc., may be considered to be a normal covalent bond, involving a pair of electrons and two single-electron orbital wave functions, one for each atom. The wave function representing it may not be closely approximated by a function of the Heitler–London type, $\psi(1)\varphi(2) - \varphi(1)\psi(2)$, but may involve ionic terms $\varphi(1)\varphi(2)$ and $\psi(1)\psi(2)$, corresponding to A^+A^- and A^-A^+, these two occurring, of course, with the same coefficient. The contribution of these terms to the normal state of the hydrogen molecule has been discussed by Slater.[4] In the wave function representing the bond between unlike atoms A and B the terms corresponding to A^+B^- and A^-B^+ will occur with the same coefficient, equal to that for A:A or B:B, if the two atoms have the same degree of electronegativity. Such a function may be called a normal covalent bond wave function, and the bond a normal covalent bond. If one atom is more electronegative than the other, the wave function can be formed by adding to the normal covalent bond wave function an additional ionic term.

[4] J. C. Slater, *Phys. Rev.*, **35**, 509 (1930).

The Additivity of the Energies of Normal Covalent Bonds. The Hydrogen Halides and the Halogen Halides.—It is found that there exists a convincing body of empirical evidence in support of the postulate[5] that *the energies of normal covalent bonds are additive;* that is

$$A:B = {}^1/_2\{A:A + B:B\}$$

where the symbol A:B means the energy of the normal covalent bond between A and B, etc. The energy of a normal covalent bond between A and B would be given by the integral $\int \psi^* H \psi d\tau$, with ψ the normalized normal covalent wave function. Inasmuch as the energy integral for any wave function for a system must be equal to or greater than the energy of the lowest state of the system, the energy of the actual bond between A and B must be at least as great as that for a normal covalent bond. Hence if the postulate of additivity is correct, the difference Δ between the actual bond energy and that predicted from additivity must be zero or positive, and the greater the ionic character of the bond, the greater will be the value of Δ.

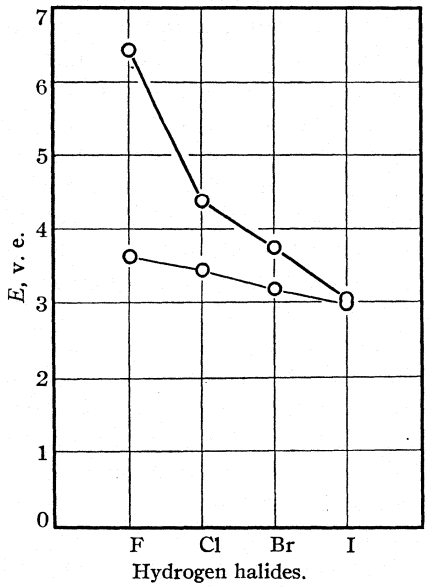


Fig. 1.—Bond energies for hydrogen halides: observed values are connected by heavy lines, values calculated for normal covalent bonds by light lines.

In Table I and Figs. 1 and 2 are given bond energies for hydrogen and the halogens, and their binary compounds, together with the deviations from additivity. The values of Δ are usually known more accurately than the bond energies themselves because they can be directly measured as heats of reaction. It is seen that *the values of* Δ *are positive for all of these compounds,* which provides strong support for the postulate. Moreover, the values are in agreement with previously formed conceptions as to the nature of the bonds in these molecules. A recent discussion[6] of energy curves has shown HF to be largely ionic, while HCl, HBr and HI are largely covalent, with HI nearly a normal covalent molecule. These descriptions are in complete accord with the course of the Δ-values.

BrCl approaches the normal covalent type still more closely than HI, with a deviation from additivity of less than 1%. The values of Δ for

[5] Linus Pauling and Don M. Yost, *Proc. Nat. Acad. Sci.*, **18**, 414 (1932).

[6] Pauling, THIS JOURNAL, **54**, 988 (1932).

TABLE I[5]

	H:H	F:F	Cl:Cl	Br:Br	I:I
Bond energy	4.44	2.80	2.468	1.962	1.535 v. e.
		HF	HCl	HBr	HI
Actual bond energy		6.39	4.38	3.74	3.07
Predicted from additivity		3.62	3.45	3.20	2.99
Δ		2.77	0.93	0.54	0.08
		ClF	BrCl	IBr	ICl
Actual bond energy		3.82	2.231	1.801	2.143
Predicted from additivity		2.63	2.215	1.748	2.001
Δ		1.19	0.016	0.053	0.142

IBr and ICl are also small, but that for ClF is even larger than for HCl, showing that the bond in chlorine fluoride is more ionic in character than that in hydrogen chloride.

It is perhaps desirable to point out that the bond type has no direct connection with ease of electrolytic dissociation in aqueous solution. Thus the nearly normal covalent molecule HI ionizes completely in water, whereas the largely ionic HF is only partially ionized.

Bond Energies for Light Atoms and Halogens.—In the calculation of bond energies from heats of formation and heats of combustion the following energies of reaction were assumed[7] in addition to those given in Table I.

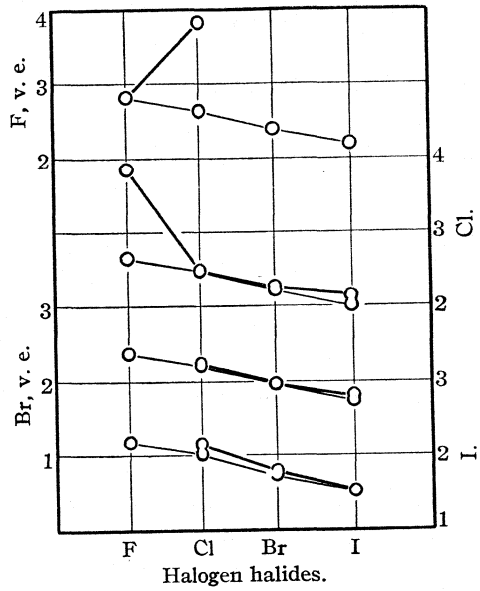


Fig. 2.—Bond energies for halogen halides.

$$2O = O_2 + 5.09 \text{ v. e.}$$
$$2N = N_2 + 9.10 \text{ v. e.}$$
$$H_2 + {}^1/_2\,O_2 = H_2O(g) + 2.508 \text{ v. e.}$$
$$H_2 + {}^1/_2\,O_2 = H_2O(l) + 2.966 \text{ v. e.}$$
$$C^3P = C_{\text{graphite}} + 6.61 \text{ v. e.}$$
$$C^{*5}S = C_{\text{graphite}} + 7.61 \text{ v. e.}$$
$$C_{\text{graphite}} + O_2 = CO_2 + 4.094 \text{ v. e.}$$
$$2Br = Br_2(l) + 2.293 \text{ v. e.}$$
$$2I = I_2(c) + 2.188 \text{ v. e.}$$

Some doubt has been thrown on the value 9.1 v. e. for the dissociation energy of N_2 by the recent experiments of Tate and Lozier,[8] whose interpre-

[7] Values of thermal quantities used throughout this paper are from "International Critical Tables," Landolt-Börnstein, or Kharasch's compilation of heats of combustion, *Bur. Standards J. Research*, **2**, 359 (1929), except where otherwise indicated.

[8] J. T. Tate and W. W. Lozier, *Phys. Rev.*, **39**, 254 (1932).

tation of their results has in turn, however, been criticized by Arnot.[9] The value 6.61 v. e. for the heat of sublimation of graphite to normal carbon atoms is very uncertain, and the assumed value of 1.00 v. e. for the excitation energy to the $2s2p^3\ ^5S$ state is also uncertain. It is not essential for the discussion of deviations from additivity that these energy quantities be known; but it is convenient to deal with definite values for bond energies, even though they are relative to an arbitrarily chosen starting point, so that the values given have been used in this paper. When accurate values of these quantities become known, the bond energies can be easily corrected accordingly.

Compounds of Oxygen and Nitrogen.—From the heat of formation of water from atoms

$$2H + O = H_2O(g) + 9.493 \text{ v. e.}$$

the H:O bond is found to have the energy 4.747 v. e. The equation[10]

$$H_2O_2(l) = H_2O(l) + {}^1/_2\,O_2 + 1.02 \text{ v. e.}$$

combined with the heat of vaporization of H_2O_2, 0.50 v. e., leads to

$$2H + 2O = H_2O_2(g) + 10.99 \text{ v. e.}$$

Making use of the postulate of the constancy of bond energies, we subtract 4.75 v. e. for each H:O bond to obtain 1.49 v. e. for the O:O bond.

The $^1\Sigma$ state of the oxygen molecule, 1.62 v. e. above the normal state, probably corresponds to a double bond between the two atoms. This gives 3.47 v. e. for O::O.

From the heat of formation of ammonia, 0.475 v. e., we obtain

$$N + 3H = NH_3 + 11.685 \text{ v. e.}$$

and the value 3.895 v. e. for the N:H bond.

The heats of formation of OF_2 (−0.40 v. e.), NF_3 (1.13 v. e.), Cl_2O (−0.79 v. e.) and NCl_3 (−2.38 v. e.), lead to the values 2.48 v. e. for O:F, 3.29 v. e. for N:F, 2.12 v. e. for Cl:O, and 1.95 v. e. for N:Cl.

Compounds of Carbon.—Heats of combustion of diamond and the aliphatic hydrocarbons show, as was pointed out by Fajans,[11] that the postulate of the constancy of bond energies is not accurate, for assuming that the H:C bond energy is the same in the higher members of the series as in methane, a value for the C:C bond energy is obtained which is 0.2 v. e. lower than that from diamond. It is difficult to decide how to treat this discrepancy. I have arbitrarily chosen to ignore diamond. The values H:C = 4.34 v. e. and C:C = 3.60 v. e. then give good agreement with experiment for the aliphatic hydrocarbons, as is seen by comparing the heats of formation ($E_{\text{obs.}}$) of gaseous molecules from atoms as calculated from heats of combustion with the sum of the bond energies ($E_{\text{calcd.}}$).

[9] F. L. Arnot, *Nature*, **129**, 617 (1932).

[10] G. L. Matheson and O. Maass, THIS JOURNAL, **51**, 674 (1929).

[11] Fajans, *Ber.*, **53**, 643 (1920); **55**, 2826 (1922); *Z. physik. Chem.*, **99**, 395 (1921).

	$E_{obs.}$, v. e.	$E_{calcd.}$, v. e.		$E_{obs.}$, v. e	$E_{calcd.}$, v. e.
CH_4	17.37	17.36	C_4H_{10}	54.20	54.20
C_2H_6	29.65	29.64	C_6H_{14}	78.77	78.76
C_3H_8	41.91	41.94	C_7H_{16}	91.00	91.05

Similar calculations for saturated cyclic hydrocarbons show that a three-membered ring is unstable to the extent of over 1 v. e., larger rings showing little strain. The table compares observed heats of combustion with those calculated from bond energies.[12]

		$Q_{obs.}$, v. e.	$Q_{calcd.}$, v. e.	Instability, v. e.
Trimethylene	C_3H_6	21.55	20.49	1.06
Methylcyclobutane	C_5H_{10}	34.31	34.15	0.16
Cyclopentane	C_5H_{10}	34.28	34.15	.13
Methylcyclopentane	C_6H_{12}	41.02	40.98	.04
Cyclohexane	C_6H_{12}	41.02	40.98	.04

Heats of combustion of gaseous hydrocarbons containing double bonds lead to the average value 6.46 v. e. for C::C.

		Q, v. e.	E, v. e.	C::C, v. e.
Ethylene	C_2H_4	14.38	23.84	6.48
Propylene	C_3H_6	21.26	36.07	6.43
Isobutylene	C_4H_8	28.07	48.37	6.45
Trimethylethylene	C_5H_{10}	34.86	60.69	6.49
Diallyl	C_6H_{10}	40.26	66.99	6.40
Hexylene	C_6H_{12}	41.66	73.00	6.52

Heats of combustion for hydrocarbons containing triple bonds are uncertain. Thomsen's values lead to C:::C = 8.68 v. e.

	Q, v. e.	E, v. e.	C:::C, v. e.
Acetylene	13.54	17.28	8.60
Allylene	20.18	29.75	8.79
Dipropargyl	38.30	54.14	8.65

It is interesting to note that the unsaturation of a double bond amounts to 0.74 v. e., this being the energy liberated by a reaction leading to the formation of two carbon–carbon single bonds in place of a double bond. For a triple bond the unsaturation is 2.1 v. e.

Five primary alcohols give an average of 3.56 v. e. for C:O, with a maximum deviation of 0.10 v. e., and six ethers give 3.55 v. e., with a maximum deviation of 0.07 v. e. Secondary and tertiary alcohols seem to be 0.3–0.5 v. e. more stable than corresponds to this C:O value. In view of the agreement between ethers and primary alcohols, we select C:O = 3.55 v. e.

Primary, secondary and tertiary amines give the following values for C:N, Thomsen's values of heats of combustion being used.

[12] The heat of combustion of ethylene oxide, C_2H_4O, combined with C:O = 3.55 v. e., shows the three-membered ring involving oxygen to be unstable to the extent of 0.67 v. e.

	C:N, v. e.		C:N, v. e.
CH_3NH_2	2.82	$(CH_3)_2NH$	2.92
$C_2H_5NH_2$	2.87	$(C_2H_5)_2NH$	2.95
$C_3H_7NH_2$	2.80	$(CH_3)_3N$	2.94

Neglecting the possibility that the bond energy in primary amines be slightly less than in secondary and tertiary amines, we take the average value 2.88 v. e. for C:N.

Cyanogen, acetonitrile and hydrogen cyanide (using Thomsen's value for heats of combustion of the first two) lead to 8.86, 8.98, and 8.74 v. e., respectively, for C:::N. The average of these, 8.86 v. e., is very nearly the mean of C:::C = 8.68 v. e. and N:::N = 9.10 v. e. (in N_2).

Heats of combustion of fluorine-substituted hydrocarbons give C:F = 5.40 v. e. as the average of eight values, maximum deviation 0.35 v. e. Twelve chlorine compounds give an average of 3.41 v. e. for C:Cl. The same value is obtained from the heat of formation of CCl_4. Three bromine compounds (heats of combustion from Thomsen) give C:Br = 2.83 v. e., and two iodine compounds, CH_3I and C_2H_5I (Thomsen), give C:I = 2.2 v. e. The last two values are uncertain. Other data, obtained by Berthelot and by Roth and Macheleldt and quoted by Swietoslawski,[13] give the value 2.45 v. e. for C:I.

Bond Energies and the Relative Electronegativity of Atoms.—In Table II there are collected the energies of single bonds obtained in the preceding sections. One additional value, obtained by a method to be described later, is also included: 1.44 v. e. for N:N. Under each bond energy is given the value for a normal covalent bond, calculated from additivity, and below that the difference Δ. It is seen that Δ is positive in twenty of the twenty-one cases. The exception, C:I, may be due to experimental error, and be not real.

Regularities observed in the Δ-values suggest that it is possible to make a rough assignment of the atoms to positions along a scale representing degree of electronegativity, with the assumption that Δ is a function of the linear separation of the loci of the two atoms on the scale, in the way that genes are mapped in a chromosome from crossover data. It is to be observed that the values of $\Delta^{1/2}$ are approximately additive (these values are given directly below those of Δ). For example, the sum of $\Delta^{1/2}$ for H:A and A:F is 2.05, 2.06, 1.91, and 2.06 for A = C, N, O, and Cl, respectively. We accordingly write

$$\Delta_{A:B} = (x_A - x_B)^2 \qquad (1)$$

with Δ measured in volt-electrons, and construct the scale shown in Figs. 3 and 4 on this basis. The reliability of the method is indicated by Fig. 3, in which four distinct procedures are illustrated. The coördinates of the elements on this scale are given in Table III.

[13] W. Swietoslawski, "Thermochemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1928.

TABLE II

	H	C	N	O	F	Cl	Br	I
H	4.44	4.34	3.89	4.75	6.39	4.38	3.74	3.07
		4.02	2.94	2.99	3.62	3.45	3.20	2.99
		0.32	0.95	1.76	2.77	0.93	0.54	0.08
		.57	.98	1.33	1.67	.97	.74	.28
	C	3.60	2.88	3.55	5.40	3.41	2.83	2.45
			2.52	2.55	3.20	3.03	2.78	2.57
			0.36	1.00	2.20	0.38	0.05	−0.12
			.60	1.00	1.48	.62	.22	
		N	1.44		3.29	1.95		
					2.12	1.95		
					1.17	0.00		
					1.08	.00		
			O	1.49	2.48	2.12		
					2.15	1.98		
					0.33	0.14		
					.58	.37		
Observed bond energy				F	2.80	3.82		
Normal covalent bond energy						2.63		
Δ						1.19		
$\Delta^{1/2}$						1.09		
					Cl	2.468	2.231	2.143
							2.215	2.001
							0.016	0.142
							.13	.38
						Br	1.962	1.801
								1.748
								0.053
								.23
							I	1.535

TABLE III

COÖRDINATES OF ELEMENTS ON THE ELECTRONEGATIVITY SCALE

H	0.00	Br	0.75
P	.10	Cl	.94
I	.40	N	.95
S	.43	O	1.40
C	.55	F	2.00

These coördinates, introduced in Equation 1, lead to values of Δ which agree with those of Table II with an average error of 0.09 v. e., excluding H:F. The calculated Δ for H:F is 4.00 v. e., 1.23 v. e. higher than observed; this indicates that Equation 1 is inaccurate when $x_A - x_B$ becomes as large as 2.

The electronegativity map may be used with considerable confidence in predicting bond energies, especially for atoms which lie near each other on the map. It will be observed that the difference in bond energy of H:A and

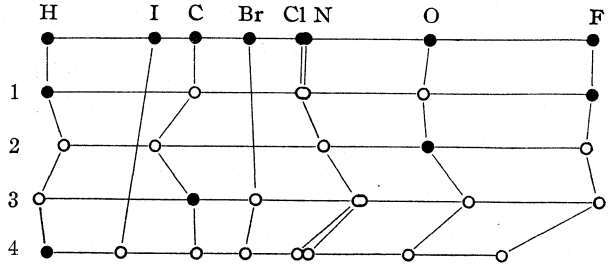


Fig. 3.—The construction of the electronegativity map. Map loci of atoms were obtained by the use of values of $\Delta^{1/2}$ relative to the atoms represented by solid circles: (1) loci taken to give the correct ratio of $\Delta^{1/2}$ for H:A and A:F. Absolute values of $\Delta^{1/2}$ are shown in the other lines, for (2) A:O, (3) C:A and (4) H:A.

A:F increases rapidly in the order A = C, Cl, O. Now the value of this difference for N is only slightly greater than for Cl, showing that the locus of N on the map should lie just to the right of that for Cl, and that in

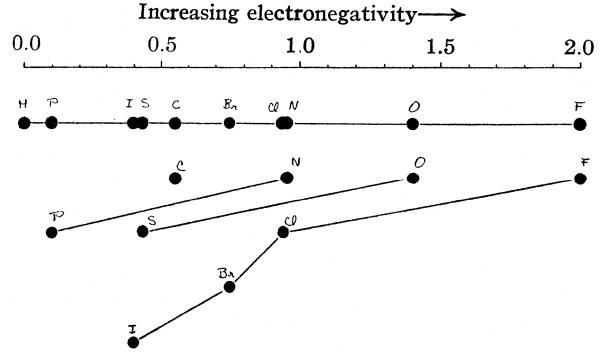


Fig. 4.—Map representing the relative degree of electronegativity of atoms.

consequence $\Delta = 0.00$ for N:Cl. The bond energies for N:Cl and Cl:Cl then lead to 1.44 v. e. for N:N, the value given in Table II. This value could be checked if the heat of formation of gaseous hydrazine were known. The predicted value is

$$N_2 + 2H_2 = N_2H_4(g) - 0.96 \text{ v. e.}$$

It may be mentioned that the heats of combustion of hydrazobenzene and azobenzene give 1.59 v. e. for N:N and 4.24 v. e. for N::N, with rather large probable errors.

From the equations

$$S(g) = S_{rhombic} + 2.89 \text{ v. e.}$$
$$S_{rh.} + Cl_2 = SCl_2(g) + 0.34 \text{ v. e.}$$
$$S_{rh.} + H_2 = H_2S + 0.23 \text{ v. e.},$$

we obtain S:Cl = 2.85 v. e. and H:S = 3.78 v. e. From

$$2S_{rh.} + Cl_2 = S_2Cl_2(g) + 0.24 \text{ v. e.}$$

we obtain, with the use of the above S:Cl value, S:S = 2.79 v. e. in S_2Cl_2. The equation

$$^1/_8\, S_8(g) = S_{rh.} + 0.11 \text{ v. e.}$$

gives S:S = 2.78 v. e., if the S_8 molecule consists of an eight-membered ring involving eight single bonds; the agreement with the S_2Cl_2 value provides strong support for this structure. From these energy values the map position of sulfur was obtained.

The S_6 molecule, supposed to contain six single bonds, is less stable than expected by 0.30 v. e., presumably because of steric effects.

From the trend of map loci with position in the periodic table phosphorus may be placed very near hydrogen on the map, perhaps at about 0.10. This requires Δ to be very small (0.01 v. e.) for H:P. From

$$^1/_4\, P_4(g) + {}^3/_2\, H_2(g) = PH_3(g) + 0.246 \text{ v. e.}$$

we obtain P:H = 2.302 v. e. + C, in which C is one-third of the energy of dissociation of $^1/_4\, P_4(g)$ into P(g). This then gives, with Δ = 0.01 v. e., the value 0.14 v. e. + $2C$ for P:P. P_4 presumably has a tetrahedral structure, with single bonds at 60° angles;[14] the bonds are 0.14 v. e. weaker than normal P:P bonds, as compared with 0.05 v. e. for S:S bonds in S_6.

The equation

$$^1/_4\, P_4(g) + {}^3/_2\, Cl_2 = PCl_3(g) + 3.30 \text{ v. e.}$$

gives P:Cl = 2.41 v. e. + C.

The extent to which Equation 1 is valid and the accuracy of the map are graphically shown in Fig. 5. The vertical lines, representing Δ-values, should increase in height with the square of their distance from the diagonal.

It is evident that the map and Equation 1 can be used for the prediction of the energies of bonds for which no experimental data are available, the values being trustworthy to about 0.05 v. e. for map distances less than 0.50, and 0.1–0.2 v. e. for distances up to 1 or 1.5. Table IV contains predicted values, with the aid of which heats of formation of purely covalent compounds containing single bonds, such as SF_2 (but not SF_6), can be calculated. In some cases all data needed for testing these values are available except heats of vaporization or sublimation. Thus the heat of formation of $S_2Br_2(l)$, 0.09 v. e., agrees with the bond energies if the heat of vaporization of S_2Br_2 be 0.44 v. e., which is a not unreasonable value (that for Br_2 being 0.33 v. e.). The somewhat doubtful value 0.0 v. e. reported

[14] R. Hultgren, *Phys. Rev.*, **40**, 891 (1932).

for the heat of formation of $S_2I_2(c)$ leads to a heat of sublimation of 0.9 v. e. (that for I_2 being 0.65 v. e.). Similarly the heats of formation of $PBr_3(l)$,

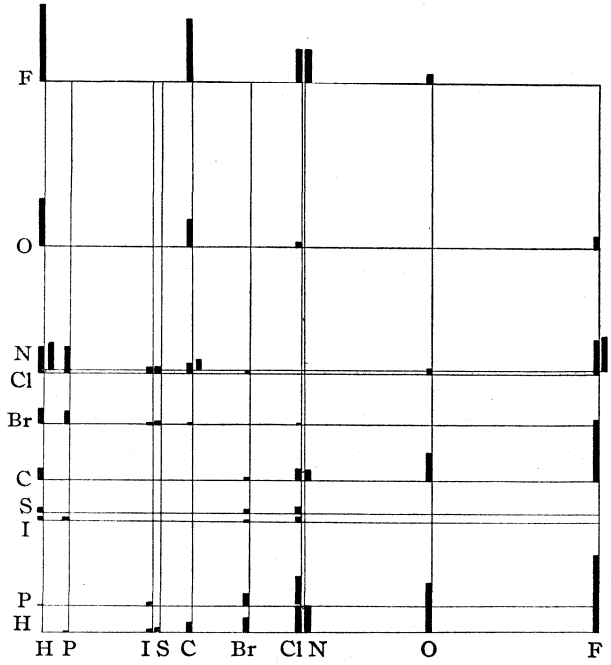


Fig. 5.—In this figure ordinates and abscissas represent loci on the electronegativity map, and the heavy vertical lines are drawn to the height Δ, the observed deviation from additivity of bonds, attributed to their ionic character. Equation 1 in the text requires that these heights increase with the square of the distance from the diagonal.

1.97 v. e., and $PI_3(c)$, 0.48 v. e., lead to the reasonable values 0.51 v. e. and 0.98 v. e. for the heat of vaporization of PBr_3 and the heat of sublimation of PI_3, respectively.

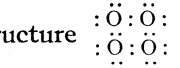
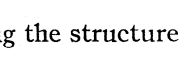
TABLE IV

PREDICTED BOND ENERGIES

N:O	1.67 v. e.	S:N	2.38 v. e.
Br:N	1.74	S:O	3.08
I:N	1.79	S:F	5.25
Br:O	2.15	P:I	0.93 + C
I:O	2.52	P:S	1.56 + C
Br:F	3.94	P:C	3.17 + C
I:F	4.72	P:Br	1.47 + C
I:S	2.16	P:N	1.51 + C
S:C	3.20	P:O	2.50 + C
S:Br	2.47	P:F	5.08 + C

Assuming that the energy of formation of crystalline silicon (with the diamond structure) is the energy of the Si:Si bonds, the heats of formation 15.70 and 6.20 v. e. of gaseous SiF_4 and $SiCl_4$ lead to values of 1.98 and 1.24 for $\Delta^{1/2}$ for Si:F and Si:Cl, respectively. These substantiate the map position of about -0.15 obtained by extrapolating the series Cl, S, P. This and many other map positions which could be similarly obtained are not included in Fig. 4 and Table III, however, because of the somewhat greater uncertainty attached to them. With this map position, the heat of formation of SiH_4 should be about 0.08 v. e., or less if the metallic character of crystalline silicon makes some contribution to its energy. The value 0.5 v. e. given in "International Critical Tables" is without doubt too large; Landolt–Börnstein reports -0.29 v. e.

Arsenic, antimony, selenium, and tellurium no doubt lie close to hydrogen on the map, so that single-bond energies can be obtained for them from the heats of formation of hydrides, as in the case of phosphorus, by assuming Δ to be very small. Crystals of selenium and tellurium contain long spiral strings, in which each atom is presumably held to two others by covalent bonds, and those of arsenic and antimony contain layers, in which each atom is presumably similarly attached to three others. With $\Delta_{M:H}$ very small, the heat of reaction of such a string or layer with hydrogen should be nearly zero, so that the observed negative heats of reaction for the crystals give just the energy necessary to separate the strings or layers in the crystals. This energy is, per atom, 1.08 v. e. for selenium, 1.52 v. e. for tellurium, 1.92 v. e. for arsenic, and 1.5 v. e. for antimony, the last value being probably too low because of error in the reported heat of formation of the hydride.

The observed value of the heat of formation of O_4 from atoms, 10.19 v. e., is so much greater than the energy of four O:O bonds, 5.96 v. e., that the structure  for this molecule must be rejected. The corresponding values for ozone are 6.15 v. e. and 4.47 v. e., causing the structure  to be rejected also. Ozone probably has a structure like that of SO_2, as suggested by Lewis. The very small heat of formation of O_4 from $2O_2$ and the ease with which dissociation occurs (even crystalline oxygen showing some paramagnetism) indicate that O_4 consists of two $^3\Sigma O_2$ molecules held together loosely by van der Waals forces, the exchange terms being larger for two triplet molecules combining to a singlet than they are for singlet molecules.

The metallic elements may also be roughly located on the map, though the significance and usefulness of their map positions is not so great as for the non-metals.

The property of electronegativity discussed in this paper and defined by Equation 1 is not analogous to the electron affinity of atoms, but is closely related to the intuitive conception of electronegativity possessed by the chemist. The relation to the periodic system is the expected one. Fluorine and oxygen are by far the most electronegative atoms, with fluorine much more electronegative than oxygen. The series C, N, O, F is almost uniform. Fluorine is much more electronegative than the other halogens, and deserves to be classed by itself as a superhalogen. OF_2 should be called oxygen fluoride, and Cl_2O chlorine oxide, the more electronegative element being written last. In nitrogen trichloride, NCl_3, nitrogen and chlorine are neither positive nor negative, the bonds being normal covalent bonds, and the molecule the best example of a normal covalent molecule that we have, other than the symmetrical molecules. Nitrogen trichloride would decompose into gaseous elementary molecules with no heat effect if elementary nitrogen contained single N:N bonds. Since the triple bond in N_2 is 4.78 v. e. more stable than three N:N bonds, half this energy quantity, 2.39 v. e., is emitted during the decomposition of NCl_3. The contribution of ionic terms, giving $\Delta = 1.17$ v. e., overcomes this for NF_3, and leads to a positive heat of formation.

Summary

After the discussion and definition of extreme ionic bonds and normal covalent bonds, values of the energy of twenty-one single bonds are obtained from experimental values of heats of formation and combustion of gaseous molecules, with the use of the assumption that the energy of formation from separated atoms of a molecule to which a single Lewis electronic structure can be assigned is the sum of constant terms representing the various bonds. The postulate of the additivity of the energies of normal covalent bonds is then formulated, and it is found that deviations from additivity, Δ, are positive for all bonds (with one doubtful exception), and increase as the ionic character of the bond increases. An assignment of atoms to positions on a map representing relative degree of electronegativity is then made with the use of the Δ-values, according to the equation $\Delta_{A:B} = (x_A - x_B)^2$, where x_A and x_B represent the coördinates of atoms A and B on the map. Values of the energy of twenty bonds for which experimental data are not available are predicted by means of this equation, and a number of questions regarding the structure of molecules are discussed.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE CATALYTIC DECOMPOSITION OF GERMANE

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Langmuir's concept of contact catalysis has given the most concrete and promising basis for the interpretation of velocities of reactions catalyzed by solid surfaces. Its initial success with the carbon monoxide–oxygen reaction as studied by Langmuir[1] has led to many applications of this theory with some degree of confidence.[2] In many cases it has not offered an entirely unequivocal explanation of the phenomena observed, yet, in the main, the later results have served to increase confidence in Langmuir's general concept of the nature of surface catalysis.

One would expect that this theory could be best applied to the simple decomposition reactions. Such reactions have been studied by Bodenstein and Kranendieck[3] with ammonia and by Stock and Bodenstein,[4] who interpreted the results of Stock, Gomolka and Heynemann[5] on the rate of decomposition of stibine on antimony surfaces. Some of these reactions have been interpreted with moderate success on the assumption that each decomposing molecule has two contact points common with the surface.

The methane analogs of the fourth group elements can be predicted to decompose heterogeneously because of the relatively few degrees of freedom possessed by their molecules and it is conceivable that their rates of decomposition might behave differently from those of the hydrides of the fifth group elements of the periodic system. Of the fourth group hydrides, germane, GeH_4, is the best suited for this purpose. It was first prepared by Voegelen,[6] who observed the formation of a metal mirror in the analogous Marsh test, an observation which has been verified qualitatively by later workers. No quantitative measurements have thus far been made on the rate of decomposition of this compound, so in view of the bearing that such studies might have upon the present adsorption theory, we undertook this investigation.

Experimental

General Method.—The thermal decomposition of germane takes place as follows

$$GeH_4 = Ge + 2H_2$$

[1] Langmuir, *Trans. Faraday Soc.*, **17**, 621 (1921).

[2] See Taylor, Reaction Velocities in Heterogeneous Systems, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, 1931.

[3] Bodenstein and Kranendieck, Nernst Festschrift, p. 99.

[4] Stock and Bodenstein, *Ber.*, **40**, 570 (1907).

[5] Stock, Gomolka and Heynemann, *ibid.*, **40**, 532 (1907).

[6] Voegelen, *Z. anorg. Chem.*, **30**, 324 (1902).

The hydride exists as a gas at room temperature, boiling point −90°, and undergoes decomposition very slowly at temperatures below 280°. Accordingly all experiments were carried out at temperatures exceeding this value. Since hydrogen is the only gaseous constituent resulting from the decomposition, the rate of the reaction was followed by observing the total pressure of the system at different intervals of time. From the total pressure one may readily calculate the pressure of the undecomposed hydride and the pressure of the hydrogen resulting from decomposition.

Apparatus.—The apparatus is shown diagrammatically in Fig. 1. The chamber A, about 300 cc. capacity, serves as a container for the reaction. It is inner-sealed into a larger chamber B, 85 mm. in diameter and about 250 mm. in length, which contains approximately 100 cc. of mercury as the heating material. The entire chamber B is inserted in the larger container C which is filled with insulating material. The mercury in B is heated by coils of resistance wire placed in lower regions of C (not shown in the figure). A is connected to the capillary manometer D, the mercury column of which is agitated during the pressure readings by a small doorbell buzzer. E leads to the vacuum pumps and also to the containers for the germane. F represents a Chromel–X–Copel thermocouple to measure the temperature of the reaction chamber. The e. m. f. of this couple was determined with a White potentiometer. G leads to a constant pressure regulator, not shown in the figure, similar in design to that described previously by Smith.[7] The mercury is boiled continuously in B as far as condenser H during the progress of a run in order to ensure a constant temperature in the entire reaction chamber. The pressure regulator was found very satisfactory for maintaining a constant pressure of mercury vapor; no difficulty was experienced in establishing a pressure constant to 0.1 mm., which corresponds to a temperature regulation of ±0.02° at 300°. For the higher temperatures, in the neighborhood of the normal boiling point of mercury, the reaction tube was heated directly with a furnace. The temperature of the furnace did not vary more than 0.5° over the short period of time required to complete the reaction.

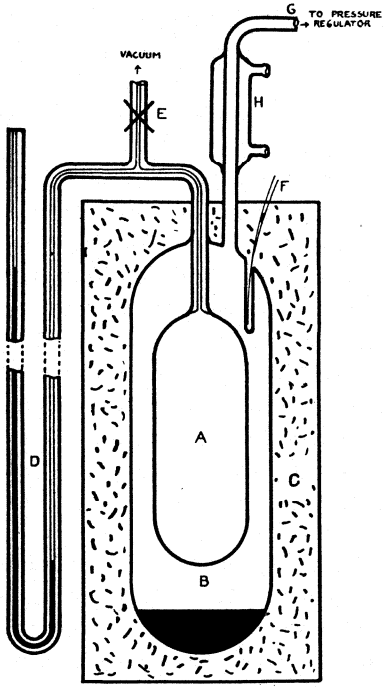

Fig. 1.—Apparatus.

Preparation of Materials.—The germane was prepared in liquid ammonia by the reaction of magnesium germanide, Mg_2Ge, with ammonium bromide.[8] The hydride was collected over water, then dried by passing through a phosphorus pentoxide tube and finally solidified at liquid air temperatures. The hydrogen present with the hydride was removed by the pumps at this low temperature. Since some higher boiling products,

[7] Smith, *Ind. Eng. Chem.*, **16**, 22 (1924).

[8] E. Seaton Carney, Thesis, Brown University, 1928.

presumably higher hydrides of germanium, remained with the germane, the mixture was fractionally distilled at −80° to ensure a pure sample of GeH_4. The molecular weight of the purified gas was found to be 76.0, which value increased to 76.5 after the sample was subjected to a second distillation.

Two samples of the hydride were decomposed for analytical purposes, one at 320° and the second at 354°, with the result that the final gas pressure was practically twice that of the original. Molecular weight determinations of the products in each of these two cases gave a value of 2.2 ± 0.1.

Approximately three liters of the purified germane were stored in a large flask at about atmospheric pressure. When a reaction was to be carried out, a portion of the hydride was condensed at liquid air temperature in a small volume adjacent to the reaction chamber. The liquid air bath was removed and the hydride was distilled as rapidly as possible into the apparatus; the time for such a distillation usually did not exceed one minute. At the higher temperatures, where the rate of decomposition of the hydride is very rapid, it was found impossible to obtain a pressure reading before an appreciable amount of the germane had dissociated. This difficulty did not appear at lower temperatures.

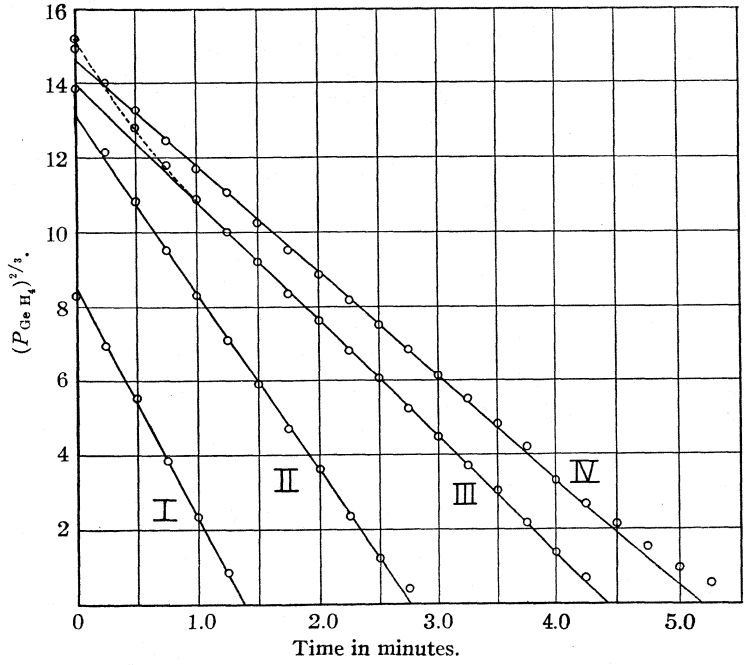

Fig. 2.

Results

The results of the investigation are shown graphically in Figs. 2, 3 and 4, in which the pressure of the undecomposed germane to the two-thirds power is plotted against the time. It is readily observed that this type of plot follows a straight line, within the limits of experimental error, at the

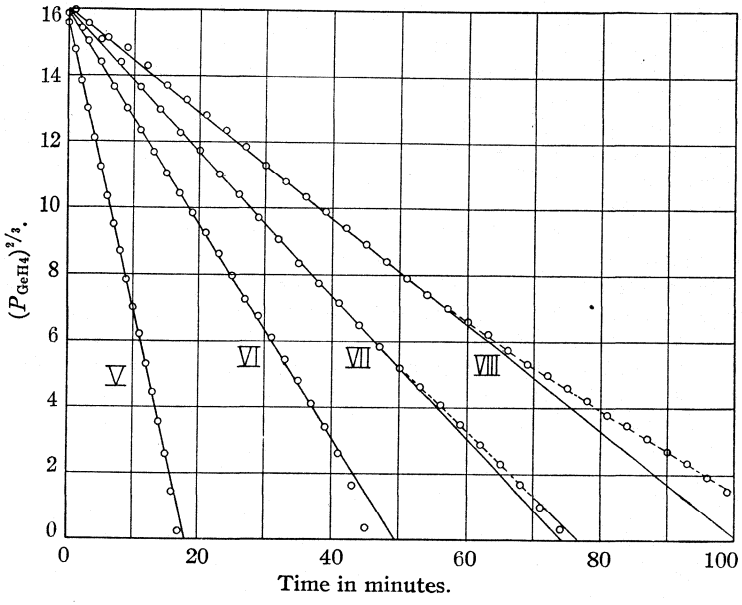

Fig. 3.

higher temperatures and also at the lower temperatures for low germanium hydride pressures. In other words

$$-\frac{dp^{2/3}}{dt} = K \qquad (1)$$

or

$$-\frac{dp}{dt} = 3/2\ Kp^{1/3} \qquad (2)$$

The slopes of these lines are given in Table I, designated by K, expressed in centimeters of germane to the two-thirds power per minute.

TABLE I

DATA FOR THE DECOMPOSITION OF GERMANE AT DIFFERENT TEMPERATURES

Run	Temperature °C.	°K.	$1/T \times 10^3$	Initial press. GeH_4, cm.	K	log K
I	374	647	1.546	23.9	6.50	0.813
II	364	637	1.570	51.4	4.73	.675
III	360	633	1.580	59.2	3.16	.500
IV	354	627	1.595	57.7	2.95	.447
V	330	603	1.658	61.9	0.845	− .073
VI	319	592	1.689	65.1	.343	− .465
VII	309	582	1.718	64.8	.215	− .668
VIII	301	574	1.742	63.4	.153	− .815
IX[9]	283	556	1.798	69.0	.040	−1.400

Figure 5 shows log K plotted against $1/T \times 10^3$.

[9] Runs X, XI and XII were carried out with initial germane pressures of 39.95, 19.70 and 10.80 cm., respectively, and at the same temperature as for Run IX.

Theoretical

To represent the experimental results of the decomposition of germane by the theory of Langmuir, certain assumptions regarding the rate of adsorption, the rate of evaporation and the decomposition rates of this compound on the germanium surface are necessary, assumptions which are different for each case to which the theory is applied. We shall assume (1) that three points of condensation are required, all of which must be simultaneously activated if evaporation is to take place, (2) that the rate of evaporation is much greater than the rate of decomposition, (3) that one-point activation of the bond will produce instability and rapid decomposition, and (4) that hydrogen inhibits at low temperatures but less as the temperature is elevated.

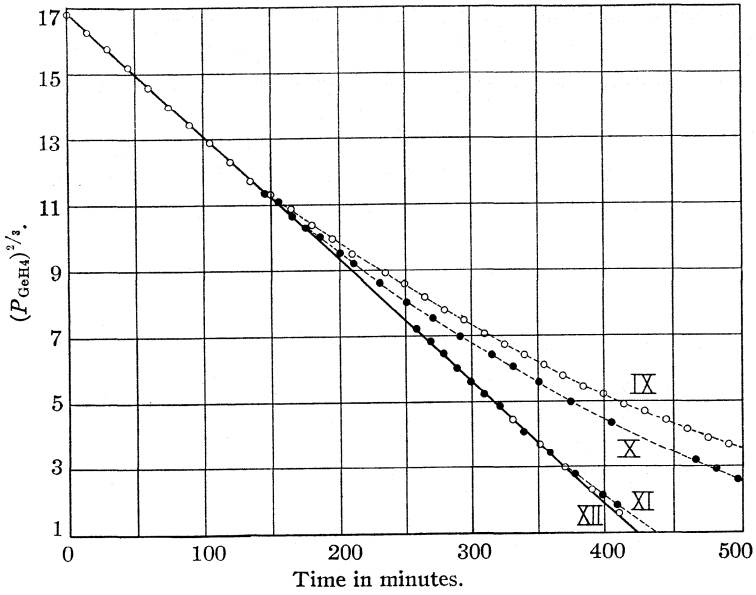

Fig. 4.

With these assumptions we obtain

$$\alpha_1\mu_1\Theta^3 = \nu_1\Theta_1^3 \quad (3)$$

$$\alpha_2\mu_2\Theta^n = \nu_2\Theta_2^n \quad (4)$$

$$w = K_1\Theta_1 \quad (5)$$

where α_1 and α_2 are the accommodation coefficients for germane and hydrogen, respectively, Θ_1 and Θ_2 the fractions of the surface covered by germane and hydrogen and Θ the uncovered surface; μ_1 and μ_2 represent the number of molecules striking the surface in unit time; ν_1 and ν_2, the specific rates of evaporation of these two gases; and K_1, the specific decomposition velocity. w is the rate of decomposition and n represents the number of

contact points for the hydrogen molecule. Using the above equations together with

$$\theta + \theta_1 + \theta_2 = 1 \tag{6}$$

we obtain

$$w = \frac{K_1 \left(\frac{\alpha_1\mu_1}{\nu_1}\right)^{1/3}}{1 + \left(\frac{\alpha_1\mu_1}{\nu_1}\right)^{1/3} + \left(\frac{\alpha_2\mu_2}{\nu_2}\right)^{1/n}} \tag{7}$$

Since μ is proportional to the pressure, we may let $\left(\frac{\alpha_1\mu_1}{\nu_1}\right)^{1/3} = A_1^{1/3}p_1^{1/3}$ and $\left(\frac{\alpha_2\mu_2}{\nu_2}\right)^{1/n} = A_2^{1/n}p^{1/n}$. We then obtain

$$w = \frac{K_1A_1^{1/3}p_1^{1/3}}{1 + A_1^{1/3}p_1^{1/3} + A_2^{1/n}p_2^{1/n}} \tag{8}$$

Using equation (8) under conditions where the inhibiting effect of hydrogen is negligible, we may let $A_2^{1/n}p_2^{1/n}$ be equal to zero. If $A_1^{1/3}\,p_1^{1/3}$ is small as compared with unity, the rate becomes

$$w = K_1A_1^{1/3}p_1^{1/3} \tag{9}$$

which corresponds to equation (2) and represents the results of our experiments. If suitable units are chosen for w, $K_1A_1^{1/3}$ becomes equal to K of

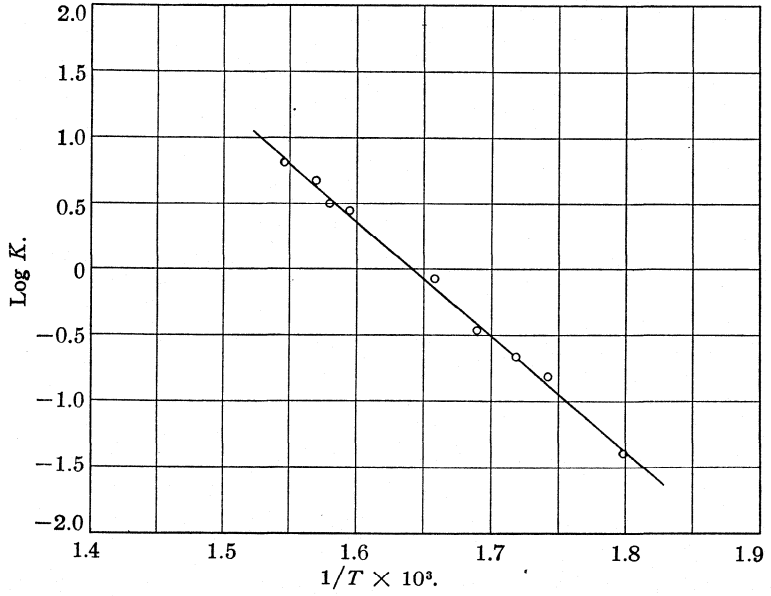

Fig. 5.

equations (1) and (2). Making $A_1^{1/3}\,p_1^{1/3}$ small is equivalent to assuming that the specific rate of evaporation is great as compared with the rate at which the molecules condense. In other words, the amount of surface occupied by the germane molecules is relatively small.

The Inhibiting Effect of Hydrogen.—With increasing temperature the specific rate of evaporation of hydrogen should increase proportionately to $e^{-q_2/kT}$, while the rate of adsorption increases as $T^{1/2}\, e^{-r/kT}$, where r is the heat of activation of adsorption of hydrogen. Adsorption is here considered in its general sense. It is not implied that this energy r is that for "secondary" adsorption.[10] A_2 should then be proportional to $T^{1/2}e^{-(r-q_2)/kT}$, where $r-q_2$ is the difference between the heats of activation of adsorption and evaporation of the hydrogen molecules on a germanium surface, and corresponds to the heat of adsorption. Since this is a negative quantity, we conclude that $A_2^{1/n}$ decreases rapidly with increasing temperature as would be expected, and at higher temperatures this term in equation (8) should become negligible.

For higher temperatures the reaction velocity should follow equation (9) over a longer range of pressures, that is, hydrogen should show a smaller inhibiting effect. Examination of the curves in Figs. 2 and 3 shows clearly that this is the case. We have not added hydrogen to the germane initially to determine its effect since any such condition could be achieved by beginning with different pressures of germane. Unfortunately we have not been able to determine the value of n without ambiguity inasmuch as this analysis requires the slope of a curve which in itself is derived from the slope of another curve. The uncertainty of any such procedure with rate data is at once apparent. Such analyses of this kind as we did make gave values of $1/n$ somewhat greater than 1; yet, on account of this uncertainty, we hesitate to give the inhibiting effect of hydrogen a definite numerical value.

Temperature Coefficient and the Heat of Activation.—The temperature coefficient of the reaction is that for the specific reaction rate $K_1A_1^{1/3}$ of equation (9). This value, as shown in Table I, is for 300 sq. cm. of apparent catalytic surface. A_1 is proportional to $e^{-H/RT}$, or $A_1^{1/3}$, to $e^{-H/3RT}$ where, by the same argument as given previously for A_2, H is the heat of adsorption of one mole of germane on germanium. K_1 is proportional to $e^{-Q/RT}$ where Q is the heat of activation of the decomposition of one mole of the hydride. $K_1A_1^{1/3}$ is then proportional to $e^{-(Q\,+\,H/3)/RT}$ or

$$K_1A_1^{1/3} = K_0e^{-(Q\,+\,H/3)/RT} \qquad (10)$$

We have defined H as the heat of *adsorption*. Q and H are of opposite signs; Q represents heat absorbed and H heat evolved. $Q + H/3$ may also be considered as the difference between the heat of activation and one-third the heat of *evaporation* (*desorption*).

Plotting log $K_1A_1^{1/3}$ or log K (equations (1) and (2)) against $1/T$, we obtain the value of an activation energy which, according to our interpretation, is equal to $Q + H/3$ (Fig. 5). The value of this quantity is calcuated from the slope of the curve and is found to be 39.7 ± 2 kilogram

[10] See Taylor, THIS JOURNAL, **53**, 578 (1931).

calories per mole. Thus it is possible to express the rate of the reaction as follows

$$w = 0.935 \times 10^{12} e^{-20,000/T} p^{1/3} \text{ (cm. Hg)}^{2/3}\text{/min. sq. cm.} \qquad (11)$$

The rate given in this equation is for 1 sq. cm. of apparent catalytic surface.

Discussion

The theory for the mechanism of the catalytic decomposition of germane was developed only after it was shown that no other rate law than the one described could represent the data for all pressures and temperatures. The decomposition time plotted against both $p^{1/2}$ and log p gave no consistent results. Plotting log p against log t, a straight line was obtained which had a slope of two-thirds. The added fact that we obtained consistent values for the temperature coefficient of the reaction (see Fig. 5) confirmed the relation that at high temperatures the rate of decomposition was proportional to $p^{1/3}$. We therefore attempted to make sufficient and reasonable assumptions to adapt these results to the general theory developed by Langmuir.

So far as we are aware this is the first case in which it has been necessary to assume a three-point contact for an adsorbed reacting molecule. However, on the basis of our knowledge of the structure of germane and crystalline germanium, such an assumption seems to us to be the most reasonable one. Like methane, the structure of germane is to be considered as tetrahedral. Metallic germanium has been shown[11] to have a diamond-type structure with octahedral cleavage. All surfaces of germanium crystals therefore have a triangular structure; that is, lines drawn between three adjacent atoms (points) on the surface form an equilateral triangle. These facts make the assumption of three contact points a reasonable one.

To develop equation (8) it has been necessary to assume that three points must be independently activated to cause evaporation of the germane molecule from the surface. Since we have no other evidence to support this assumption, it hardly seems advisable to give too detailed a picture of this mechanism, yet we can see no reason why such an assumption would not be a valid one.

We have also assumed that only one point is highly activated when dissociation takes place. We have no way at present of determining how and when the hydrogen molecule is subsequently formed.

The further assumption we have made, that only a small fraction of the condensing molecules dissociate and that equilibrium is essentially maintained between the condensing and the evaporating molecules, is a common one in chemical kinetics. A similar assumption regarding equilibrium between activated and non-activated molecules is made in developing some

[11] See Ewald and Hermann, "Strukturbericht," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931, p. 54.

of the theories of homogeneous reaction rates, which theories have been applied with a moderate degree of success.

Run III (Fig. 2) was started with a glass surface rather than with one on which germanium had already been deposited. As may be seen from the figure, the initial rate in this run was greater for the glass than for the germanium surface. A simple calculation, assuming a plane contact surface, shows that the deposit of a layer of germanium several thousand molecules thick was necessary before the rate became the same as that for the usual germanium surface. The catalytic activity of the first layers deposited on the glass is greater than that for the ordinary germanium crystal surface. The effect may be ascribed to the porosity of the glass but it also may be ascribed to the irregular crystal surface which is probably first formed. There can be no question that the catalytic activity is greatly influenced by the spacing and the geometry of the atoms at the surface.

Several runs, not described here, were made to demonstrate that the reaction is a heterogeneous one. Reaction cells were filled with glass wool and under these conditions the reaction at 340° was immeasurably faster than with the smaller surface.

The decomposition of antimony hydride has been studied by Stock and his co-workers.[5,12] These authors show that the rate of decomposition is proportional to p^m where m varies from 0.4 at 0° to 0.7 at 75°. At 25° the rate is proportional to $p^{0.5}$. According to their results the hydrogen produced in the decomposition of the hydride does not have an inhibiting effect. Applying the Langmuir theory in this case, the term in the denominator of the rate equation, similar to our equation (8), very probably cannot be neglected. The neglecting of this term is equivalent to assuming that only a very small fraction of the surface is covered by the reaction molecules. In the experiments with stibine, the conditions of lower temperature and higher molecular weight of the stibine would undoubtedly result in a greater amount of surface covered and the denominator term might therefore be of significance. A closer analysis of these results with a view to their extension are now being undertaken. In the case of the decomposition of arsine[12,13] there are not sufficient data for analysis.

Summary

1. Experiments are described in which the catalytic rates of decomposition of germane, GeH_4, on a germanium surface are determined.

2. The rates of decomposition at higher temperatures are found to be proportional to the one-third power of the undissociated germane pressure.

3. At lower temperatures the hydrogen formed in the reaction displays an inhibiting effect.

[12] Stock and Guthmann, *Ber.*, **37**, 885 (1904); Echeandia, Thesis, Berlin, 1909; Stock, *Z. physik. Chem.*, **50**, 111 (1905).

[13] Stock, Echeandia and Voigt, *Ber.*, **41**, 1319 (1908).

4. By making assumptions applicable in this case an equation, based on Langmuir's adsorption theory, is developed; this equation is in agreement with the experimental results. The essential assumption made is that of three-point contact between the germane molecule and the germanium surface.

5. The temperature coefficient and the heat of activation have been determined. The significance of this energy term has been discussed in the light of the proposed theory.

6. A discussion of the validity of the assumptions made and of similar work in this field concludes the article.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A STUDY OF VAN DER WAALS FORCES BETWEEN TETRAHALIDE MOLECULES

BY J. H. HILDEBRAND AND J. M. CARTER

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The theoretical and experimental investigations of the general problem of solubility conducted by the senior author and collaborators during a period of years have made evident the importance of a more accurate knowledge than we now possess of intermolecular forces between like and unlike molecules in the simplest possible cases, where the molecules are non-polar and where the molecular field, as shown by recent applications of wave mechanics, is spherical. While the noble gases are theoretically satisfactory for such an investigation, we selected the tetrahalides as practically far more suitable. They are not only available in large quantities, but their molecular volumes and intermolecular forces represent a wide range of variation. We are making a systematic study of certain properties of six tetrahalides and their solutions. The properties thus far measured are the expansion on mixing and the thermal pressure coefficient, $(\partial p/\partial T)_V$, from which can be calculated the important quantity, $(\partial E/\partial V)_T$. There is now under way, as a further part of the general program, a study of the activities of the same substances in their binary solutions.

Preparation and Purification of Materials.—Stock U. S. P. carbon tetrachloride, about 1500 cc., was shaken with C. P. sodium hydroxide sticks, and a small quantity of distilled water for two days. The liquid was then decanted, filtered, and the process repeated. After standing in contact with phosphorus pentoxide overnight, it was distilled from fresh phosphorus pentoxide. The distilling apparatus was of Pyrex glass, with all connections fused, except the connection to the receiving flask, which was a cork covered with tin foil, and the cork holding the thermometer, inserted in the distilling flask, which was also covered with tin foil. The first and last portions of the distillate were discarded, although the boiling point rose only 0.08° during the entire run. The fraction retained boiled at 76.37 to 76.43° (754 mm.). The purified material was kept in the dark, in a Pyrex flask, with a tin foil-covered stopper.

Baker and Adamson stannic chloride, colorless and free from sediment, was filtered through glass wool into a Pyrex distilling apparatus, with all joints fused. The distilling flask contained phosphorus pentoxide, and the receiving flask was connected through a phosphorus pentoxide tube to the atmosphere, or to a vacuum pump. The thermometer was hung from a glass hook inside the neck of the distilling flask, so that there would be no possibility of moisture entering the apparatus. Stannic chloride proved to be the most difficult material to obtain absolutely anhydrous, as it forms a hydrate which is extraordinarily stable at temperatures up nearly to the boiling point of water. To remove all water, and any traces of hydrochlorica cid resulting from hydrolysis, the liquid was refluxed for several hours, not allowing any appreciable amount to distil into the condenser. The distilling flask was then cooled, and the apparatus partially evacuated, while the condenser, connecting tubes and receiving flask were flamed. This was repeated three times. Finally, the liquid was distilled, discarding the first portion by keeping the receiving flask heated to a higher temperature than the boiling point. The middle portion was distilled slowly and showed a boiling point of 114.0 to 114.1° at 760 mm. The receiving flask was then sealed off. To ensure keeping the liquid dry, the receiving flask was equipped with a device which enabled the flask to be sealed on to another apparatus for removing a part of the liquid, and subsequently to be sealed off again, without allowing access of moisture.

Kahlbaum's silicon tetrachloride was treated in the same manner as the stannic chloride, and showed a boiling point of 57.50–57.55° at 755 mm.

Kahlbaum's titanium tetrachloride, treated in the same way, showed a boiling point of 135.6–135.8° at 758 mm. Silicon tetrabromide was prepared from amorphous silicon. This was placed in a long combustion tube in a furnace. Connections for introducing dry nitrogen and bromine were fused to one end of the tube, and a receiving flask and drying tube to the outer end. Air and moisture were removed by heating the tube gently, while a current of dry nitrogen was passed through. The temperature was then raised to just below a red heat, while dry bromine was passed through slowly in a current of nitrogen. The silicon tetrabromide collected in the receiving flask, which was cooled with water. In spite of precautions taken to ensure the absence of oxygen, the silicon in time became covered with a white coating, which stopped the reaction. Three runs gave approximately 500 cc. of silicon bromide. This was heated, while connected to a vacuum, to remove excess bromine, and mercury was then added to remove the last traces. It was then purified in the same manner as stannic chloride and showed a boiling point of 152.8–152.9° at 758 mm.

To prepare stannic bromide, lead-free tin was placed in a large distilling flask, sealed to a condenser and receiving flask, and also to a tube leading to a flask of dry bromine. After thorough drying of the system, dry bromine was slowly distilled onto the tin, while the neck of the distilling flask was kept cold by a jet of air cooled to −50°. The reaction was started by slightly warming the tin, and kept at a convenient speed by regulating the flow of bromine. The addition of bromine was continued until there was only a slight amount of tin left in the flask. The product was then purified in the same way as the stannic chloride. It boiled at 203.3–203.4° at 760 mm. The liquid was almost colorless, and solidified at 33.0° to a clear colorless solid. It was stored in contact with lead-free tin foil.

The expansion on mixing was determined in a dilatometer designed by the senior author and illustrated in Fig. 1. The two liquids were in their respective bulbs, separated by mercury. The reversed pear shape of the bulbs permitted a variation in the proportions of the two liquids by increasing the volume of mercury. The capillaries were calibrated by determining the weight of a thread of mercury required to fill them, and tested for uniformity by running a short thread of mercury along them.

Before making a determination, the apparatus was dried by passing a current of dried air through it. The liquids were introduced while the apparatus was placed in a box dried with phosphorus pentoxide, and in such a way that contact with air was avoided as much as possible. The amounts of the liquids used were determined by weighing the apparatus after the addition of each.

After the apparatus had been filled, rubber tubes connected to calcium chloride tubes were placed over the ends of the capillaries, and the apparatus immersed to the bottoms of the capillaries in a thermostat. After the levels of the liquids in the capillaries had become constant, they were read on the graduations, and the apparatus tilted to allow the liquids to mix. As soon as the levels had come to equilibrium, readings were again taken, and the tube again tilted. This was repeated until further mixing caused no change in the levels.

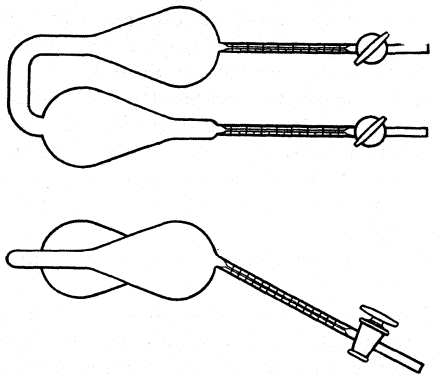

Fig. 1.

All determinations were made at 25.000 ± 0.001°, except those involving stannic bromide, which were made at 35.000 ± 0.005°.

In the case of the mixtures of carbon tetrachloride with titanium tetrachloride and with stannic chloride, after the determination of the expansion on mixing, the temperature of the thermostat was raised to 30.000 ± 0.002°, and the expansion of the mixture determined. The accuracy of the results is not as great as for the expansion on mixing, as corrections must be applied for the expansion of the Pyrex apparatus and of the mercury.

The expansion of the mixture of carbon and tin tetrachlorides, which showed the largest expansion, was determined at three compositions, to test the form of the function; the expansions of the others were determined at approximately 50 mole per cent. Biron[1] has used for the relation between expansion and composition the formula $\Delta V/V = k\ N_1N_2$, where

TABLE I

EXPANSION ON MIXING

$t = 25°$ except for solutions containing $SnBr_4$, where $t = 35°$

Solution	Mole fractions	100 $\Delta V/V$ observed	100 $\Delta V/V$ calcd. at 50 mole per cent.	$k = \frac{\Delta V}{V_{N_1N_2}} \times 10^5$
CCl_4–$SiCl_4$	0.511–0.489	0.014	0.014	56
CCl_4–$TiCl_4$	.513– .487	.083	.083	340
CCl_4–$SnCl_4$	.636– .364	.374		1617
CCl_4–$SnCl_4$	.445– .555	.403	.408	1633
CCl_4–$SnCl_4$	.247– .753	.303		1630
CCl_4–$SiBr_4$	.612– .388	.175	.184	732
CCl_4–$SnBr_4$	.533– .467	.220	.221	884
$SiCl_4$–$SnBr_4$	.509– .491	.111	.111	444
$SiBr_4$–$SnBr_4$	.487– .513	.093	.093	372

[1] Biron, *J. Russ. Phys.-Chem. Soc.*, **41**, 569 (1909).

N_1 and N_2 are the respective mole fractions. It should be noted that $N_1 + N_2 = 1$, but both letters are retained for the sake of symmetry.

Table I summarizes the results. The close agreement of the three values of k for the mixture above mentioned shows the validity of the Biron relation. If k is given the value 0.01632, the calculated and observed values of 100 $\Delta V/V$ for the three mixtures agree as follows: 0.374–0.377, 0.403–0.403, 0.303–0.303. A discussion of the relation of these expansions to the properties of the pure substances will be deferred until later.

The coefficient of expansion was determined for two mixtures, carbon tetrachloride with titanium tetrachloride and with stannic chloride. This was used as a check on the calculation of the volumes of the same solutions at 30° from the known volumes of the pure liquids at 30° by assuming that the same per cent. expansion had taken place on mixing as was found at 25°.

The following results were obtained

	Obs.	Calcd.
CCl_4–$TiCl_4$	0.00115	0.001133
CCl_4–$SnCl_4$	.001205	.001202

The agreement is so good that we felt justified in calculating the molal volumes and coefficients of expansion of the other mixtures on the assumption that at each temperature the liquids mixed with the same per cent. increase in volume as was found at 25°. The expansion should probably be smaller at increased temperatures but, as the expansion is so small in any case, it was felt that no significant error would be introduced by taking the same value at all temperatures between 20 and 40°.

The apparatus and procedure for the determination of the thermal pressure, $(\partial p/\partial T)_V$, was substantially that of Westwater, Frantz and Hildebrand[2] except that all of the containing bulbs were shorter, 10 cm., and wider, 3 cm., instead of 45 cm. and 1.5 cm., respectively, as in the earlier work. This increased the accuracy of the correction for the pressure of the mercury in the bomb. Results with both bulbs were in complete agreement.

The ice-point of the resistance thermometer was redetermined and found to be unchanged. A recalculation of the previous calibration discovered a small error, which had the effect of giving values of $(\partial p/\partial T)_V$ too high, by about 0.5%. At the close of the investigation the thermometer was sent to the Bureau of Standards for recalibration; the results agreed with our recalculation.

The high pressure manometer having broken, it was not considered necessary to repair it, as the linear relationship between pressure and temperature had been sufficiently established by the previous work. This reduced

[2] W. Westwater, H. W. Frantz and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928); Hildebrand, *ibid.*, **34**, 649 (1929).

the pressure range from 20 to 15 atmospheres. The other two manometers were recalibrated, giving agreement with the earlier calibration.

Constant volume was maintained by use of a delicate relay and a dry cell. The relay was connected to the 110-volt lighting circuit in which a lamp was placed. In view of the extremely low current passed at the contact of the mercury and the platinum wire, it is not believed that any emulsification with the liquids took place. The ease with which contact could be broken and re-established at pressures hardly distinguishable supports this.

The runs were made in practically the same manner. At least seven observations were made in each temperature interval, usually with both increasing and decreasing temperatures. It was found easy to hold the temperature constant to within 0.001° for ten minutes, while taking an observation, and the pressure to within less than 0.02 atm., usually to 0.01 atm. Check readings were made at each point. Different points were never more than 0.02 atm. off a straight line.

The corrections for the thermal expansion and the compressibility of the Pyrex bulb were made in the same way as formerly. The values of the compressibility, usually unknown, were determined by successive approximations from the coefficient of expansion and the experimentally measured thermal pressure coefficient.

The values of T_1, the temperature for $P = 1$ atm., and of $(\Delta P/\Delta T)_V$ were determined from the experimental points by a least square calculation based upon the linear relationship between P and T. Table II shows the agreement for one run between the observed and smoothed out pressures. This may be taken as a fair sample of the accuracy obtained throughout the investigation.

TABLE II

DEVIATION OF OBSERVED PRESSURES FROM LINEAR RELATIONSHIP

Run 1 for CCl_4 t	P, atmospheres Obs.	Calcd.	Diff.
20.396		1.00	
20.416	1.24	1.23	+0.01
20.557	2.86	2.87	− .01
20.760	5.23	5.26	− .03
20.899	6.86	6.85	+ .01
21.078	8.95	8.93	+ .02
21.257	11.01	11.01	.00
21.363	12.24	12.24	.00
21.576	14.73	14.72	+ .01

The results for all the pure liquids investigated are summarized in Table III. The molal volumes have been calculated from the known densities as given in the "International Critical Tables." The values of the van der Waals a have been calculated from the thermodynamic equation for the change in energy with volume

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \quad (2)$$

together with the equation

$$a = v^2(\partial E/\partial V)_T \quad (3)$$

previously found to be applicable to these data. The values of a given are in atm. $\times$ $\overline{cc.}^2$ and v is the molal volume. The constancy of a shown in both Tables III and IV again bears witness to the accuracy of Equation 3 for this range.

The corresponding data for mixtures are given in Table IV.

TABLE III

THERMAL PRESSURE COEFFICIENTS, $(\partial P/\partial T)_V$, ENERGY–VOLUME COEFFICIENTS, $(\partial E/\partial V)_T$, AND VAN DER WAALS "$a$" FOR PURE LIQUIDS

Substance	t, °C. at 1 atm.	$(\partial P/T\partial)_V$, atm. per degree Obs.	Correc.	Molal volume, cc.	a, atm. $\times$ liters^2
CCl_4	20.40	11.63	11.40	96.54	31.18
	20.63	11.63	11.40	96.57	31.23
	25.84	11.23	11.02	97.19	31.18
	31.25	10.92	10.72	97.84	31.23
	37.09	10.55	10.36	98.56	31.22
					31.21
$SiCl_4$	21.43	8.86	8.76	114.79	33.98
	27.51	8.55	8.46	115.76	34.06
	33.62	8.21	8.12	116.78	34.01
	35.82	8.10	8.01	117.17	33.96
					34.00
$SiBr_4$	20.72	11.63	11.43	126.02	53.35
	24.97	11.37	11.18	126.51	53.31
	31.23	11.03	10.84	127.22	53.39
	36.48	10.75	10.57	127.69	53.38
					53.36
$TiCl_4$	21.78	12.03	11.74	110.14	42.00
	25.04	11.77	11.49	110.53	41.86
	29.99	11.46	11.20	111.09	41.89
	36.21	11.06	10.82	111.83	41.87
					41.90
$SnCl_4$	24.71	11.13	10.91	117.59	44.85
	27.35	10.92	10.71	118.02	44.80
	32.07	10.64	10.44	118.68	44.86
	37.12	10.33	10.14	119.38	44.84
					44.84
$SnBr_4$	32.98	12.64	12.24	131.51	64.79
	35.03	12.50	12.11	131.72	64.76_5
	38.47	12.29	11.91	132.12	64.82
					64.79

TABLE IV

THERMAL PRESSURE COEFFICIENTS AND VAN DER WAALS a FOR SOLUTIONS. COMPOSITION IS 50 MOLE PER CENT. EXCEPT AS STATED

Substance	t, °C., at 1 atm.	$(\partial P/\partial T)_V$, atm. per degree Obs.	Correc.	Molal volume, cc.	a, atm. × liters^2
CCl_4–$SiCl_4$	21.03	10.13	9.98	105.68	32.79
	25.10	9.90	9.74	106.25	32.82
	29.68	9.57	9.44	106.90	32.68
	35.87	9.26	9.13	107.81	32.81
				Av.	32.78
CCl_4–$TiCl_4$	20.69	11.85	11.59	103.40	36.42
	25.43	11.55	11.30	103.95	36.47
	31.10	11.23	11.00	104.63	36.66
	36.68	10.77	10.65	105.28	36.58
					36.53
CCl_4–$SnCl_4$ 75 25	23.13	11.54	11.22	102.33	34.82
	29.38	11.00	10.80	103.11	34.74
	35.51	10.64	10.46	103.89	34.85
					38.41
CCl_4–$SnCl_4$ 50 50	21.71	11.38	11.26	107.42	38.31
	25.32	11.26	11.05	107.89	38.40
	30.41	10.94	10.74	108.54	38.41
	35.65	10.59	10.40	109.22	38.27
					38.35
CCl_4–$SnCl_4$ 25 75	22.76	11.33	11.11	112.59	41.68
	28.43	10.96	10.75	113.36	41.67
	34.36	10.61	10.42	114.16	41.77
					41.71
CCl_4–$SiBr_4$	20.36	11.77	11.44	111.47	41.58
	27.09	11.31	11.04	112.24	41.76
	30.67	11.07	10.81	112.66	41.69
	34.92	10.80	10.56	113.16	41.67
					41.68
CCl_4–$SnBr_4$	22.16	12.61	12.27	113.77	46.89
	26.14	12.31	11.98	114.24	46.79
	32.43	11.89	11.61	114.97	46.84
	35.23	11.66	11.44	115.30	46.90
					46.85_5
$SiCl_4$–$SiBr_4$	23.87	10.26	9.98	120.80	43.26
	27.43	9.90	9.74	121.29	43.07
	31.96	9.71	9.55	121.93	43.32
	35.73	9.53	9.38	122.47	43.45
					43.27_5

TABLE IV (*Concluded*)

Substance	t, °C., at 1 atm.	$(\partial P/\partial T)_V$, atm. per degree Obs.	Correc.	Molal volume, cc.	a, atm. × liters²
$SiCl_4$–$SnBr_4$	20.53	11.26	11.03	122.53	48.64
	26.18	10.90	10.69	123.28	48.64
	30.34	10.67	10.47	123.86	48.77
	35.78	10.34	10.15	124.64	48.72
					48.69
$SiBr_4$–$SnBr_4$	23.10	12.51	12.13	128.46	59.29
	27.62	12.19	11.83	128.97	59.20
	31.89	11.90	11.56	129.44	59.10
	37.03	11.58	11.26	130.02	59.05
					59.16

Table V gives data for the pure liquids at 25° recalculated from the mean values of a found in Table III. Values for other temperatures are here omitted because they can readily be calculated.

TABLE V

DATA FOR PURE LIQUIDS AT 25°

Subs.	Molal volume, cc.	$(\partial P/\partial T)_V$, atm./deg.	$(\partial E/\partial V)_T$, atm.	$v(\partial E/\partial V)_T$, liter-atm.	$v^2(\partial E/\partial V)_T = a$ atm. × liters²
CCl_4	97.09	11.11	3311	321.4	31.21
$SiCl_4$	115.36	8.57	2554	294.7	34.00
$TiCl_4$	110.50	11.51	3430	379.2	41.90
$SnCl_4$	117.64	10.86	3236	381.2	44.84
$SiBr_4$	126.52	11.18	3332	421.8	53.36
$SnBr_4$	130.62	12.74	3799	496.3	64.79

Table VI gives experimental values of three different functions for the solutions at 25°, $(\partial E/\partial V)_T$, $v(\partial E/\partial V)_T$ and $v^2(\partial E/\partial V)_T = a$, in comparison with values calculated from the corresponding functions of the pure liquids. The first two are calculated on additive basis, the a on the basis of the oft used assumption[3] that a for the mixture is given by

$$a = N_1^2 a_1 + 2N_1N_2a_{12} + N_2^2 a_2 \qquad (4)$$

and that a_{12}, referring to the constant of attraction for unlike molecules, is given by

$$a_{12} = \sqrt{a_1 a_2} \qquad (5)$$

Substituting 5 in 4 gives

$$a = (N_1\sqrt{a_1} + N_2\sqrt{a_2})^2 \qquad (6)$$

It will be observed that the best arrangement between observed and calculated values is for additivity of $v(\partial E/\partial V)_T$. Except for the mixtures of carbon tetrachloride with stannic chloride, the agreement is probably within the limit of error. The fact that this particular system shows the largest deviation is very striking, for if these tetrahalides are arranged in series according to molal volumes, boiling points, or any of the three

[3] *Cf.* J. J. van Laar and R. Lorenz, *Z. anorg. allgem. Chem.*, **171**, 41 (1928).

functions given in Table V, stannic chloride occupies an intermediate position. The anomaly suggests that this substance, while probably possessing a tetrahedral molecule,[4] may contain bonds more nearly ionic than do the other liquids here represented. The bonds in carbon tetrachloride would probably be the least ionic of the substances used, hence this pair shows the largest expansion on mixing. It will be interesting to learn, as a result of work now in progress, what correlation there may be with deviations from Raoult's law.

TABLE VI

PROPERTIES OF TETRAHALIDE SOLUTIONS AT 25°. COMPOSITION IS 50 MOLE PER CENT. EXCEPT AS NOTED

Solution	$(\partial E/\partial V)_T$, atm. Obs.	Calcd.	% Diff.	$v(\partial E/\partial V)_T$, liter-atm. Obs.	Calcd.	% Diff.	$v^2(\partial E/\partial V)_T$, liters^2 × atm. Obs.	Calcd. (6)	% Diff.
CCl_4–$SiCl_4$	2903	2982	−0.7	308.4	308.1	0.1	32.78	32.58	0.6
CCl_4–$TiCl_4$	3382	3371	.3	351.6	350.2	.4	36.53	36.35	0.5
CCl_4–$SnCl_4$									
75 25	3308	3292	.5	339.1	336.4	.9	34.81	34.38	1.2
50 50	3296	3274	.7	355.3	351.3	1.1	38.55	37.72	2.1
25 75	3269	3255	.4	369.2	366.3	0.8	41.71	41.20	1.2
CCl_4–$SiBr_4$	3320	3322	.0	372.0	371.6	.1	41.68	41.54	0.3
CCl_4–$SnBr_4$	3597	3555	1.2	410.5	408.8	.4	46.86	46.46	.8
$SiCl_4$–$SiBr_4$	2956	2943	0.4	357.8	358.3	− .1	43.28	43.14	.3
$SiCl_4$–$SnBr_4$	3209	3177	1.0	395.4	395.5	.0	48.69	48.17	1.1
$SiBr_4$–$SnBr_4$	3570	3566	0.1	459.6	459.0	.1	59.16	58.94	0.4
Mean square			0.41			0.30			1.03

It is expected to correlate the energy functions for the solutions and the pure components with the behavior of regular solutions, defined by the senior author as solutions in which there is complete randomness of molecular distribution, so that the entropy of mixing is the same as in an ideal solution of the same composition. This makes it possible to calculate the deviation from ideality of the partial molal free energies of the components of a regular solution from the heat or energy of mixing. This study is now in progress for the substances here considered.

We will add some further remarks upon the attraction constants for the pure substances. First, the assumption that $(\partial E/\partial V)_T$ is a pure function of volume for the small range here studied is justified by the linear relation between P and T. If $(\partial^2 P/\partial T^2)_V = 0$, it can be seen by differentiation of Equation 2 with respect to T at constant V that $(\partial(\partial E/\partial V)_T/\partial T)_V = 0$, hence $(\partial E/\partial V)_T = f(V)$. The curvature of the P–T curve can hardly exceed 0.001 atm. per degree, which would correspond to a change of $\partial E/\partial V$ with temperature of only 0.01%. This cannot, however, be strictly true for the entire change in volume from liquid to vapor, unless the specific heat at constant volume is independent of the volume,[5] *i. e.*, $(\partial C_V/\partial V)_T = 0$.

[4] *Cf.* R. Wierl, *Ann. Physik*, **8**, 521 (1931).

[5] (a) J. H. Hildebrand, *Phys. Rev.*, **34**, 984 (1929); (b) *Z. Physik*, **67**, 127 (1930).

For the substances studied this is probably very nearly but not quite true; hence a for volumes so different as liquid and gas might be expected to show a small difference. The only evidence on this point has already been given in the case of carbon tetrachloride. For the other substances the necessary data of sufficient accuracy are not yet at hand but are being obtained through measurements of vapor pressure.

Second, if we dismiss any departure of $\partial E/\partial V$ from being a pure volume function as a negligible effect of higher order, the simple form of the function, a/v^2, calls for some comment. For a dilute gas this form results, as is well known, from the kinetic theory. The law of force between the molecules determines the magnitude of a but not the exponent of V, all laws of intermolecular attraction yielding V^2. The intermolecular forces are operative chiefly during binary collisions whose frequency varies as the square of the concentration. The closeness of approach during a collision, however, is not affected by the volume. In dealing with solids, on the other hand, it has always been assumed that a change in volume is accompanied by a corresponding change in mean molecular distance. If this is true, an intermolecular potential proportional to $1/r^m$ would correspond to $\partial E/\partial V$ proportional to $1/V^{(m/3)+1}$. The quantum mechanical analysis of van der Waals forces by London[6] has led to $m = 6$, which corresponds to $\partial E/\partial V$ proportional to $1/V^3$. The fact that the liquids yield $1/V^2$ instead of $1/V^3$ may be interpreted as indicating that they are much nearer to gases in their nature than to solids. This is in harmony with the existence of more degrees of freedom in the liquid than in the solid. The correspondence might be expected to be less for polar molecules and we have cited elsewhere[5a] the strong departure of liquid methyl alcohol from the $1/V^2$ relation.

We may also recall the deviation from the $1/V^2$ relation when the liquid is so highly compressed, or strongly cooled, that repulsive forces begin to play an important role.[5a] An accurate study of $\partial E/\partial V$ under pressures between 1 atm. and 1000 atm. would probably reveal the necessity of substituting some more complicated function of volume, even in the range studied in this investigation.

Third, it is of interest to ask how closely the attraction constant depends upon the size for molecules surrounded by the same halogen. Table VII gives again the values of a for the tetrachlorides under investigation together with the interhalogen distance, in Ångströms, as determined by Wierl[4] for the gaseous molecules by electron diffraction. The last column gives the ratio of the former quantity to the latter. If the one were a function of the other this ratio should change in some regular way. It is evident that this is approximately but not accurately the case. We may hazard the guess that the bonds between central atom and the chlorine atoms are not

[6] F. London, *Z. Physik*, **63**, 245 (1930).

completely buried within the molecules, but influence the external field, as already suggested in connection with stannic chloride.

TABLE VII

RELATION BETWEEN VAN DER WAALS a AND INTERHALOGEN DISTANCE, l

Subs.	a atm. × liters²	l, Å.	Ratio
CCl_4	31.21	2.98	10.5
$SiCl_4$	34.00	3.29	10.3
$TiCl_4$	41.90	3.61	11.6
$SnCl_4$	44.84	3.81	11.8

Finally, it is possible to calculate the compressibility from our figures for $\partial P/\partial T$ together with the coefficients of expansion to be got from the density–temperature functions. The compressibility at 25° is given in Table VIII for the five substances which are liquid at this temperature.

TABLE VIII

COMPRESSIBILITIES AT 25°, IN RECIPROCAL ATMOSPHERES

	$\left(\frac{\partial P}{\partial T}\right)_V$ atm./deg.	$\frac{1}{V_{25}}\left(\frac{\partial V}{\partial T}\right)_p \times 10^6$	$\frac{1}{V_{25}}\left(\frac{\partial V}{\partial p}\right)_T \times 10^7$
CCl_4	11.11	1228	1105
$SiCl_4$	8.57	1416	1652
$TiCl_4$	11.51	1033	898
$SnCl_4$	10.86	1173	1080
$SiBr_4$	11.18	968	866

Summary

Certain properties of six liquid tetrahalides and seven of their binary solutions have been investigated as part of a systematic study of forces between like and unlike molecules of a high degree of symmetry.

The expansion on mixing was measured for seven liquid pairs, and is expressed by the value of 10^5k in the equation, $\Delta V/V = k\ N_1N_2$, (N_1 and N_2 are the respective mole fractions) with the following results: CCl_4–$SiCl_4$, 56; CCl_4–$TiCl_4$, 340; CCl_4–$SnCl_4$, 1632; CCl_4–$SiBr_4$, 732; CCl_4–$SnBr_4$, 884; $SiCl_4$–SnBr, 444; SiBr–$SnBr_4$, 372.

The thermal pressure coefficient, $(\partial p/\partial T)_V$, was measured with precision for the six pure liquids and for the liquid pairs mentioned above. The volume coefficient of energy was calculated by the equation, $(\partial E/\partial V)_T = T(\partial p/\partial T)_V - P$. It is a pure volume function, a/v^2, within a few tenths of a per cent. for the range studied. The values of a for the pure liquids, in liters² × atmospheres, for a mole of liquid, are, CCl_4, 31.21; $SiCl_4$, 34.00; $TiCl_4$, 41.90; $SnCl_4$, 44.84; $SiBr_4$, 53.36; SnBr, 64.79. The values of a for seven mixtures are given in the text, and their calculation from the values for the pure substances is shown and discussed.

The validity of the calculation of $(\partial E/\partial V)_T$ as a pure volume function is examined.

The exponent 2 in a/v^2 indicates that the liquids are like gases, from a kinetic standpoint, for if the molecules were uniformly spaced, the inverse sixth power of intermolecular potential, deduced by London for van der Waals forces, would lead to a/V^3.

The magnitude of a is approximately but not exactly a function of the interhalogen distance for the tetrachlorides.

The following values of compressibility at 25° were calculated: CCl_4, 1105; $SiCl_4$, 1652; $TiCl_4$, 898; $SnCl_4$, 1080; $SiBr_4$, 866; each in reciprocal atmospheres $\times 10^7$.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

NITROGEN COMPOUNDS OF GERMANIUM. II. EQUILIBRIUM IN THE SYSTEM Ge–NH_3–Ge_3N_4–H_2. THE DISSOCIATION OF GERMANIC NITRIDE[1]

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Introduction

Finely-divided germanium has been shown to react with ammonia gas at temperatures ranging from 600–750° to produce germanic nitride according to the equation[2]

$$3Ge + 4NH_3 = Ge_3N_4 + 6H_2 \quad (1)$$

This reaction was found to be readily reversible in the same temperature interval. Since germanium and germanic nitride exist as solid phases at these temperatures, the equilibrium constant for the reaction may be expressed as[3]

$$K_1 = (f_{H_2})^6/(f_{NH_3})^4 \quad (2)$$

From the ammonia equilibrium

$$2N_2 + 6H_2 = 4NH_3 \quad (3)$$

an expression for the constant may be written as

$$K_2 = (f_{NH_3})^4/(f_{N_2})^2(f_{H_2})^6 \quad (4)$$

It then follows that

$$K_1 \times K_2 = K_3 = 1/(f_{N_2})^2 \quad (5)$$

Germanic nitride is known to dissociate at high temperatures to yield nitrogen and metallic germanium[2,4,5]

$$Ge_3N_4 = 3Ge + 2N_2 \quad (6)$$

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[1] Presented at the meeting of the American Chemical Society in Indianapolis, Indiana, April, 1931.

[2] Johnson, THIS JOURNAL, **52**, 5160 (1930).

[3] The fugacity is used in this paper in place of the pressure since the magnitude of the latter assumes relatively high values. At low pressures the two terms are identical.

[4] Schwarz and Schenk, *Ber.*, **63**, 296 (1930).

[5] Hart, Master of Science Thesis, University of Chicago, August, 1930.

For this equilibrium (6) we may write

$$K_4 = 1/K_3 = (f_{N_2})^2 \qquad (7)$$

Since K_2 has been determined experimentally over a considerable temperature range, it is evident that when K_1 is known, K_4 and the pressure of nitrogen in equilibrium with germanic nitride and metallic germanium may be readily calculated for reaction (6). It was found necessary to resort to this indirect method for a determination of K_4 since the dissociation of germanic nitride, as will be shown later, cannot be determined directly.

The present paper describes the determination of K_1 at the temperatures 610, 614, 638, 654 and 664°. It was not found practical to employ a static method for the determination of this equilibrium since, at these temperatures, ammonia is readily dissociated. Accordingly, a dynamic method was used which consisted in passing different mixtures of ammonia and hydrogen over finely-divided germanium at a definite temperature. The formation of germanic nitride was easily observed by the color and the increase in weight of the germanium.

The values obtained indirectly, as described above, for K_4 show why germanic nitride is not produced when metallic germanium is heated with nitrogen at ordinary pressures. The only explanation of the apparent stability of germanic nitride, even at temperatures as high as 500°, is that the rate of dissociation to germanium and nitrogen must be exceedingly low.

Experimental

Materials.—Small amounts of purified germanic oxide were reduced with hydrogen at 600° to the gray germanium powder. For a further purification, the metal was heated in chlorine at 250° to form $GeCl_4$, the chloride was hydrolyzed to the oxide, and finally the oxide was again reduced with hydrogen to germanium. Small samples of the oxide were used in this reduction process in order to ensure complete reaction.

Anhydrous ammonia of commerce was siphoned from its container into a steel cylinder containing several small pieces of sodium which served to remove the water completely. In the course of an experiment the ammonia was allowed to escape from this cylinder as a gas.

Tank hydrogen of the best grade was used without further purification. The presence of a small amount of water or oxygen in the hydrogen was not objectionable in the experiments.

Apparatus and Procedure.—The apparatus used in the investigation is shown in Fig. 1. Approximately 1 g. of the gray germanium powder was placed in a boat and inserted into a Vitreosil tube P which in turn was heated by an electric furnace J. The temperature of the furnace was measured by a platinum–platinum-rhodium thermocouple K calibrated by the usual Bureau of Standards metals. The e. m. f. developed by the thermocouple was measured with a White potentiometer. The temperature of the furnace was readily controlled with outside rheostats with a variation of not more than ±1° during the course of an experiment.

Ammonia and hydrogen were allowed to enter at A_1 and A_2, respectively, at a rate dependent upon the composition of the mixture desired for a given experiment. The composition of the gas mixture was controlled by the calibrated flowmeters C_1 and C_2, the capillaries of which were obtained from broken thermometer stems. Some of these

capillaries were sufficiently small to allow a gas flow of less than 20 cc. per minute with a pressure difference of 10 cm. in the two arms of the flowmeter. Flowmeters with larger capillaries were used when rates as high as 300–350 cc. per minute were found necessary for certain compositions. In order to maintain a constant pressure in the flowmeters, the mercury levels in the blow-off tubes B_1 and B_2 were adjusted accordingly. Thus a constant flow of ammonia and hydrogen could be readily maintained with any excess amount of either gas passing through the tubes B_1 and B_2 continuously. The inlet of each of these tubes contained a small capillary inner-sealed in the side wall so as to produce small bubbles of the exit gases and thus avoid any appreciable disturbances in the height of the mercury columns in the flowmeters.

D_1 and D_2 were employed as traps to catch any mercury that might be removed from the meters due to the introduction of too much gas in the initial stages of a run. These traps were found to be advantageous in that the mercury could be easily returned to the meters without the necessity of dismantling the apparatus.

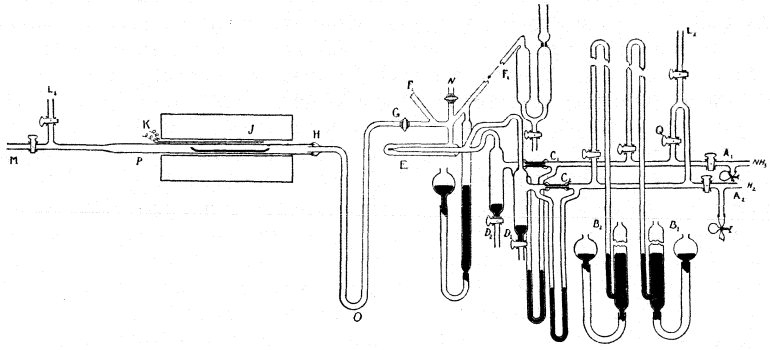


Fig. 1.

When the gases had passed through the meters at a definite rate of flow, they were allowed to enter chamber E through a small opening as shown in the figure. This chamber served to mix the hydrogen and ammonia before entering the furnace and coming in contact with the germanium. A de Khotinsky seal was made at H between the Pyrex and Vitreosil tubes. The U-tube O was employed merely to obtain some flexibility in making the seal at H.

F_1 represents a gas absorption pipet which was filled with glass tubes in order to obtain as high a surface area as possible. (F_2 leads to a second pipet of the same type not shown in the figure.) These pipets contained 50 cc. of approximately 0.1 *N* hydrochloric acid protected from gases of the atmosphere such as ammonia and moisture by a calcium chloride tube. In a given experiment the flowmeters were set to give only approximate values of the composition of the gas mixture, while accurate values were obtained through the absorption of the mixture by the hydrochloric acid in the pipets. The excess hydrochloric acid was titrated with approximately 0.1 *N* sodium hydroxide with methyl orange as the indicator. The percentage of ammonia in the different gas mixtures was thus obtained from the titration values. In order to be certain of a constant gas composition throughout an experiment, four hours for the usual case, a sample of the gas mixture was collected in F_1 during the first hour and a second sample collected in F_2 during the fourth hour. In general, a variation between the two samples was found not to exceed 0.5% ammonia.

During the course of a determination, the exit gases were allowed to pass through the tube at M into the atmosphere. Stopcock G was opened when the furnace had

reached a definite and constant temperature to permit the gases to come in contact with the germanium. It was closed when samples of the gas mixture were collected in the absorption pipets. (Between the main tubes and F_1 and F_2 were inserted stopcocks to control flow of the gases into the pipets. These stopcocks are not shown in the figure.) G was also closed at the beginning of a determination during the process of establishing a satisfactory gas flow. In this procedure the exit gases were allowed to pass into the atmosphere through N. L_1 and L_2 represent stopcocks leading to a mercury vapor pump supported by a Hyvac oil pump. According to the position of these stopcocks, it was possible to evacuate the entire apparatus on both sides of the flowmeters at the same time. This was found to be essential in the evacuation of the system since the capillaries of the flowmeters were of such a diameter as to be comparable with the mean free path of the gas molecules at low pressures.

The above description of the apparatus indicates the procedure followed to determine the equilibrium relations for equation (1) at a given temperature. When the gases had passed through the apparatus for a period of about four hours, the furnace was rapidly cooled to a temperature below that required for any appreciable reaction between ammonia and germanium. The composition of the gas mixture was maintained throughout the cooling. Then the seal at H was removed and finally the boat was taken from the tube in the furnace. Any increase in weight of the boat and contents was due to the presence of Ge_3N_4. In order to establish the presence of Ge_3N_4, in several instances the contents of the boat were reduced with hydrogen at 700°, the ammonia produced was collected in standard acid solution and determined as nitrogen. The nitrogen determination was found to check with the original increase in weight of the germanium. In the initial experiments at a given temperature, a composition of the gas mixture was used which would produce a considerable quantity of Ge_3N_4 during a four-hour heating. In the subsequent experiments, the ammonia content of the mixture was reduced until no reaction resulted with the germanium. These experiments were repeated several times at each temperature. By this procedure it was found possible to obtain equilibrium values quite accurately to approximately $\pm 0.5\%$ of ammonia.

Results

Table I gives a set of typical data at five temperatures. Column 1 of the table gives the temperature; column 2 the percentage of ammonia in the gas mixture, the first value representing an analysis of the mixture taken during the first hour of the experiment while the second value is obtained from a sample taken during the last hour; column 3, the weight of Ge_3N_4 calculated from the increase in weight due to nitrogen; column 4, the rate of flow of the gases through the meters; and column 5, the time of flow at the temperature in question. All of these data were checked several times by additional experiments.

Table II shows the equilibrium data recorded and calculated from the results given in Table I. The values given in column 3 for the percentage of ammonia in the equilibrium mixture are derived from a large amount of data, a typical set of which is recorded in Table I. In calculating K_1, partial pressures were taken to be identical with the fugacities at the temperatures and pressures employed in our experiments. It is surprising that these equilibrium values can be easily obtained and duplicated with a considerable degree of accuracy. The method employed allows for some

TABLE I

RESULTS OBTAINED IN PASSING MIXTURES OF AMMONIA AND HYDROGEN OVER GERMANIUM POWDER AT DIFFERENT TEMPERATURES

Temp., °K.	Composition of gas mixture, % NH_3	Ge_3N_4 formed, g.	Rate of flow, cc./minute H_2	Rate of flow, cc./minute NH_3	Time, hrs.
883	95.3–95.7	0.328	29	...	4
	91.2–91.6	.103	44	...	4
	90.4–90.5	.024	47	...	4
	89.9–89.9	No reaction	44	...	4
	89.6–89.8	No reaction	44	...	4
887	92.6–93.0	0.078	37	...	3.5
	89.4–90.1	.029	47	...	4
	89.0–88.5	No reaction	48	324	4
911	92.2– ..	0.141	35	...	4
	91.6–91.3	.093	35	325	4
	89.2–88.8	.078	35	295	4
	88.2–88.3	.049	35	275	4
	88.2–88.1	.049	35	270	4
	84.5–84.8	.029	35	206	4
	84.4–84.6	.019	35	214	4
	82.3–82.1	No reaction	23	123	3
	79.7–79.3	No reaction	23	105	4
927	85.7–85.9	0.054	52	289	3
	82.0–82.2	.029	74	319	4
	80.8–80.9	No reaction	79	319	3
937	84.3–83.8	0.268	52	304	3
	81.0–81.5	.195	80	316	3
	79.2– ..	.054	79	290	3.5
	77.7–78.0	No reaction	92	288	2.5
	74.2–75.3	No reaction	74	267	3

errors such as those due to changes in the rate of flow of the gases and changes in temperature of the reactants. However, these errors must be small in magnitude since the results of the experiments are readily reproducible. On the other hand, the values given for K_1 cannot be highly accurate since a small deviation in the percentage of ammonia at equilibrium becomes greatly magnified in the calculation of K_1.

TABLE II

EQUILIBRIUM DATA FOR THE REACTION $3Ge + 4NH_3 = Ge_3N_4 + 6H_2$

Temp., °K.	$10^3/T$	NH_3 at equilibrium, %	$K_1 = (f_{H_2})^6/(f_{NH_3})^4$	Free energy, ΔF (cal.)
883	1.133	90.0 ± 0.2	1.52×10^{-6}	23,500
887	1.128	89.0 ± .3	2.82×10^{-6}	22,500
911	1.097	84.0 ± .4	3.37×10^{-5}	18,600
927	1.079	81.3 ± .4	9.97×10^{-5}	17,000
937	1.067	78.5 ± .4	2.60×10^{-4}	15,400

In Fig. 2 are plotted the values of $\log K_1$ against $1/T$. A straight line is drawn through the five points in this plot. The maximum deviation of

any one point from this line is well within the limits of the deviations expressed in column 3 of Table II.

Thermodynamic Calculations.—The free energy increase (ΔF) accompanying reaction (1) is noted in the last column of Table II. It is derived from the equilibrium constant K_1 by means of the equation $\Delta F = -RT \ln K_1$, where K_1 is defined as above, T is the absolute temperature and R has a value of 1.987 cal./mole degree.

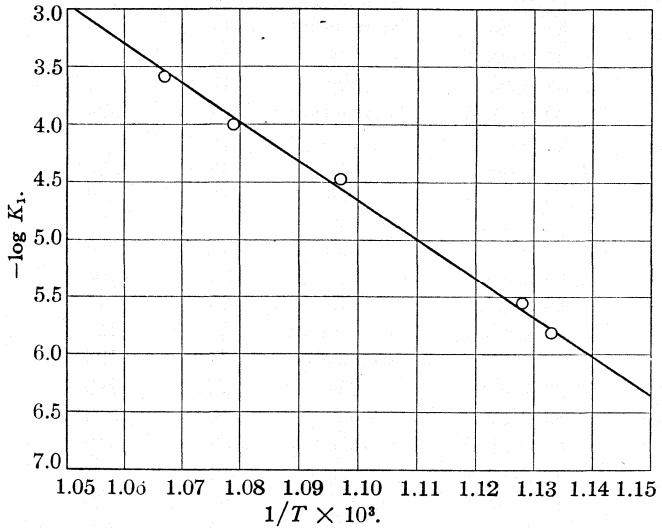


Fig. 2.

Since no data are available for the specific heat of germanic nitride, it is not possible to obtain an accurate value for ΔH of reaction (1). However, the slope of the curve in Fig. 2 gives an average value of ΔH over the temperature range between 883 and 937°K. According to this calculation, ΔH is 155,600 calories.

The dissociation pressure of germanic nitride may be calculated, as previously shown, by combining the equilibrium constant determined for reaction (1) with the known values[6] of K_2 for the ammonia equilibrium. The product of these two constants gives K_3, which is equal to the reciprocal of the square of the fugacity of the nitrogen. Since germanic nitride and germanium exist as solid phases, $K_4 = 1/K_3 = (f_{N_2})^2$ the equilibrium expression for the dissociation of germanic nitride. The free energy change accompanying the dissociation may be calculated as described above. The data are given in Table III.

[6] The equilibrium constant for the reaction, $1/2N_2 + 3/2H_2 = NH_3$, was calculated from the general free energy equation given by Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 557. This constant was then raised to the fourth power in order to satisfy equation (3).

TABLE III

DATA FOR THE DISSOCIATION OF GERMANIC NITRIDE

Temp., °K.	$K_2 \times 10^{12}$	$K_4 \times 10^{-16}$	$f_{N_2} \times 10^{-8}$ (atm.)	Free energy ΔF, in cal.
883	3.351	19.63	4.43	−69,900
887	2.930	12.10	3.48	−69,300
911	1.334	2.224	1.49	−68,150
927	0.8027	1.250	1.12	−68,300
937	0.5916	0.6501	0.806	−67,800

An average value of the heat effect, between the temperatures 883 and 937°K., accompanying reaction (6) may be obtained from the plot of log K_4 against $1/T$. This procedure gives a value of $\Delta H = -102{,}000$ calories. By adding the ΔH values for equations (1) and (3), one obtains $\Delta H = -103{,}000$ calories for reaction (6).

Discussion

The results of this investigation are in accord with the failure to prepare germanic nitride directly from germanium and nitrogen at atmospheric pressure.[7] They also show the impossibility of preparing this nitride from its elements at any pressure experimentally attainable. The equilibrium fugacities calculated for the dissociation of germanic nitride are not to be taken as being highly precise, inasmuch as any small error in the determination of K_1 becomes considerably magnified in the calculation of K_4.

The procedure followed in the work under discussion is similar to that employed by Emmett, Hendricks and Brunauer[8] in the determination of the dissociation pressure of Fe_4N. Their calculations give a dissociation pressure of 5600 atmospheres for Fe_4N at 525°. They identified the Fe_4N phase in a determination of the equilibrium, $2Fe_4N + 3H_2 = 2NH_3 + 8Fe$, by means of x-ray powder photographs. We were not compelled to use this method of identification since it has been shown that Ge_3N_4 is the only new phase that appears when germanium reacts with ammonia gas and that only germanium and ammonia are produced when Ge_3N_4 is reduced with hydrogen.[2] In the case of the action of dry ammonia on iron, several nitrides of the element have been shown to be present.

Since germanic nitride is known to be thermally stable at a temperature as high as 500° and since the calculated nitrogen fugacity in equilibrium with germanium and the nitride at 650° is of the order of magnitude of 1×10^8 atmospheres, it must be concluded that the rate of dissociation at low temperatures is exceedingly low. The data given in Table III show the nitride to be less stable thermally at the lower than at the higher temperatures; on the other hand, it does not appear to dissociate to any measurable extent at ordinary temperatures.

[7] Experiments carried out in this Laboratory. The results of this work will be discussed in a later paper in connection with the properties of germanous nitride.

[8] Emmett, Hendricks and Brunauer, THIS JOURNAL, **52**, 1456 (1930).

The results obtained indirectly for the dissociation of Ge_3N_4 are not analogous to those found for the dissociation of Si_3N_4.[9] The pressure of nitrogen in equilibrium with silicon and silicon nitride is only a few mm. at 1600°K., and this pressure is found to increase with increasing temperature up to 1800°K. Likewise, the sign of the heat effect accompanying the dissociation of Si_3N_4 is positive in contrast to the negative value found for the Ge_3N_4 dissociation.

In conclusion, we would like to thank Professor T. R. Hogness for the helpful suggestions and criticisms offered in the preparation of this article.

Summary

The equilibrium in the system Ge–NH_3–Ge_3N_4–H_2 has been determined by a dynamic method at temperatures ranging from 883 to 937°K.

Known data for the ammonia equilibrium are used to calculate the dissociation pressure of germanic nitride. The results demonstrate the failure to produce germanic nitride by heating metallic germanium with nitrogen.

The free energy and heat content changes are calculated from the log K values and the log K–$1/T$ plots, respectively, according to the usual procedures.

[9] Hincke and Brantley, THIS JOURNAL, **52**, 48 (1930).

CHICAGO, ILLINOIS

[CONTRIBUTION FROM VANDERBILT UNIVERSITY]

SOME REACTIONS OF VANADIUM CARBIDE

BY S. E. OLDHAM AND W. P. FISHEL

RECEIVED MAY 28, 1932 PUBLISHED SEPTEMBER 5, 1932

Chemically pure vanadium carbide, obtained from The Vanadium Corporation of America, was used in these experiments. Analysis corresponded to the simple formula, VC.

Vanadium carbide was found not to react with aqueous hydrochloric acid at ordinary or elevated temperatures. With nitric acid at room temperature, there was only a slight reaction, but on heating it dissolved rapidly. Prolonged heating produced an orange precipitate of hydrated vanadium pentoxide, or vanadic acid. Perchloric acid did not react with the carbide at room temperature, but boiling produced a vigorous reaction and eventually an orange precipitate as in the case of nitric acid. Large amounts of chlorine were liberated along with carbon monoxide, carbon dioxide, oxygen and some hydrocarbons. Sulfuric acid had no effect until raised to the temperature at which it became a strong oxidizing agent.

When placed in a combustion tube and heated to a temperature of 750° or higher in a current of dry hydrogen chloride, vanadium carbide reacted to form methane and hydrogen as gaseous products and vanadium dichlo-

ride, trichloride and carbon as solids. This is contrary to statements by Moissan[1] and Friend[2] that the carbide does not react with hydrogen chloride at red heat. The dichloride, especially at lower temperatures, is the chief solid product formed. An average of analyses on the dichloride was: V, 41.97%; Cl, 58.90%. No carbon dioxide was found in the gases given off by the reaction. After being freed from hydrogen chloride, the evolved gases were exploded over mercury and extracted for carbon dioxide in an Orsat apparatus. Averages of analyses on gases collected at the indicated temperatures were

Temp., °C.	815	880	950	985	1025
Methane, %	24.2	21.9	26.4	27.1	27.5
Hydrogen, %	45.5	41.4	40.6	38.1	38.2

From the contraction on explosion and the amount of carbon dioxide found, the gases were assumed to be methane and hydrogen. These gases were collected from one to one and one-half hours after the first signs of reaction. Analyses on gases caught after five hours gave a methane content of 19.3% and a hydrogen content of 53.5%. Small quantities of VCl_3 were produced in all runs, but considerable amounts were produced when the reaction was allowed to go on for five hours. A decided increase in the hydrogen content of the evolved gases was also noticed. This was probably due to a secondary reaction of VCl_2 with HCl.

The vanadium dichloride is a green solid which when thrown upon water does not sink at once, but floats on the surface of the liquid. It dissolves slowly to give a lavender solution which precipitates silver from a solution of silver nitrate and decolorizes indigo, litmus and potassium permanganate solutions. The dichloride is stable in moist air for some length of time, contrary to the statement of Friend[2] that it is an exceedingly hygroscopic compound. It dissolves readily in nitric acid with the liberation of chlorine or hydrogen chloride. Analysis for chlorine was made by first dissolving in potassium hydroxide solution to retain the chlorine and then acidifying with nitric acid. On treatment with potassium hydroxide, it seemed to dissolve and immediately reprecipitate as a black solid, probably $V(OH)_2$.

The fact that part of the carbon goes to form methane while the remainder is changed to elementary carbon indicates that some of the carbon atoms in vanadium carbide bear a different relation to the vanadium than others, and that the molecular formula is $(VC)_n$.

Summary

Vanadium carbide reacts with hydrogen chloride at elevated temperatures forming methane, hydrogen, vanadium dichloride and some vana-

[1] Moissan, *Compt. rend.*, **122**, 1297 (1896).

[2] Friend, "Text-Book of Inorganic Chemistry," Vol. VI, iii, p. 104.

dium trichloride. It is insoluble in aqueous hydrochloric acid, but is soluble in hot oxidizing acids forming hydrated pentoxides.

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

REACTIONS OF COMPOUNDS WITH EVEN NUMBERS OF ELECTRONS. NITROGEN TRICHLORIDE AND NITROGEN TETROXIDE

BY WILLIAM ALBERT NOYES

RECEIVED MAY 31, 1932 PUBLISHED SEPTEMBER 5, 1932

Some years ago it was suggested[1] that if we assume that the pair of electrons forming a covalence remain with one of the atoms which separates during a chemical reaction, a reconciliation between the positive–negative theory of the reactions of non-electrolytes and Lewis's theory of shared electrons could be effected. A further, very important, reconciliation between the older valence theories and Lewis's theory, has been furnished by the sharp distinction between doubled covalences and semipolar unions given us by Sugden's parachor,[2] and by the optically active sulfoxides of Phillips and his co-workers.[3]

In the first paper referred to it was pointed out that compounds having a covalence may, in reactions, separate either into electrically neutral parts, each with an odd electron, or into positive and negative ions by the method suggested above. Coleman and Howells[4] have shown that nitrogen trichloride reacts with butylene in the latter manner, the positive chlorine going to the end carbon atom.

In an extensive study of the reaction between nitric oxide, which has an odd electron, and nitrogen trichloride, it has been shown[5] that the nitric oxide takes an electrically neutral chlorine atom, with an odd electron, from the trichloride, leaving the ephemeral compound, nitrogen dichloride, also with an odd electron.

Nitrogen tetroxide is a compound containing only paired electrons, although it begins to dissociate to two molecules of nitrogen dioxide, each with an odd electron, at temperatures below zero. It has seemed of interest, therefore, to study the reaction of this compound with nitrogen trichloride.

It was expected that the reaction would prove to be a typical covalence reaction, the positive chlorine ion going to the negative oxygen, the nega-

[1] W. A. Noyes, THIS JOURNAL, **45**, 2959 (1923).

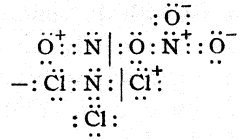
[2] Sugden, *J. Chem. Soc.*, **127**, 1525 (1925).

[3] Phillips, *ibid.*, **127**, 2552 (1925); Harrison, Kenyon and Phillips, *ibid.*, 2079 (1926).

[4] G. H. Coleman and H. P. Howells, THIS JOURNAL, **45**, 3084 (1923).

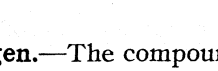
[5] *Ibid.*, **50**, 2902 (1928); **52**, 428 (1930); **53**, 2137 (1931).

tive dichloride ion (not the electrically neutral dichloride with an odd electron) combining with the positive nitric oxide ion to form the same dichlorodinitrogen oxide which was formed in the reactions of nitric oxide. At the temperatures it was necessary to use, the dichlorodinitrogen oxide decomposes at once to chlorine and nitrous oxide, as in the former experiments.



In the majority of the experiments tried the nitrogen tetroxide was condensed in the reaction bulb described in the former papers, the external bulb, in which nitric oxide was condensed for experiments at −150°, being omitted to secure a direct contact with the cooling solutions and give a better temperature control. With the nitrogen tetroxide at −80°, a cooled solution of nitrogen trichloride in chloroform was added, the bulb was evacuated and allowed to warm up slowly to −45° or above. When a solution containing 25% of the trichloride was used the reaction sometimes became very rapid, almost explosive, at −35°. There appears to be no appreciable reaction at −80°. At −45 to −35° the reaction proceeds slowly, with little change in color and a slow evolution of nitrous oxide and then of chlorine. After a time the solution became red from the formation of nitrosyl chloride.

The products of the reaction were distilled through the series of seven U-tubes and were separated and analyzed as for the experiments with nitric oxide and nitrogen trichloride, previously described. The results varied between wide limits and conditions for a smooth, fairly quantitative reaction have not been found. It does not seem worth while, therefore, to give the results of individual experiments. Fifteen or more experiments were tried under varying conditions. The following products have been found:



Nitrogen and Oxygen.—The compound, , supposed to be one of the initial products of the reaction seems to decompose to oxygen and nitryl chloride, NO_2Cl. The larger part of the nitrogen trichloride always decomposed to nitrogen and chlorine. The gases not condensed in a U-tube surrounded by liquid air were analyzed and found to contain 95 to 96% of nitrogen and 4 to 5% of oxygen. It was thought at one time that chlorine monoxide might be formed. Some qualitative indications of its presence were seen in a few experiments but no satisfactory evidence was secured.

Nitrous oxide was always found. The amount varied from 0.03 to

0.44 mol for each mol of nitrogen tetroxide used. The largest amount was found in an experiment in which about 2.9 mols of nitrogen tetroxide was used with 29 mols of nitrogen trichloride. In other experiments the quantities found were much smaller.

Chlorine.—Nearly all the nitrogen trichloride decomposed to nitrogen and chlorine and none of the trichloride was found at the end of any experiment. This is in marked contrast with the conduct of nitric oxide reported in other papers. This may have been partly due to the higher temperature necessary to bring about any interaction between the trichloride and tetroxide but probably also because of some catalytic effect of the nitrogen tetroxide and dioxide on the trichloride.

Nitrosyl chloride was found in varying amounts. A number of different explanations may be given for this but without better experimental evidence it is useless to speculate.

Nitryl chloride, NO_2Cl, was found several times among the products of the reaction. The following analysis demonstrated its presence: gas, 1.51 mg. mol.; wt., 0.1146; N, 1.46 mg. at.; Cl, 1.59 mg. at.; O, 2.36 mg. at. This corresponds to mg. mol., Cl_2, 0.05; NO_2Cl, 0.90; NOCl, 0.56.

For a discussion of the existence of nitryl chloride see the following paper.

Nitrogen tetroxide was partly left unchanged at the end of the experiments.

Summary

1. The interaction of nitrogen trichloride dissolved in chloroform and nitrogen tetroxide, at 0 to −35°, gives nitrogen, oxygen, nitrous oxide, chlorine, nitryl chloride and nitrosyl chloride. The nitrogen trichloride is all decomposed and the nitrogen tetroxide is, in part, either unchanged or regenerated in the reaction.

2. The formation of nitrous oxide is most simply explained by supposing an initial covalence reaction in which the positive $\dot{\ddot{O}}::\dot{\ddot{N}}^{+}$ group combines with the negative $:\dot{\ddot{C}}\dot{\ddot{l}}:\dot{\ddot{N}}:^{-}$ to form the same dichlorodinitrogen oxide which is formed by the interaction of nitric oxide and nitrogen trichloride. Nitrous oxide is formed from this by the loss of chlorine.

3. Nitryl chloride, NO_2Cl, is another product of the reaction.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

REDISCOVERY OF NITRYL CHLORIDE

BY WILLIAM ALBERT NOYES

RECEIVED MAY 31, 1932 PUBLISHED SEPTEMBER 5, 1932

In the study of the reaction between nitrogen trichloride and nitrogen tetroxide described in the preceding paper, nitryl chloride, NO_2Cl was discovered as one of the products of the reaction. An examination of the literature showed that Richard Müller described a preparation of the compound by the action of hydrochloric acid on nitrogen tetroxide.[1] Hassenberg prepared it by passing nitrogen dioxide mixed with an excess of chlorine through a hot tube.[2] Odet and Vignon prepared it by passing the vapor of phosphorus oxychloride over lead or silver nitrate.[3] Exner[4] prepared the compound by the method of Hassenberg and also by that of Odet and Vignon and tried experiments which indicated that he actually had the compound in his hands.

W. Collingwood Williams,[5] and Gutbier and Lohman,[6] repeated the experiment of Hassenberg, but failed to get any satisfactory evidence of the formation of nitryl chloride. Geuther[7] also tried, unsuccessfully, to obtain the compound by dropping cooled nitrogen tetroxide on cool phosphorus pentachloride. After these futile attempts, chemists generally believed that the earlier workers had been in error and the compound was omitted from textbooks and handbooks.

After discovering that the compound is formed by the interaction of nitrogen trichloride and nitrogen tetroxide, an examination of the articles cited led to the conclusion that some of the earlier workers were more careful than their critics. Especially, no one seems to have repeated the experiments of Müller, and Williams used temperatures too low and too high for a successful result.

Müller gives the equation

$$3NO_2 + 3HCl = 2NOCl + NO_2Cl + H_2O$$

The first experiments by his method seemed to give only very small quantities of nitryl chloride but finally a gas was obtained which gave the following results: gas, 2.61 mg. mol.; N, 2.87 mg. at.; Cl, 1.89 mg. at.; O, 4.54 mg. at. These results give four simultaneous equations from

[1] Richard Müller, *Ann.*, **122**, 1 (1862).
[2] Hassenberg, *J. prakt. Chem.*, [2] **4**, 11 (1871).
[3] Odet and Vignon, *Compt. rend.*, **70**, 96 (1870).
[4] Exner, *Wien. akad. Ber.*, **65**, II, 120 (1872).
[5] Williams, *J. Chem. Soc.*, **49**, 222 (1886).
[6] Gutbier and Lohmann, *J. prakt. Chem.*, [2] **71**, 182 (1905).
[7] Geuther, *Ann.*, **245**, 98 (1888).

which the following composition can be calculated:[8] mg. mol, NOCl, 1.20; NO_2Cl, 0.69; NO_2, 0.46, N_2O_4, 0.26.

Müller did not determine nitrogen in his compound, his determination of the molecular weight does not indicate a pure compound and since he gives a boiling point of $+5°$, while Schumacher[10] has found a boiling point of about $-13°$, it seems probable that he had a mixture containing nitrosyl chloride and nitrogen tetroxide as well as nitryl chloride.

After removing the nitrosyl chloride and nitryl chloride in a current of air, nitric acid remained, as Müller states. This was entirely free from chlorine and had a composition closely approaching that of a monohydrate, or orthonitric acid, H_3NO_4. Pickering demonstrated[9] the existence of this hydrate. Its formation is probably the reason why the nitryl chloride is not hydrolyzed by the water formed in the reaction.

Nitryl chloride has been obtained by passing the vapor of phosphorus pentachloride over carefully dried lead nitrate. As the method of Schumacher, to be referred to below, is much superior to this, details and analyses need not be given.

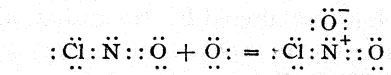
To test the method of Hassenberg some nitrogen tetroxide and an excess of chlorine were sealed in a tube in such amounts that they gave a pressure of about six atmospheres at 270°. The tube was heated for two hours in boiling toluene without apparent result, for eighteen hours in boiling naphthalene (218°), with the appearance of a reddish color after cooling to a temperature at which nitrogen tetroxide is colorless, and for five hours in an air-bath, 230–250° in the upper part and at about 300° below. After cooling, the gas remaining in the tube was transferred to a tube in which it could be weighed and analyzed. The results of the analysis were: mg. mol. Cl_2, 1.66; NOCl, 0.05; NO_2Cl, 0.63; NO_2, 0.19.

After the work described in this paper was nearly complete, Mr. Colin W. Whittaker, of the Division of Fixed Nitrogen Investigations in the Bureau of Chemistry and Soils, in Washington, called my attention to the papers of Schumacher and Sprenger,[10] which I had overlooked. They have prepared nitryl chloride by the action of ozone on nitrosyl chloride. Evidently the ozone adds an electrically neutral oxygen atom to the unshared electrons of the nitrogen atom

[8] The Editor has very kindly called my attention to the fact that nitrogen tetroxide is dissociated to the dioxide only to the extent of about 25% at 30°, the temperature of the experiment and that the ratio of the two reported is improbable. The dilution of the gases would increase the dissociation but it is evident that the results are not very accurate or reliable and the evidence for nitryl chloride is not very satisfactory in this case. I am of the opinion that the compound was present. Considerable time has been spent on the subject and it is not of sufficient importance to justify further work.

[9] Pickering, *J. Chem. Soc.*, **63**, 436 (1893).

[10] Schumacher and Sprenger, *Z. anorg. allgem. Chem.*, **182**, 139 (1929); *Z. Elektrochem.*, **35**, 653 (1929); *Z. physik. Chem.*, **B12**, 115 (1931).



Their determinations of vapor pressure indicate a boiling point of −13°, which throws discredit on the boiling point given by Müller. They state that the compound is completely decomposed at 170° and assume that it decomposes to nitrogen dioxide and chlorine and that these do not combine at any temperature. The experiments recorded above do not altogether agree with this. They also indicate that nitryl chloride decomposes to nitrosyl chloride and oxygen as well as to nitrogen dioxide and chlorine.

Summary

Nitryl chloride has been prepared by the action of hydrochloric acid on nitrogen tetroxide, by the action of phosphorus pentachloride on lead nitrate, and by the union of nitrogen dioxide and chlorine.

The method of Schumacher and Sprenger by the action of ozone on nitrosyl chloride is undoubtedly better. That method, combined with the method of Whittaker, Lundstrom and Merz[11] for preparing nitrosyl chloride will make nitryl chloride and nitrosyl chloride easily accessible for both laboratory and commercial use.

[11] Whittaker, Lundstrom and Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE EFFECT OF SUPERSONIC RADIATION ON BROM THYMOL BLUE

BY A. R. OLSON AND N. B. GARDEN

RECEIVED MAY 31, 1932 PUBLISHED SEPTEMBER 5, 1932

In 1929, Schmitt, Johnson and Olson[1] reported that various substances can be oxidized by subjecting solutions of such substances to ultrasonic vibrations under such conditions that air or oxygen can be cavitated from the solutions. In particular, experiments were conducted upon dilute aqueous solutions of brom thymol blue, without specifying how dilute those solutions were. Quoting from their article, "Subsequent tests showed that when a dilute aqueous solution of brom thymol blue (to which sufficient sodium hydroxide was added to produce a blue green color) was radiated, the solution changed to yellow in a very short time. It was easy to demonstrate that comparatively few of the dye molecules were destroyed in the process of radiation, for addition of alkali caused a prompt return of the blue color. Other indicators, such as brom phenol blue and litmus were affected in a similar manner. Whatever the process may be, there is no

[1] Schmitt, Johnson and Olson, THIS JOURNAL, **51**, 370 (1929).

doubt that dye molecules were altered by the radiation and gave rise to hydrogen ions." An attempt to repeat some of this work was made by Szu-chih Liu and Hsien Wu.[2] They confirmed the conclusion of Schmitt, Johnson and Olson, that the presence of oxygen was necessary, but stated that "the indicators are permanently destroyed under the influence of ultrasonic radiation. A change of hydrogen-ion concentration may occur as a result of this destruction, but the fading of the color is due to the destruction of the indicator and not to any change in the hydrogen-ion concentration." They based this conclusion on the observation that the indicator solution became colorless without passing through the yellow stage, and that the addition of alkali did not cause the return of the blue color.

The only point at issue between the two groups of investigators is the concentration of hydrogen ion produced, and the concentration of indicator molecules which remain after radiation, since both groups agree that some indicator molecules are destroyed. The most obvious explanation of the apparent discrepancy between the two investigations lies in the probable difference of the initial concentration of indicator and hydrogen ion. Nevertheless, the experiments have been repeated and extended as described below.

The oscillator was essentially the same as that used by Schmitt, Johnson and Olson. The brom thymol blue was identical with that used in the original investigation. It was not recrystallized or purified, but was dried at 108° for two hours; 0.25 g. was shaken with a liter of distilled water, and then decanted. This solution, which corresponds closely with that used by Schmitt, Johnson and Olson, will be called Solution A. Another liter of distilled water was poured upon the residual crystals, and after shaking and standing for some time, it was decanted. This solution will be referred to as Solution B. A third solution, C, was made by dissolving 0.081 g. of the indicator in a liter of water. This corresponds to a concentration of 1.3×10^{-4} M. The usual stock indicator solution is made by dissolving 0.04 g. of indicator in 100 cc. of 95% alcohol, which corresponds to 6×10^{-4} mole liter, and so the titration is carried out with an indicator concentration of about 3×10^{-6} M. This procedure was not followed, in order to avoid the introduction of any extraneous material. The P_H values were determined by comparing with Clark's[3] color chart.

Solution A appeared to be more orange than B. The behavior of these two solutions toward alkali also appeared to be different. The addition of one drop of 0.05 N sodium hydroxide to 10 cc. of B produced a deep blue color which faded in a few minutes to a yellowish green. With

[2] Szu-chih Liu and Hsien Wu, THIS JOURNAL, **54**, 791 (1932).

[3] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1920.

A, on the other hand, several times as much alkali was required to produce the blue color, and this turned rather quickly to yellow. On standing in Pyrex glass for a few days, B required more sodium hydroxide than A to produce the same color. The commercial indicator therefore probably is inhomogeneous, which is not surprising in view of the complicated structure of this molecule.

When a small amount of freshly prepared solution A, to which sufficient sodium hydroxide had been added to give a blue green color, was divided into two parts, one of which was kept for a control and the other subjected to radiation, the radiated sample quickly turned yellowish green and then yellow. When more sodium hydroxide was added to this sample, the blue-green color was reëstablished. Further radiation again turned this yellow. This process was repeated several times but the color became less intense until finally all the dye molecules were destroyed. This completely confirmed the results reported by Schmitt, Johnson and Olson.

With a fresh solution of B, on the other hand, the radiated sample gradually faded in color without turning yellow so that after half an hour's exposure the solution was water white. The addition of alkali did not cause a return of color, which is in accord with the observations of Szu-chih and Hsien Wu.

In order to determine whether this difference in behavior was due to differences in hydrogen-ion concentration or whether it was due to difference in the characteristic end-points of the two samples of indicator, the experiments were repeated using hydrogen electrodes to determine the change in the hydrogen-ion concentration. Two hydrogen electrodes were used, one in the radiated sample and one in the control. The two samples were connected by a bridge which was fitted with a stopcock that was opened only when readings were taken.

Under these conditions it was found that when solution A was radiated until it turned yellow, the hydrogen-ion concentration was 2.5 times that of the control. On the other hand, when solution B was radiated until the color faded, its hydrogen-ion concentration was 5 times that of the control, thus showing that solution A was much more sensitive to the hydrogen-ion concentration than solution B.

In the work of Szu-chih Liu and Hsien Wu the indicator for their samples was taken from a 0.0006 M solution which they had made, but 20 drops were used per 100 cc. in the solution subjected to radiation so that their indicator concentration was 5 times that normally used for titration or about 1.7×10^{-5} M. This corresponds to one-tenth the concentration of solution C.

If the P_H of a solution of pure C is adjusted to slightly above the 7.6, possibly around 8, then the color fades slowly and does not give the yellow acid color. Upon radiation various dilutions of solution C were then

tried, starting in each case with the P_H color for 7.2 and it was found that the yellow color was obtained down to a composition of 4 cc. of solution C with 46 cc. of water and 2 drops of 0.05 N sodium hydroxide. With this solution and those more dilute than 0.000015 M of indicator, the indicator was apparently decomposed without change of color. With a P_H of 7.6 it required a much greater concentration of indicator to produce a yellow color. These results confirm the explanation offered above for the apparent discrepancy between the two investigations.

Tests were then made to detect whether the vibrations had a direct or an indirect effect upon the indicator by adjusting a basic solution to such a value that the 7.2 P_H color was given upon the addition of an equal volume of solution C. Samples of this were put in three test-tubes which had been carefully rinsed with the solution. To one was added the indicator solution and this colored one along with a clear one was placed in the vibrating carbon tetrachloride. After ten minutes' radiation the samples were removed and all three brought to the same temperature. The indicator solution was then added to the other two samples. That sample which was exposed with the dye present in solution showed the usual change in color to the acid side and the clear solution which was exposed likewise showed more acid but not so great as in the first case.

This demonstrates rather conclusively that the vibrations produce effects in addition to those produced on the indicator molecules, such as hydrogen peroxide formation as suggested by Schmitt, Johnson and Olson or solution of, or adsorption by the glass.

A solution of indicator which has turned yellow due to ultrasonics can be restored to the green color by boiling so that the presence of a volatile acid is indicated. Such a solution can again be made acid by further radiation and the volatile acid again removed. Each time this is done the color is less pronounced. The process can be repeated until the color is completely destroyed. This definitely removes the possibility that the carbon dioxide of the air can be entirely responsible for the color change.

Conclusions

It has definitely been shown that the observations of Szu-chih Liu and Hsien Wu and of Schmitt, Johnson and Olson are not necessarily in conflict and that the variation of indicator and hydrogen-ion concentrations presents one explanation of the differing results.

There is also the possibility that the brom thymol blue obtained for use as indicator is not a homogeneous substance and that the compounds used by the two sets of experimenters differed.

The results definitely prove that the hydrogen-ion concentration does change upon the destruction of the indicator.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE DENSITY OF SOLUTIONS OF SODIUM, POTASSIUM AND SODIUM BROMIDE IN LIQUID AMMONIA

BY WARREN C. JOHNSON AND ALBERT W. MEYER

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Kraus and Lucasse[1] observed, in their studies of concentrated solutions of sodium and of potassium in liquid ammonia, a rather abrupt change in the conductivity in passing from saturated solutions to those more dilute in the alkali metal. They were able to determine with considerable accuracy the composition of the saturated solution at the point of discontinuity. Since the volume of the cell employed could be measured approximately, they estimated the density of a saturated solution of sodium in liquid ammonia to be 0.54 and that of a saturated solution of potassium as 0.632.

Of particular interest in these observations is the fact that in both cases the density of the saturated solution is markedly lower than the densities of the constituents comprising the solution. In other words the process of solution of the alkali metal in liquid ammonia is accompanied by a substantial increase in volume. Later, the density of solutions of sodium in ammonia was measured directly with a Westphal balance over a considerable range of concentration, from 32.6 gram molecules of ammonia per gram atom of sodium to the saturation point.[2] The density of the saturated solution was found to be in good agreement with the estimated value of Kraus and Lucasse,[1b] and to increase with dilution to approach that of pure liquid ammonia.

The unusually large volume increase was interpreted as being due to the electron freed from the constraints of the metal, since studies of other physical properties of these solutions were sufficiently conclusive to show the sodium present as normal sodium ions.[3]

In view of the interesting properties of these solutions, it was deemed advisable to measure the density of solutions of potassium in liquid ammonia at different concentrations. In addition, the density of saturated and also highly diluted solutions of sodium is determined as a verification of the method employed. In order to demonstrate the unique behavior of the metal solutions in contrast to that of solutions of salts in liquid ammonia, similar measurements are made with sodium bromide solutions.

Apparatus and Procedure

The apparatus employed throughout the investigation was identical with that formerly used for the sodium solutions.[2] Several other types of apparatus were de-

[1] Kraus and Lucasse, (a) THIS JOURNAL, **43**, 2538 (1921); (b) *ibid.*, **44**, 1941 (1922).

[2] Kraus, Carney and Johnson, *ibid.*, **49**, 2206 (1927).

[3] See Kraus, *ibid.*, **43**, 749 (1921), and previous articles.

signed and tested in the preliminary experiments, but they were discarded as inferior to the above in simplicity and in ease of manipulation.

Metallic potassium was introduced into the bottom of the density tube by the method described by Kraus and Lucasse.[1a] At the end of a series of measurements the ammonia was allowed to evaporate and the last trace was removed by the vacuum pumps. The metal was dissolved in an alcohol–ether mixture, the solution was partially evaporated to remove the organic solvents, and then titrated with approximately 1 *N* hydrochloric acid. A small excess of the acid was added to the solution, the solvent was evaporated in a platinum dish and finally the metal was determined as chloride in order to check the titration results. A similar procedure was used for the determination of sodium. In the case of sodium bromide, a weighed amount of the salt was placed in the density tube before the addition of ammonia.

The alkali metals used in the experiments were found to be free from iron; the potassium contained a small amount of sodium. The sodium bromide was crystallized twice from water solution and was thoroughly dried at 110°.

Former measurements[4] of the vapor pressure of solutions of potassium in liquid ammonia furnished data for the composition of the saturated solution as well as for corrections for the amount of ammonia in the vapor phase to be applied in the calculation of the concentration of the solution whose density was to be measured. In the case of the sodium and sodium bromide solutions, the concentration was sufficiently low in each instance to allow for a vapor phase correction on the basis of the vapor pressure of pure ammonia at the temperature in question.[5]

The temperature of the solutions was measured with a calibrated alcohol thermometer to read to ±0.05° between 0 and −50°. Due to changes in the barometric pressure during a period of several hours required for a determination, it was not found possible to control the temperature of the liquid ammonia bath with a variation of less than ±0.2°.

Results

The density values for saturated and dilute solutions of sodium in liquid ammonia are given in Table I. The concentration of the solution is expressed in terms of the number of gram molecules of ammonia per gram atom of sodium. The volume change per gram atom of sodium, ΔV, is calculated from the equation

$$\Delta V = \frac{N \times 17.032 + 22.997}{D_s} - \left(\frac{N \times 17.032}{D_{NH_3}} + \frac{22.997}{D_{Na}}\right)$$

where N represents the concentration as expressed above, D_s the density of the solution, D_{Na} the density of metallic sodium at −33.8°, and D_{NH_3} the density of pure ammonia at the same temperature. At this temperature the density of liquid ammonia is 0.6821,[6] while that of sodium is 0.9805 according to the data of Dewar[7] at low temperatures and of Richards and Brink[8] at ordinary temperatures.

[4] Johnson and Meyer, *J. Phys. Chem.*, **33**, 1922 (1929).

[5] For the vapor pressure of liquid ammonia at different temperatures, see Cragoe, Meyers and Taylor, *Bureau of Standards, Scientific Papers*, No. 369, p. 33, 1920.

[6] Cragoe and Harper, *Bur. Standards, Sci. Papers*, **420**, 313 (1921).

[7] Dewar, *Chem. News*, **85**, 277 (1902).

[8] Richards and Brink, THIS JOURNAL, **29**, 117 (1907).

TABLE I

DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA

$t = -33.8°$. 0.5307 g. of sodium

NH_3, g.	NH_3/Na	Density	ΔV, cc.
Saturated soln.	5.48	0.5781	41.01
14.873	37.84	.6603	43.03
18.882	48.04	.6653	41.95
21.684	55.17	.6681	40.45
25.210	64.14	.6704	39.51

A large excess of sodium was employed in the determination of the density of the saturated solution, the result of which is shown in the above table. For the composition of this solution, the value of 5.48 gram molecules of ammonia per gram atom of sodium was taken from former data on the vapor pressure of sodium solutions.[2]

The density of solutions of potassium in liquid ammonia was measured from the saturation point to a concentration as low as 34.08 gram molecules of ammonia per gram atom of potassium. The volume change is calculated as described above. At the temperature of the measurements, $-33.2°$, the density of liquid ammonia is 0.6816,[6] while that of metallic potassium is taken as 0.86.[9] The data for the potassium solutions are given in Table II.

TABLE II

DENSITY OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AT $-33.2°$

NH_3, g.	NH_3/K	Density	ΔV, cc.
	Series I: 1.5718 g. of potassium		
Satd. soln.	4.95	0.6282	27.28
11.105	16.22	.6583	28.30
15.870	23.18	.6659	26.91
18.322	26.76	.6685	26.15
20.978	30.64	.6701	26.08
23.333	34.08	.6721	24.73
	Series II: 2.6025 g. of potassium		
Satd. soln.	4.95	0.6282	27.28
7.9695	7.03	.6351	29.00
10.940	9.65	.6433	29.67
12.697	11.20	.6483	29.20
14.963	13.20	.6522	29.36
20.122	17.75	.6598	28.44

In order to point out the abnormal behavior of metals dissolved in liquid ammonia, a series of density measurements was made with sodium bromide solutions. A rather abrupt change was found to take place in the density in

[9] This value is selected from the data of Richards and Brink,[8] at 20°, since measurements are not available at low temperatures. The density of metallic potassium is probably 1–2% greater at $-33.5°$ than at 20°; however, the value taken at the latter temperature has only a small effect on the volume change as calculated from the above equation.

passing from the saturated solutions to those containing a smaller amount of dissolved salt. An extrapolation of the density curves, representative of the saturated and dilute solutions, respectively, gave a value of 45.00 gram molecules of ammonia per gram molecule of sodium bromide for the composition of the saturated solution. In other words, at $-33.2°$, 13.43 g. of sodium bromide is dissolved by 100 g. of liquid ammonia. Such an extrapolation is subject to error; however, in this case, the error must not be greater than 3–4%. The results of these density measurements are shown in Table III. The volume change accompanying the process of solution is not given in the table but may be readily calculated in a manner previously described.

TABLE III

DENSITY OF SOLUTIONS OF SODIUM BROMIDE IN LIQUID AMMONIA AT $-33.2°$

NH_3, g.	NH_3/NaBr	Density
Series I: 1.0445 g. of sodium bromide		
Satd. soln.	45.00	0.7417
11.410	66.00	.7273
14.921	86.33	.7204
17.670	102.21	.7153
Series II: 0.5143 g. of sodium bromide		
12.085	141.98	0.7073
19.646	230.85	.6983
26.920	316.29	.6941
29.803	350.15	.6933

Discussion

The density of solutions of sodium in liquid ammonia is shown in Fig. 1, curve I, with the mole fraction of the metal plotted as abscissa and the density as ordinate. The circles represent former data[2] while the disks are taken from the values given in Table I above. The value for a saturated solution is practically identical with the earlier work of Kraus, Carney and Johnson, in that the latter report a value of 0.5782 while that of our work is found to be 0.5781 at the same temperature. The values found at low concentrations lie well upon the line extrapolated from the earlier data to zero concentration, in other words, to the value of the density of pure liquid ammonia at $-33.8°$. Although our values at low concentrations are not as consistent among themselves as those at the higher concentrations, they are sufficient to demonstrate the applicability of the method. These less consistent results may be attributed in part to the greater tendency of the alkali metals to react with ammonia in dilute solutions.

In Fig. 2, curve I, the density of potassium solutions is plotted against the concentration of the dissolved metal in a manner frequently employed for this type of work. It is observed that the density increases continuously with decreasing concentration of metal to approach the density

of pure ammonia. The form of the curve is the same as that found for sodium solutions. The density of a saturated solution of potassium in

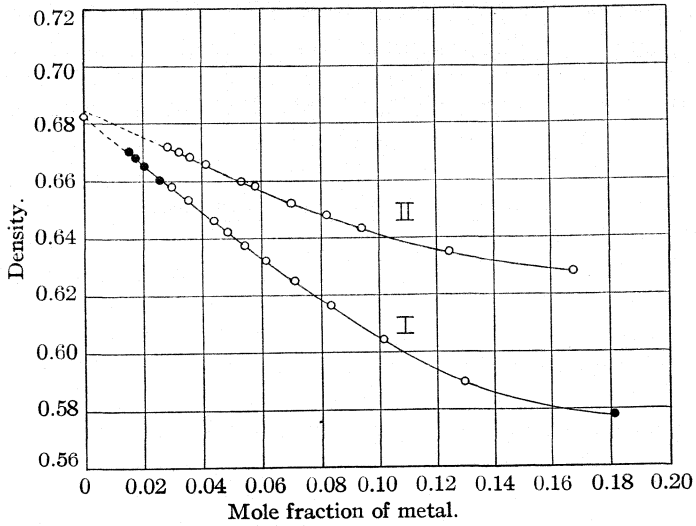


Fig. 1.—Density of solution of sodium and of potassium.

ammonia is found to be 0.6282, which is in good agreement with the estimated value (0.632) of Kraus and Lucasse.[1]

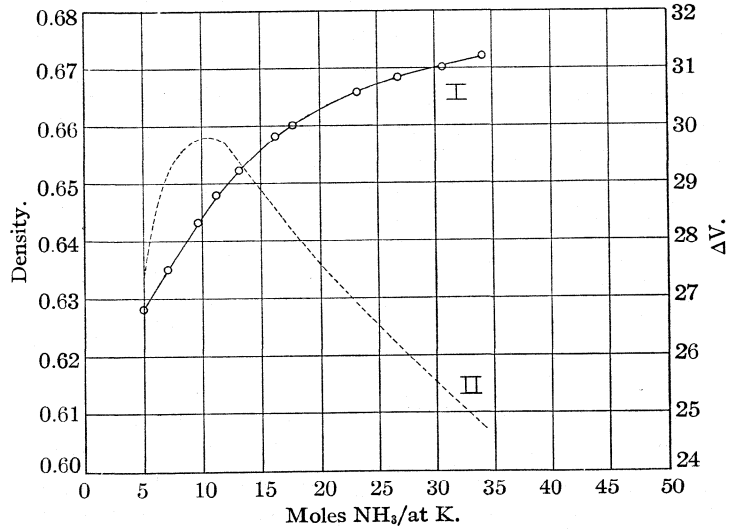


Fig. 2.—Density and volume change for potassium solution at −33.2°.

Figure 1, curve II, shows the mole fraction of potassium plotted against the density. In this case, it is readily seen that the density of potassium

solutions is somewhat greater than that of sodium solutions at equivalent mole fractions. The two curves approach each other at low concentrations and should practically coincide at zero concentration. The fact that the potassium curve lies above the sodium curve at zero concentration of dissolved metal, though the temperature of the former is 0.6° higher than that of the latter, can be accounted for by the difficulties encountered in temperature control and by the greater reactivity of metallic potassium in dilute ammonia solutions. The potassium curve extrapolates to a value of 0.6844 at zero concentration while the density of pure ammonia at −33.2° is 0.6816. In other words, the values given at the lower concentrations are about 0.4% too high for the temperature in question. However, the major part of this error may be attributed to fluctuations in the temperature.

The volume change accompanying the process of solution of potassium in ammonia is found to be considerable in magnitude. The variation of this change with concentration of the solution is shown in Fig. 2, curve II. Since the volume change, ΔV, is very sensitive to small variations in the density, the above-mentioned plot was made by taking values from the smooth density curve (I). The form of the volume change curve closely resembles the analogous curve for sodium solutions. It passes through a maximum at a concentration of about 10.5 gram molecules of ammonia per gram atom of potassium while the corresponding value for the sodium solutions is 11.25. Evidently, some similar change is taking place in these concentrated solutions of sodium and of potassium which we are unable to explain with the data at our disposal. The volume change accompanying the formation of a saturated solution of potassium in ammonia is 27.28 cc. per gram atom of metal, while the maximum volume change is 29.80 cc. The corresponding volume changes for sodium solutions are 40.96 cc. and 43.37 cc., respectively. It may be possible to account for the differences in the values for sodium and potassium solutions by the relative atomic and ionic radii of the metals alone. In other words, it would appear that the function of the negative constituent, presumably the ammoniated electron, is the same in both solutions.

An examination of curve I, Fig. 3, which shows the density of solutions of sodium bromide in liquid ammonia as a function of the concentration, points out the normal behavior of salt solutions. In this case, the density of the saturated solution is 0.7417, which value is found to decrease with decreasing salt concentration to approach the density of pure ammonia. Since the density of this solution is markedly higher than the density of pure liquid ammonia, it is to be concluded that the effect of the sodium ion is to decrease the volume of the solution. Thus, the actual volume increase, due to the negative constituent present as a result of solution of metallic sodium in ammonia, must be very large to overcome the effect of the normal sodium ion. It would be interesting to compare the partial

molal volume of sodium bromide with the partial molal volume of sodium in relatively dilute ammonia solutions in order to obtain a better conception of the relative effects of the negative constituents in relation to the volume change. Such a comparison would require more data than we have at our disposal at the present time.

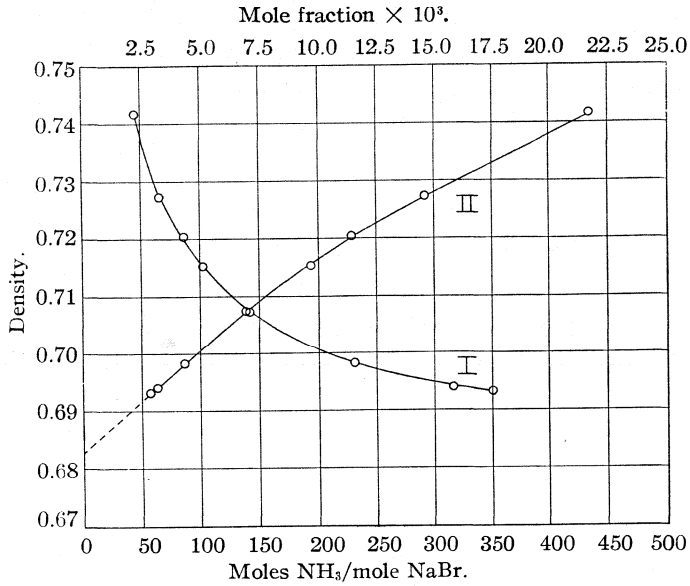


Fig. 3.—Density of solution of sodium bromide in ammonia at −33.2°.

Curve II, Fig. 3, shows the mole fraction of sodium bromide plotted against the density. In the more dilute solutions the curve follows a straight line which, upon extrapolation to zero concentration, intersects the density axis at a value of 0.6828. This value is slightly greater than the density of pure ammonia at −33.2°, namely, 0.6816, but is well within the limits of error due to fluctuations in the temperature.

Summary

The density of saturated and dilute solutions of sodium in liquid ammonia at −33.8° has been determined to check the method and former data.

Similar measurements have been made for solutions of potassium in liquid ammonia, the results of which resemble closely those found for sodium solutions. The density of a saturated solution of potassium in ammonia is 0.6282 at −33.2°; with decreasing concentration of metal, the density increases to approach that of pure ammonia.

The increase in volume accompanying the solution of potassium in liquid ammonia has been calculated from the density values. The volume

increase for a saturated solution is 27.28 cc. per gram atom of potassium. It is found to increase at lower concentrations to a maximum value of 29.80 cc. and then to decrease in solutions containing a smaller amount of dissolved metal.

In order to point out the abnormal behavior of solutions of metals in liquid ammonia, the density of solutions of sodium bromide has been measured at $-33.2°$ over a considerable concentration range. The density of these solutions is found to decrease with decreasing concentration of sodium bromide in a normal manner.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS DIVISION, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.]

THE THERMAL DECOMPOSITION OF AZINES

BY LOUIS B. HOWARD AND GUIDO E. HILBERT

A NOTE ON THE THERMAL DECOMPOSITION OF BENZALDAZINE UNDER 1000 ATMOSPHERES PRESSURE OF NITROGEN, HYDROGEN AND AMMONIA

WITH R. WIEBE AND V. L. GADDY

RECEIVED JUNE 4, 1932 PUBLISHED SEPTEMBER 5, 1932

THE THERMAL DECOMPOSITION OF AZINES

Curtius and Jay[1] observed that aldazines, notably benzaldazine, decompose upon distillation into stilbenes and nitrogen. Later Meisenheimer[2] pointed out that benzonitrile was also one of the thermal decomposition products of benzaldazine and postulated two simultaneous reactions.

$$C_6H_5CH{=}N{-}N{=}CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + N_2 \quad (1)$$

$$C_6H_5CH{=}N{-}N{=}CHC_6H_5 \longrightarrow 2C_6H_5CN + H_2 \quad (2)$$

The most comprehensive study was that of Pascal and Normand,[3] who demonstrated in the case of benzaldazine that in addition to stilbene and nitrogen, some ammonia, a small amount of phenanthrene and a stable compound containing nuclear nitrogen were also produced. Azines in which the ortho position of the benzene ring was substituted yielded none of the phenanthrene derivatives. They suggested that the stable nuclear nitrogen compound (yield 15%) had the empirical formula of $C_{28}H_{23}N_3$ (melting point 261° and boiling point 460°) and probably was identical with the unknown product obtained by Curtius and Blumer[4] in the pyrolysis of benzoinhydrazone. The purposes of the present investigation were to

[1] Curtius and Jay, *J. prakt. Chem.*, [2] **39**, 45 (1889).

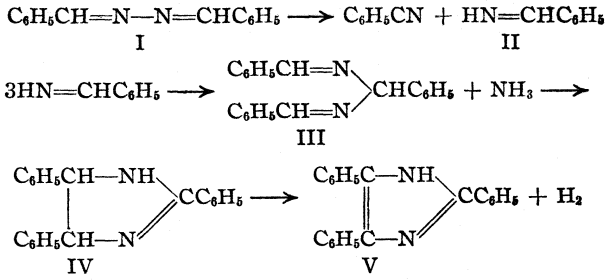
[2] Meisenheimer and Heim, *Ann.*, **355**, 274 (1907).

[3] Pascal and Normand, *Bull. soc. chim.*, [4] **9**, 1029 (1911); [4] **9**, 1059 (1911); [4] **11**, 21 (1912).

[4] Curtius and Blumer, *J. prakt. Chem.*, [2] **52**, 126 (1895).

identify the extremely stable nitrogen compound of Pascal and Normand, to determine if analogous substances are formed in the decomposition of other aldazines, and to develop a satisfactory mechanism to explain the formation of the various products. In addition, a semi-quantitative study of the decomposition products of benzaldazine was made in order to ascertain whether the pyrolysis was appreciably affected by the application of 1000 atmospheres pressure of nitrogen, hydrogen, and ammonia.

The findings of the French investigators on the formation of the nuclear nitrogen compound have been confirmed. The product (17% yield) on purification, however, melted somewhat higher (m. p. 275°) and the analytical value for nitrogen was considerably lower than previously reported. It emitted visible light on oxidation, which is a property characteristic of lophine (V) with which it was subsequently shown to be identical. Since lophine is readily obtained by the pyrolysis of hydrobenzamide (III) under similar conditions[5] the following mechanism immediately suggests itself. It is known that benzalimine (II) is easily converted with



the elimination of ammonia[6] to hydrobenzamide and that the latter probably passes through amarine (IV) to form lophine (V). This mechanism in which all of the steps, with the exception of the first (I–II), have been well established, offers a simple and reasonable explanation for the formation of the ammonia and benzonitrile as well as the lophine. The azine must simultaneously decompose in another manner to yield stilbene and nitrogen as expressed in equation (1).

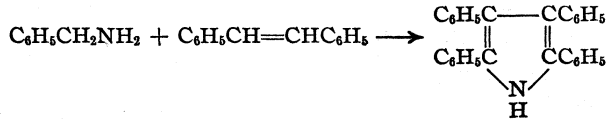
A number of other mechanisms for the formation of lophine are theoretically possible. One of these consists of the interaction of two moles of benzonitrile with an intermediate benzal radical. This was readily shown to be improbable since the pyrolysis of the azine in the presence of a large excess of the nitrile did not lead to any increase in the yield of lophine.

[5] Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1928, p. 247.

[6] Busch, *Ber.*, **29**, 2143 (1896); Escourrou, *Bull. soc. chim.*, [4] **45**, 742 (1929), found that benzalimine was considerably more stable than reported by Busch, but was broken down to ammonia and hydrobenzamide upon boiling below 175° at 10 mm. pressure.

Moreover, when the pyrolysis was carried out in the presence of copper powder, which in this case appeared to be a dehydrogenating catalyst, the yields of both lophine (12.3 to 1.4%) and stilbene (41 to 9.6%) diminished considerably, whereas that of benzonitrile was greatly increased (8.6 to 38.4%). Virtually the same result was obtained by raising the temperature of decomposition. This was effected by placing the azine in a steel bomb which was plunged into a metal bath already heated to the desired temperature. Under these conditions it seems probable that equation (2) represents the main course of the reaction and that the toluene observed arose as a result of the liberated hydrogen.

A further possibility for the formation of lophine was the reduction of part of the benzaldazine to benzyl or dibenzylamine[7] and the subsequent interaction of either of these with stilbene, or pyrolysis *per se*. Accordingly, both benzylamine and dibenzylamine were heated alone at 300° for forty hours and found to produce a mixture of lophine and tetraphenylpyrrole. Since it was felt that the low yield of lophine was due, possibly, to an insufficient amount of stilbene formed in the pyrolysis of the amines, the thermal decomposition was carried out in the presence of stilbene. The yield of tetraphenylpyrrole was increased markedly (9 to 22%) and lophine, instead of being augmented, was found to be absent except in experiments which had been subjected to rapid heating. The presence of the small amounts of lophine in such cases was evidently due to a pyrolysis of benzylamine *per se*. The insignificant amount of lophine formed, coupled with the fact that the pyrolysis of benzaldazine only occasionally gave a detectable amount of tetraphenylpyrrole, seemingly eliminated the possibility of lophine formation by such a mechanism. The formation of tetraphenylpyrrole from benzylamine and stilbene is very interesting al-



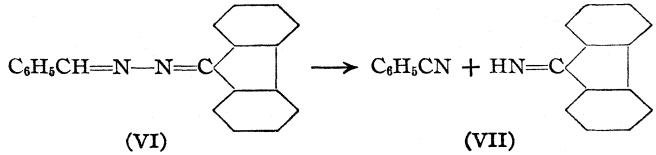
though the mechanism of its formation is not entirely obvious. It apparently arises from the interaction of some intermediate decomposition product of benzylamine, other than benzalimine, and stilbene.

It has been pointed out to us by Dr. P. H. Emmett of this Laboratory that any possible reaction between benzalimine (II) and some other molecular species of the system to give lophine (V) would be favored tremendously from the kinetic standpoint over the trimolecular reaction proposed ($3II \longrightarrow III + NH_3$). The only reaction that appears to have any possibility of taking place is that occurring between benzalimine and

[7] There is little doubt that reducing conditions are present since both toluene and dibenzyl derivatives were obtained in the pyrolysis of anisaldazine and the dibenzyl derivative from tolualdazine (see experimental).

benzaldazine. The pyrolysis of benzaldazine in the presence of either benzalimine or benzaldehyde, however, did not lead to any increase in the yield of lophine above the normal amount expected from the individual reactants.

An effort to capture the intermediate benzalimine as N-phenylbenzalimine by pyrolysis in the presence of a large excess of aniline was unsuccessful. Since a direct method of proof of the intermediate imine formation in the case of benzaldazine was not available, it was necessary to study the thermal decomposition of an azine, the expected imine of which would be stable and isolable as such. Such an example happened to be benzalfluorenoneazine (VI), which upon decomposition produced benzonitrile and 9-iminofluorene (VII). This affords excellent evidence supporting



(VI) (VII)

the postulated mechanism of lophine formation.

A determination of the yields of lophine, benzonitrile and stilbene resulting from the pyrolysis of benzaldazine at 300° indicated that the reaction proceeded according to equation (1) to the extent of fifty mole per cent., and according to equation (3) to the extent of about twenty-five mole per cent. Unidentifiable residues in the form of tars constituted the balance. The yield of benzonitrile was somewhat less than that equivalent to the lophine, but this discrepancy may well have been due to the difficulty of complete separation and to possible partial polymerization.[8]

In order to determine whether or not other aldazines also produced analogous lophines, anisaldazine, di-*o*-chlorobenzaldazine and *p*-tolualdazine were prepared and pyrolyzed. In none of these cases was the lophine derivative isolated in the pure condition. There can, however, be little doubt that trimethyllophine was formed from *p*-tolualdazine since certain fractions, when tested with warm alcoholic potassium hydroxide and oxygen, gave the strong characteristic emission of light. In addition, *p*-tolualdazine yielded the stilbene, dibenzyl, nitrile and polymeric nitrile derivatives and a product which probably was *p*-xylene. From anisaldazine the corresponding stilbene, dibenzyl, toluene and nitrile derivatives were isolated. Di-*o*-chlorobenzaldazine formed the stilbene and nitrile derivatives and an unidentified base in small yield. Considerable hydrogen chloride and ammonium chloride were formed, indicating a rather complete degradation of much of the azine, which may well have accounted for the absence of the analogous lophine.

[8] In the pyrolysis of *p*-tolualdazine, a product that apparently is the polymeric toluic nitrile, was actually isolated.

The possibility that the unknown trimethoxylophine and tri-*o*-chlorolophine could not be prepared from the corresponding benzhydramides was suggested by the failure to obtain either from the azines. Accordingly, hydroanisamide was pyrolyzed and found to yield no compound which corresponded in composition to trimethoxylophine. Only a buff-colored powder which could neither be crystallized nor rigorously purified was obtained. On the other hand tri-*o*-chlorohydrobenzamide gave a small yield of tri-*o*-chlorolophine hydrochloride along with much hydrogen chloride and ammonium chloride. Trimethyllophine[9] may be obtained in fairly good yield from hydrotoluamide but its properties are such as to make its separation from the pyrolysis products of *p*-tolualdazine much more difficult than that encountered with lophine.

It has actually been found, as Pascal and Normand[3] suggested, that the nuclear nitrogen compound (lophine), obtained in the pyrolysis of benzaldazine, is identical with the previously unidentified product of similar properties, isolated by Curtius and Blumer[4] in the thermal decomposition of benzoinhydrazone. In addition to the other products obtained by Curtius and Blumer the presence of a small amount of a substance resembling tetraphenylfuran was observed.

Ketazines, in general, may be characterized as being considerably more stable (thermally) than aldazines and as being particularly reluctant to evolve free nitrogen with the formation of ethylenes. That this stability is not due to symmetry alone, as might be suggested in the case of benzophenoneketazine, is shown by the results obtained from the pyrolysis of acetophenoneketazine and the mixed ketazine of benzophenone and fluorenone. All three of these ketazines require higher temperatures to bring about decomposition than the aldazines studied and tend to eliminate benzonitrile instead of nitrogen. However, if one of the groups has a thermal lability approaching or exceeding that of hydrogen, such as the benzoyl group in bis-benzilketazine, the stability decreases as is shown by the fact that decomposition of this compound occurs at 250–270° to yield benzonitrile and benzoic acid.[10]

One is prone to question the usefulness of electronic interpretations as applied to thermal decompositions, especially those occurring at relatively high temperatures, such as the pyrolysis of the azines. Nevertheless, it is of interest to note several rather significant relationships. If the influence which the group R has upon the linkage between the carbon and hydrogen

(A) (B)

[9] Gattermann, *Ann.*, **347**, 367 (1906); Fürth, *Monatsh.*, **27**, 843 (1906).

[10] Ritter and Wiedeman, THIS JOURNAL, **51**, 3586 (1929).

atoms (A) is considered, one should expect that an increase in the "electronegativity" of this radical[11] will tend to increase the instability (thermal dissociability) of the C—H linkage. The increasing ease in the elimination of hydrogen, according to equation (2) will be accompanied simultaneously by an increase in the amount of reduction products. The results are in accord with this point of view as in the pyrolysis of di-*o*-chlorobenzaldazine, benzaldazine, *p*-tolualdazine and anisaldazine, the first two compounds form negligible amounts, the third isolable amounts, and the last good yields of the toluene and dibenzyl derivatives. As might be expected, there is an accompanying increase in nitrile and decrease in lophine derivatives.[12]

A second implication of the concept is encountered in the case of the ketazines, in which group R_1 is substituted for the hydrogen atom (B) and may be of greater or weaker "electronegativity" than the substituted hydrogen atom. The ease of elimination of this group will also depend upon its own relative "negativity;" a decrease in the "negativity" tends to increase the ease of removal. It is not surprising then to find benzophenoneketazine exhibiting a markedly greater stability than benzaldazine. Acetophenoneketazine, as expected, occupies an intermediate position and yields benzonitrile. If the tendency had been toward the elimination of the more negative group, we should have obtained acetonitrile, of which not a trace was observed. Bis-benzilketazine is even more readily broken down than benzaldazine and again with the elimination of the weakly "negative" benzoyl group. Furthermore, as the radical ($R_1RC=$) becomes relatively more "positive" by virtue of the attachment of the more "electronegative" groups R and R_1, the ketazines become more polar with a decreasing tendency to decompose thermally with the ejection of molecular nitrogen.

We are greatly indebted to Dr. Reid T. Milner and Mrs. Mildred S. Sherman for carrying out the microanalyses recorded.

Experimental

Pyrolysis of Benzaldazine by Distillation.—One hundred grams of benzaldazine (m. p. 93°)[13] was heated gradually in a short-necked distilling flask until a fairly rapid evolution of gas containing much ammonia took place. The flask was maintained at this temperature (290–310°) for ten hours during which time 6.8 g. of pale yellow oil distilled over. The residue (82.0 g.), which upon cooling solidified to a hard brown resin, was extracted and washed with a total of 500 cc. of ether. A pale gray, crystalline residue (17.0 g.) was obtained; m. p. 255–265°. Recrystallization from pyridine yielded fine colorless needles which melted at 276°. A dilute solution in alcoholic

[11] The radicals, methyl, *o*-chlorophenyl, phenyl, *p*-tolyl and *p*-anisyl are placed in the order of increasing "electronegativity;" see Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

[12] The failure to isolate the lophine derivative from *o*-chlorobenzaldazine is believed to be due to a more complete degradation as a result of chlorine elimination.

[13] Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 103 (1928).

potassium hydroxide emitted visible light when saturated with oxygen at 60°. When mixed with lophine prepared from hydrobenzamide[14] there was no depression of the melting point.

Anal. Calcd. for $C_{21}H_{16}N_2$: N, 9.46. Found: N, 9.32.

From alcoholic hydrogen chloride the known salt was obtained which melted at 159–161° with evolution of gas.

The ether extract was evaporated to dryness and the residue distilled until no more stilbene passed over. The solidified distillate was crystallized from alcohol to yield the characteristic glistening plates which melted at 123°; yield 40 g. When mixed with an authentic specimen there was no depression of the melting point.

The oil (b. p. 190°) which distilled over during the pyrolysis had the characteristic odor of benzonitrile, and was hydrolyzed by alcoholic potassium hydroxide to benzoic acid.

Pyrolysis of Benzaldazine in Sealed Tubes.—The general procedure in these experiments was to seal the azine in evacuated glass tubes and to heat in an electric furnace for a given length of time at the designated temperature. In every case a considerable pressure of nitrogen and ammonia developed. The tube was made part of a three-legged system which was evacuated and then by proper manipulation of heating and cooling baths the benzonitrile was distilled into one leg and the stilbene into the other. The residues were extracted with ether to obtain the lophine in a reasonably pure condition.

TABLE I

	Azine, g.	Temp., °C.	Time, hours	Lophine, g.	Benzonitrile, g.	Stilbene, g.
I	2.08	300	18	0.255	0.180	0.850
II	2.08	300	5	.260	n. d.	n. d.
III[a]	2.08	300	18	.245	n. d.	n. d.
IV[b]	2.08	300	5	.030	0.800	0.200
V	10.4	325	5	.80[c]	1.50[d]	3.80
VI[e]	6.24	300	5	1.25	n. d.	n. d.
VII[f]	1.04	300	5	0.48	n. d.	n. d.

[a] The azine was heated with 4.0 g. of benzonitrile. [b] The azine was heated with 1.0 g. of copper–bronze powder. Lophine that was heated with copper powder, under the same conditions, was recovered quantitatively. [c] Partial evaporation of the ether extract of the lophine deposited some crystalline material which after trituration with benzene and crystallization from alcohol melted at 208–209°; yield 0.29. When mixed with tetraphenylpyrrole there was no depression of the melting point. [d] An odor of toluene was noted in the benzonitrile but none was separated. [e] The azine was heated with 6.36 g. (2 mols) of benzaldehyde. No odor of ammonia was detectable and the yield of lophine corresponded very closely to the normal amount from the azine (*ca.* 0.78 g.) in addition to that (*ca.* 0.39 g.) which was expected to form by the interaction of the benzaldehyde and ammonia. [f] The azine was added to a liquid ammonia solution of benzalimine prepared from 0.5 g. of hydrobenzamide [Strain, THIS JOURNAL, **49**, 1561 (1927)] and allowed to stand for four days. Since no interaction occurred at room temperature the tube was opened to boil off the ammonia, sealed, and plunged into the furnace at 300°. Here again the yield of lophine was remarkably close to the normal individual yields of the azine (*ca.* 0.13 g.) and the hydrobenzamide (*ca.* 0.35 g.).

Pyrolysis of Benzaldazine in a Steel Bomb.—A sample of 20.8 g. of benzaldazine contained in a glass bulb with a capillary opening was sealed in a steel bomb which

[14] Pinner, *Ber.*, **35**, 4140 (1902).

was plunged into a metal bath of large capacity previously heated to 325° and allowed to remain there for five hours. The reaction mixture was a thin, dark brown paste and the products were worked up in the usual manner. The yield of lophine was 0.51 g., of stilbene 8.25 g., of benzonitrile 3.04 g. and of toluene 0.26 g. (b. p. 111° and yielded the characteristic dinitro derivative melting at 70°).

Preparation of Aldazines.—The aldazines used in this work were most conveniently prepared by the following typical procedure. A cold solution of one mole of anisaldehyde in 400 cc. of 95% alcohol was treated by slow addition and stirring with one mole of 90% hydrazine hydrate. The precipitated azine was filtered from the cold solution and crystallized from a mixture of alcohol and benzene to give a yield of 125 g. (93%), m. p. 167–179° (liquid crystal).

Pyrolysis of Anisaldazine.—Fifty grams of the azine was heated in a short-necked distilling flask until an evolution of gas rich in ammonia began. The heat was removed but the reaction gained speed and an oil began to distil over. After the initial vigorous action had abated, heat was again applied until no further distillate passed. A considerable amount of charred residue remained which was not amenable to the isolation of a pure product. The material collected was redistilled to give 5 g. of a clear oil between 170 and 220°, 5 g. of a pale yellow oily solid between 220–270°, and finally a much higher melting solid between 270–330°. An intractable tarry residue remained.

The oil was thrice fractionated to give a portion of 1.7 g. which distilled between 174–178°. Its strong anise-like odor and boiling point suggested that it was the methyl ether of *p*-cresol (b. p. 175°). This was confirmed by oxidation with neutral permanganate to anisic acid.

The oily solid was extracted with boiling water (in which it was largely soluble), filtered and cooled. Beautiful white needles were obtained which, when dry, melted at 60°. Their identity with anisonitrile was confirmed by hydrolysis in potassium hydroxide solution to anisic acid.

The higher melting solid was crystallized from benzene to give brilliant glistening plates which melted at 205–207°. Recrystallization from a mixture of alcohol and benzene gave pure di-*p*-methoxystilbene; m. p. 215°. A portion was reduced with hydrogen and platinum oxide catalyst to the corresponding di-*p*-methoxydibenzyl; m. p. 126°. Concentration of the original benzene filtrate gave a crop of crystals which melted at 120–135°. They were treated with a sufficient quantity of boiling alcohol to dissolve about three-fourths of the material, filtered and chilled. About 1 g. of white plate-like crystals melting at 124–125° was obtained. Two recrystallizations from alcohol gave a product melting at 126–126.5°. Its identity with di-*p*-methoxydibenzyl was confirmed by the undepressed melting point when mixed with an authentic specimen.

Pyrolysis of Di-*o*-chlorobenzaldazine.—Twenty grams of the azine (m. p. 141°) was distilled from a short-necked flask. Hydrogen chloride was first evolved, then an oily somewhat yellowish distillate and finally a portion which solidified to a white solid in the side tube of the flask. Further heating gave only complete charring. The whole distillate was decolorized with charcoal and crystallized from alcohol to yield white needles of pure di-*o*-chlorostilbene; m. p. 97–98°. An attempt to separate pure *o*-chlorobenzonitrile from the filtrate of the first stilbene crystallization was unsuccessful. The impure material, which had a strong nitrile odor, was hydrolyzed directly with alcoholic potassium hydroxide and yielded an appreciable amount of *o*-chlorobenzoic acid; m. p. 137–139°.

In a second experiment 2.77 g. of the azine was heated in a sealed evacuated tube at 300° for eighteen hours. Upon opening the tube considerable gas containing hydrogen chloride escaped. The residue was extracted with 10 cc. of acetone which left a pale

buff colored product which melted at 250–255° (dec.). It was found to be insoluble in acetone, benzene, ether and water, but very soluble in alcohol. It gave a Beilstein test for halogen. An alcoholic solution on treatment with ammonium hydroxide yielded a white precipitate. The mixture was warmed to dissolve the precipitate and then cooled, depositing minute crystals which melted at 163–164°. When mixed with a sample of tri-*o*-chlorolophine (m. p. 167°) it melted at about 140°. There was an insufficient amount for further study. Since tri-*o*-chlorolophine hydrochloride, in which we were mainly interested, was insoluble in acetone, the original filtrate from the buff colored product was discarded.

Pyrolysis of *p*-Tolualdazine.—Ten grams of the azine (m. p. 153°) was heated in a sealed, evacuated tube at 325° for two hours. When cold, the material remained as a dark colored semi-solid mass and upon opening the tube a pressure of ammonia and nitrogen was released. The material was transferred to a vacuum sublimation apparatus and finally heated to 240°. An oil passed over (*ca.* 0.5 g.) which solidified upon cooling to 0°. It was taken up in 4–5 volumes of alcohol and chilled to deposit plate-like crystals which were worked on clay plate with a little solvent and dried. The product was very soluble in ether, melted at about 80° and was probably *p,p'*-dimethyldibenzyl (m. p. 82–86°). The filtrate from these crystals was evaporated and the residue distilled. A small fraction passed over at 140° (perhaps some *p*-xylene). The main portion, however, boiled constantly at 215°. Its identity as *p*-toluic nitrile was confirmed by hydrolysis with 60% sulfuric acid to *p*-toluic acid which after recrystallization from water melted at 175°.

After the removal of the oily products, a white solid sublimed into the receiver. It was crystallized from alcohol to give the pure 4,4'-dimethylstilbene melting at 177–178°. Greenish-yellow crystals collected on a hotter section of the vessel and were removed, extracted with hot alcohol, filtered and worked on clay plate with a little ether. A pale yellow crystalline material remained which melted at 250–260°; its properties were similar to those of polymeric toluic nitrile.[15] Concentration of the filtrate and the washings of this product yielded a small amount of the crude stilbene (m. p. 170°). Further concentration yielded only resins from which tri-*p*-methyllophine could not be isolated. The filtrates and resins gave the characteristic light emission when warmed with alcoholic potassium hydroxide, thus strongly indicating the presence of the lophine. Neither the polymeric nitrile nor the crude stilbene gave any visible emission.

Pyrolysis of Benzal Fluorenone Azine.—This mixed azine was prepared by the method of Staudinger and Kupfer,[16] who reported a melting point of 82–84° after crystallization from alcohol. Since our compound melted at 91–92° after one crystallization from alcohol, it was analyzed.

Anal. Calcd. for $C_{20}H_{14}N_2$: N, 9.93. Found: N, 10.05, 9.81.

Five grams of the azine was heated in a nitrogen-filled sealed tube at 275° for about two hours. Considerable pressure of ammonia and nitrogen was released upon opening. The contents of the tube were fractionally distilled and the maximum temperature that the bath finally attained was 250°. The first fraction (0.39 g.) was identified as benzonitrile. The higher boiling portion of the distillate was a yellow solid which crystallized from ligroin in tufts of dense yellow crystals, melting at 121–122°. A mixed melting point with an authentic specimen of 9-iminofluorene was not depressed. Its identity was further confirmed by hydrolysis with dilute hydrochloric acid to fluorenone. The residue of 3.5 g. of a black brittle solid was extracted and washed with 35 cc. of

[15] Gattermann, *Ann.*, **347**, 367 (1906).

[16] Staudinger and Kupfer, *Ber.*, **44**, 2207 (1911).

acetone to leave 0.54 g. of an olive brown solid which melted between 280–300° and which could not be further purified.

Preparation of Some Hydrobenzamide and Lophine Analogs

Preparation of Hydroanisamide.—Hydroanisamide has been previously reported by Délépine[17] and Fischer and Prause.[18] It was more rapidly prepared by the following modification. A solution of 50 g. of anisaldehyde in 150 cc. of alcohol and 50 cc. of concentrated aqueous ammonia was allowed to stand in the cold for two days. Shaking induced crystallization and the beautiful white product so obtained was collected, washed with alcohol and desiccated; m. p. 126–127°; yield 92% of the theoretical.

Attempt to Prepare Trimethoxylophine.—Twenty grams of hydroanisamide heated in an open flask to 275° underwent an exothermic reaction with the evolution of much ammonia. The temperature was raised to and maintained at 310° for a few minutes until the reaction subsided. Trituration of the cooled dark brown product with ether yielded only a buff colored powder (m. p. 150–160°) which could neither be crystallized from any ordinary solvents nor further purified. Oxidation with permanganate in acetone gave some anisic acid.

Anal. Calcd. for $C_{25}H_{22}O_4N_2$:[19] C, 72.50; H, 5.36; N, 6.77. Found: C, 73.31, 72.99; H, 5.62, 5.24; N, 6.76, 6.78.

The original ether extracts yielded an intractable tar.

Preparation of Tri-*o*-chlorohydrobenzamide.—A solution of 62 g. of *o*-chlorobenzaldehyde in 150 cc. of 95% alcohol was treated in the cold with 50 cc. of concentrated aqueous ammonia. Within an hour a layer of oily appearance began to form at the bottom of the stoppered flask and after two days had solidified to a hard cake which was finely divided and crystallized from alcohol to a light buff colored product which melted at 98–100°. One recrystallization from acetone gave a pure white product which melted at 101–102°.

Anal. Calcd. for $C_{21}H_{15}Cl_3N_2$: N, 6.98. Found: N, 6.98 (Kjeldahl).

Tri-*o*-chlorolophine.—Ten grams of tri-*o*-chlorohydrobenzamide was heated on an oil-bath in a long-necked round-bottomed flask. At 240° some hydrogen chloride began to escape and a small amount of liquid distilled up into the neck of the flask. The temperature was raised to and maintained at 305° for one-half hour. A small amount of white solid which had sublimed up into the neck was found to be ammonium chloride. The dark brown residue was extracted in the cold with 50 cc. of acetone, which left 2 g. of a light buff colored product. This product which was found to contain both halogen (Beilstein) and nitrogen (sodium fusion) was insoluble in water, acetone and ether, but readily soluble in methyl, ethyl and butyl alcohols from which solution it was precipitated by the addition of ether as a white microcrystalline product which melted at 330° to a brown liquid. It analyzed well for tri-*o*-chlorolophine hydrochloride.

Anal. Calcd. for $C_{21}H_{14}N_2Cl_4$: N, 6.42. Found: N, 6.49, 6.39 (Kjeldahl).

The hydrochloride did not separate from a hot saturated solution upon chilling or diluting with as much as five parts of water but the addition of a drop of hydrochloric acid or a little ammonium chloride solution induced crystallization at once. A portion of the hydrochloride dissolved in a little alcohol was diluted with much water and made ammoniacal. The white precipitate which immediately formed was dried on a clay plate and crystallized from dilute methyl alcohol in clumps of small colorless needles

[17] Délépine, *Compt. rend.*, **126**, 343 (1898); m. p. 125–127°.

[18] Fischer and Prause, *J. prakt. Chem.*, [2] **77**, 129 (1908); m. p. 130°.

[19] Trimethoxylophine would have the composition $C_{24}H_{22}O_3N_2$.

which melted at 169–170°, and were found to be very soluble in all ordinary organic solvents.

Anal. Calcd. for $C_{21}H_{13}N_2Cl_3$: C, 63.08; H, 3.28. Found: C, 63.46, 63.46; H, 3.38, 3.31.

A solution in warm alcoholic potassium hydroxide did not emit visible light upon saturating with oxygen.

The Pyrolysis of Benzoin Hydrazone.—Benzoin hydrazone was prepared and pyrolyzed by the method of Curtius and Blumer.[20] Besides the tetraphenylpyrazine (m. p. 246°) and the bis-benzilketazine (m. p. 202°) we obtained a small amount of white crystalline material which deposited from the alcoholic solution of the pyrolysis product upon standing for a day or two after the pyrazine and ketazine had been removed. It was triturated with a little ether and recrystallized from alcohol to a pure white crystalline product which melted at 173°. It was possibly tetraphenylfuran. A portion of the filtrate, after the isolation of each of the various products, was tested for light emission in alcoholic potassium hydroxide. In every case a strong emission was observed which persisted after the product of m. p. 173° was removed. This filtrate after standing for three weeks deposited some yellowish material which after trituration with ether sintered at 200° but was not completely melted up to 260°. As it was impossible to purify it satisfactorily by crystallization,[21] it was sublimed in a small test-tube. The color was removed from the dark product obtained by washing with ether, m. p. 271–273°. When mixed with known lophine the melting point was 272–274°. Both this product and the one melting at 200–260° gave excellent chemiluminescence.

The Formation of Lophine and Tetraphenylpyrrole in the Thermal Decomposition of Benzylamine

Pyrolysis of Benzylamine.—A bomb tube containing 5 g. of benzylamine was gradually heated over a period of four hours to 300° and allowed to remain at this temperature for forty-four hours. A considerable pressure of ammonia developed and the reaction mixture was a yellowish brown, semi-solid, crystalline mass. It was thoroughly triturated with 30 cc. of ether and the insoluble colorless needles collected and identified as lophine; wt. 0.43 g., m. p. 270°. The ether was removed from the filtrate and the residue treated with 25 cc. of boiling alcohol and cooled. The crystals that separated were removed by filtration. The alcohol filtrate on evaporation yielded an additional amount of the same product. The total precipitate (0.40 g., m. p. 206°) was recrystallized several times from boiling alcohol in which it was slightly soluble and from which it separated as stout needles melting at 215° (corr.). It was insoluble in water, soluble to the extent of 1 g. in 100 cc. of ether and did not form a hydrochloride. The properties and analysis agreed well for those of tetraphenylpyrrole.

Anal. Calcd. for $C_{28}H_{21}N$: C, 90.52; H, 3.77; N, 5.70. Found: C, 90.19, 90.45; H, 3.75, 3.91; N, 5.73, 5.65.

Toluene, benzonitrile, stilbene and dibenzyl were also formed. These received only a superficial examination as we were mainly interested in the nuclear nitrogenous products.

Pyrolysis of Benzylamine in the Presence of Stilbene.—Five cubic centimeters of benzylamine and two grams of stilbene were heated under the same conditions as described above. Much ammonia was formed and the reaction product was a pale

[20] Curtius and Blumer, *J. prakt. Chem.*, [2] **52**, 124 (1895).

[21] Curtius and Blumer[20] were unable to purify their product above a melting point of 261° by crystallization although they were unquestionably dealing with this impure lophine.

yellow solid. It was treated with 30 cc. of ether and filtered. The insoluble matter was shown to be tetraphenylpyrrole. The filtrate was worked up in the usual manner and the combined pyrrole weighed 1.10 g. The various fractions did not exhibit chemiluminescence, indicating the absence of lophine. In one experiment, however, 0.07 g. of lophine was isolated.

Experiments in which the ratio of benzylamine to stilbene was increased tended to decrease the yield of tetraphenylpyrrole. A typical example was an experiment involving 5 g. of benzylamine and 1 g. of stilbene; the yield of the pyrrole was 0.70 g. and lophine was found to be absent. The reaction was appreciably affected by increasing the rate of heating and resulted in the formation of a marked amount of lophine. One experiment, in which the bomb tube containing 5 g. of benzylamine and 1 g. of stilbene was introduced into the furnace heated to 300°, yielded 0.20 g. of lophine and 0.66 g. of tetraphenylpyrrole.

A solution of benzaldehyde, or benzyl alcohol, or benzyl ether with stilbene heated to 300° for forty hours did not yield any tetraphenylfuran.

Pyrolysis of Dibenzylamine in the Presence of Stilbene.—Five grams of dibenzylamine and 3 g. of stilbene were heated under the same conditions as given above. The results of the experiment in general were quite similar. The yield of tetraphenylpyrrole was 1.0 g. and lophine was absent.

Pyrolysis of the Ketazines

Benzophenoneketazine.—This ketazine (m. p. 163–164°) was heated in a sealed evacuated tube at 300° for eighteen hours. Upon opening, the tube was still partially evacuated and although a distinct odor of benzonitrile was present the ketazine was recovered almost quantitatively.

In another experiment, a container with 5 g. of ketazine *in vacuo* was heated at 350° for one hour. It was cooled and the pressure found to be less than atmospheric. The brown oil had a faint odor of ammonia and on distillation yielded 0.7 g. of benzonitrile. Further distillation under diminished pressure gave fractions of 1.3 g. between 160–175° at 4 mm. of a colorless oil and 0.7 g. between 190–225° at 6 mm. of a yellow viscous oil. These products were not identified. A tarry residue remained.

Acetophenoneketazine.—A portion of 50 g. (m. p. 121–122°) heated in a long-necked distilling flask began to decompose at a temperature of 296–340° and a fraction weighing 8.0 g. of a pale yellow oil boiling at 185–210° was collected. The oil smelled strongly of ammonia and benzonitrile. A second fraction of 2.8 g. of a pale yellow oil passed as the temperature of the residue increased to 370°. The combined distillate was fractionated and after repeated distillation a portion of 1.3 g. of pure ethylbenzene (b. p. 135.5°) was obtained which was confirmed by oxidation with aqueous permanganate to benzoic acid. Most of the remaining distillate was benzonitrile (b. p. 186°) which was hydrolyzed by alcoholic potassium hydroxide to benzoic acid. The residues were discarded because of their tarry nature.

Mixed Ketazine of Fluorenone and Benzophenone.—This compound was prepared by warming for one-half hour on the water-bath a solution of 18.0 g. of fluorenone and 19.6 g. of benzophenonehydrazone in 100 cc. of glacial acetic acid. The solution became deep red orange in color and after standing overnight deposited 33.7 g. of orange colored crystals; m. p. 105–107°; yield 94% of the theoretical. Recrystallization from glacial acetic acid gave two crystalline forms. The one form separated on rapid cooling as feathery tufts and the other on slow cooling as prismatic blocks. The ketazine was extremely soluble in cold ether, benzene, acetone and dioxane and quite soluble in hot ligroin, alcohol and acetic acid; m. p. 109–110°.

Anal. Calcd. for $C_{26}H_{18}N_2$: C, 87.11; H, 5.06; N, 7.83. Found: C, 87.07, 87.01; H, 4.77, 5.18; N, 7.97, 7.92.

Ten grams of the ketazine was heated gradually in a small distilling flask to 340° before any decomposition was noticeable. Between 350–360° a slow decomposition took place with the elimination of a small amount of ammonia and the distillation of about 1 g. of oil in one and one-half hours. On standing the oil deposited pale yellow needles which were identified as 9-iminofluorene (hydrolyzed by dilute acid to fluorenone), m. p. 123°.

Anal. Calcd. for $C_{13}H_9N$: C, 87.15; H, 5.03. Found: C, 87.23, 86.98; H, 5.19, 5.44.

The oil from the needles was purified by distillation and identified as benzonitrile. The residue solidified to a brittle tar on cooling.

A NOTE ON THE THERMAL DECOMPOSITION OF BENZALDAZINE AT 1000 ATMOSPHERES PRESSURE OF NITROGEN, HYDROGEN AND AMMONIA

Benzaldazine was selected from the azines studied since its decomposition products were the most convenient to isolate. In each experiment 20.8 g. of benzaldazine was placed in a glass container inserted in a Rezistal bomb, which was then charged with 1000 atmospheres of the desired gas. The bomb was then placed in a controlled temperature metal bath for five hours. Some representative results are given in the following table.

TABLE II

	333 atm. H_2 300°, g.	1000 atm. H_2 275°, g.	1000 atm. H_2 300–315°, g.	1000 atm. N_2 280°, g.	1000 atm. NH_3 282°, g.	1000 atm. NH_3 245°, g.
Lophine	2.46[a]	2.31[b]	0.30	2.1[c]	3.05[b,d]	3.46[b,d]
Benzonitrile	1.57	2.20	4.00	0.90	0.53	0.8[e]
Stilbene	8.00	5.00	4.57	4.08	.93	.46
Toluene	n. d.	Odor	0.60	n. d.	.42	n. d.

[a] Tetraphenylpyrrole (0.89 g.) was isolated. [b] A trace of cyaphenine was detected. [c] Unchanged azine (1.85 g.) was recovered. [d] A compound in the form of fine colorless needles which was quite soluble in benzene and ligroin, less soluble in ether and difficultly soluble in methyl and ethyl alcohols was isolated; yield 0.2–0.3 g. It was exceedingly difficult to purify either by crystallization or vacuum sublimation and in the purest form obtained melted at 185–187°. It does not form a hydrochloride with hydrochloric acid in benzene or ether solution. It distils without decomposition. *Anal.* Found: C, 87.29, 87.02; H, 5.40, 5.42; N, 7.30, 7.68. [e] Not too much significance must be placed upon the benzonitrile determinations in this case.

Very little if any change was effected by the application of high pressures of nitrogen and hydrogen. The thermal decomposition in the presence of ammonia, however, proved to be quite complex. This was possibly due to a partial ammonolysis of the azine. It is interesting to note that the decomposition temperature in this case was considerably lower.

Summary

The thermal decomposition of benzaldazine has been studied. In addition to the well-known breakdown to form stilbene and nitrogen an appreciable side reaction takes place in which benzonitrile and benzal-

imine, that is subsequently converted to lophine, are simultaneously formed. As evidence in favor of this mechanism it has been shown that the degradation of benzalfluorenoneazine yields benzonitrile and 9-iminofluorene.

A number of other aldazines and ketazines have been pyrolyzed and the decomposition products isolated and identified. In general, when the lophine analog is difficult or impossible to make by the usual method, it is also absent in the pyrolysis of the azine.

Lophine and tetraphenylpyrrole are products of the decomposition of benzyl and dibenzylamine. The pyrolysis in the presence of stilbene leads solely to tetraphenylpyrrole.

High pressures of nitrogen and hydrogen did not appreciably affect the course of the decomposition of benzaldazine.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

ENERGY EXCHANGES BETWEEN UNLIKE MOLECULES. THE DECOMPOSITION OF METHYL ETHER, ETHYL ETHER, ACETONE AND THEIR BINARY MIXTURES[1]

BY LOUIS S. KASSEL[2]

RECEIVED JUNE 9, 1932 PUBLISHED SEPTEMBER 5, 1932

Steacie[3] has recently reported that in mixtures of methyl ether and ethyl ether, each substance decomposes at the rate to be expected from its partial pressure. The decomposition of each of these substances is a homogeneous unimolecular reaction the rate of which, in the usual pressure range, has fallen considerably below the limiting high-pressure value. The conclusion to be drawn from Steacie's report, therefore, is that collisional transfer of energy takes place much more readily when two molecules of ethyl or of methyl ether collide, than when a molecule of ethyl ether collides with one of methyl ether. Such a conclusion is somewhat surprising, since it is a rather more extreme example of specificity than has yet been reported for energy transfers of this character. No directly comparable experiments have been made, but it is known, for example, that ethane is very effective in activating azomethane;[4] the only inert gases which have previously

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[3] Steacie, THIS JOURNAL, **54**, 1695 (1932); *J. Phys. Chem.*, **36**, 1652 (1932). I am indebted to Dr Steacie for permitting me to see his complete paper in advance of its publication.

[4] Ramsperger, *J. Phys. Chem.*, **34**, 669 (1930).

been found to be inefficient in transferring energy are such simple ones as helium, nitrogen and carbon dioxide; and in the case of the small reactant molecule nitrous oxide, it is found that activations are produced efficiently by carbon dioxide, and only slightly less so by nitrogen and oxygen. The one striking irregularity in the scheme is furnished by hydrogen, which exhibits remarkably high efficiency in activating a variety of molecules. The case reported by Steacie, then, would be the first in which it had been found that unlike molecules of comparable complexity were not efficient in producing mutual activations. Since there was available here apparatus which could conveniently be used to test this conclusion, the following experiments were made.

Experimental Method

The reaction vessel was contained in a nichrome-wound furnace which had been designed primarily for work at about 800°; the temperature was controlled automatically by a platinum–platinum–rhodium thermocouple and a Leeds and Northrup controlling potentiometer; there were short period variations of about 2–3°, but throughout the entire work the average temperature was quite constant. There may have been a temperature gradient along the reaction vessel of as much as 5°, but this also did not vary during the work. Hence, it may be supposed that the absolute temperature might be in error by about this amount; actually, the difference in temperature scale from Hinshelwood and Steacie is less than 3°. The temperature used throughout the work, as recorded by the thermocouple, was 487°.

The reaction vessel was a Pyrex flask of about 500 cc. capacity; the attached mercury manometer was of wide bore, and the necessary correction for outside volume was made in the usual way.

C. P. grades of ethyl ether and acetone were used without further purification, except for the pumping out of permanent gases. Methyl ether was made in the apparatus from methyl alcohol and sulfuric acid, separated from methyl alcohol by fractionation, and stored in a cooled trap.

Since these reactions take place in several stages, intermediate products such as aldehydes accumulating in considerable amounts, it seemed desirable to focus attention on the early stages of the reaction; pressure readings were taken at five-minute intervals up to twenty-five minutes, the initial pressure being obtained by a short extrapolation of early, more frequent readings. The manometer was read with an accurate cathetometer, and, except at the very lowest pressures, no appreciable error was possible.

Results and Calculations

The experimental results for methyl and ethyl ethers and their 1:1 mixture are recorded in Tables I to III in terms of the accumulated fractional

pressure increase, $\Delta P_t/P_0$, at five-minute intervals; these have been corrected for the outside volume. It is found that by plotting $\Delta P_t/P_0$ against

TABLE I

VALUES OF $\Delta P_t/P_0$ FOR ETHYL ETHER

Run	P_0	$\Delta P_5/P_0$	$\Delta P_{10}/P_0$	$\Delta P_{15}/P_0$	$\Delta P_{20}/P_0$	$\Delta P_{25}/P_0$
25	35.81	0.172	0.332	0.471	0.594	0.716
69	29.38	.145	.296	.427	.558	.674
45	27.55	.124	.272	.429	.562	.677
26	22.54	.137	.291	.425	.540	.646
7	21.53	.146	.293	.423	.534	.642
40	16.98	.107	.209	.324	.422	.533
6	16.89	.106	.235	.371	.488	.588
12	14.45	.079	.176	.286	.404	.508
18	14.20	.097	.206	.319	.428	.520
11	13.59	.113	.216	.310	.406	.515
70	13.50	.092	.187	.281	.377	.487
19	11.44	.097	.190	.278	.362	.454
8	11.03	.090	.201	.313	.409	.489
71	10.30	.093	.187	.269	.368	.450
27	9.31	.080	.163	.251	.342	.439
13	7.31	.078	.156	.228	.302	.363
20	5.72	.064	.136	.220	.297	.365
72	5.58	.054	.118	.178	.256	.324
28	5.00	.074	.140	.199	.270	.335
21	2.83	.058	.121	.168	.227	.282
29	2.65	.063	.113	.155	.213	.281
73	2.59	.044	.083	.113	.157	.196

TABLE II

VALUES OF $\Delta P_t/P_0$ FOR METHYL ETHER

Run	P_0	$\Delta P_5/P_0$	$\Delta P_{10}/P_0$	$\Delta P_{15}/P_0$	$\Delta P_{20}/P_0$	$\Delta P_{25}/P_0$
62	36.10	0.121	0.276	0.417	0.532	0.628
46	30.09	.093	.210	.345	.477	.590
53	29.60	.117	.245	.380	.514	.627
54	23.19	.096	.218	.346	.458	.552
34	21.70	.113	.242	.376	.506	.616
63	18.77	.067	.148	.231	.314	.402
47	15.02	.076	.162	.249	.330	.409
31	14.44	.094	.188	.276	.354	.429
55	12.00	.065	.138	.222	.301	.378
35	11.06	.079	.162	.248	.342	.431
64	9.78	.042	.095	.169	.241	.317
48	7.51	.033	.068	.110	.161	.219
32	6.95	.066	.127	.193	.259	.318
56	6.27	.036	.077	.118	.161	.198
36	5.29	.042	.082	.124	.166	.215
65	4.72	.031	.059	.097	.139	.179
33	3.61	.031	.065	.105	.157	.194
57	3.18	.035	.056	.084	.105	.136
66	2.71	.021	.041	.065	.090	.106

TABLE III

VALUES OF $\Delta P_t/P_0$ FOR METHYL ETHER–ETHYL ETHER MIXTURES

Run	P_0	$\Delta P_5/P_0$	$\Delta P_{10}/P_0$	$\Delta P_{15}/P_0$	$\Delta P_{20}/P_0$	$\Delta P_{25}/P_0$
41	32.07	0.113	0.252	0.381	0.493	0.586
49	26.97	.103	.210	.311	.402	.490
37	26.54	.109	.228	.338	.436	.521
42	16.53	.078	.156	.233	.318	.408
58	16.03	.070	.139	.214	.286	.358
50	13.50	.069	.151	.244	.337	.408
38	13.43	.076	.156	.233	.308	.373
59	8.37	.046	.094	.142	.195	.244
43	7.92	.052	.117	.173	.227	.283
39	6.35	.056	.118	.180	.231	.282
51	6.17	.058	.118	.168	.214	.265
44	4.42	.055	.108	.156	.202	.242
60	4.36	.038	.074	.110	.148	.184
52	3.31	.040	.074	.107	.141	.174
61	2.35	.033	.066	.104	.132	.160

log P_0, lines of only slight curvature are obtained. The experimental results have therefore been smoothed by fitting them to formulas of the type

$$\Delta P_t/P_0 = A + B \log P_0 + C (\log P_0)^2$$

which are, of course, purely empirical. The fitting has been done by least squares, to remove any possible doubt as to its objectivity. Figure 1 shows a typical set of experimental points and the smoothing curve adopted.

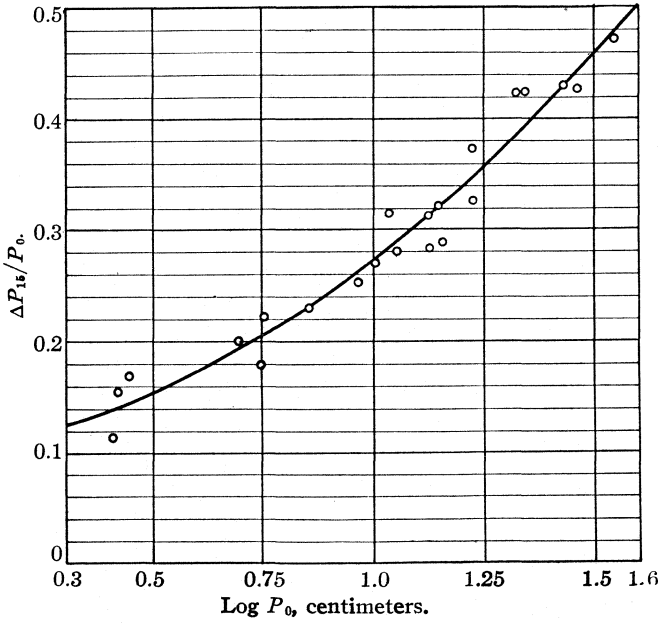

Fig. 1.—Values of $\Delta P_{15}/P_0$ for ethyl ether.

From the smoothed curves values of $\Delta P_t/P_0$ at five-minute intervals, for $\log P_0 = 0.50, 1.00, 1.50$, for both ethers and the 1:1 mixture were determined; these values are used in constructing Table IV.

TABLE IV

VALUES OF $(1/t)(\Delta P_t/P_0)$

		$\Delta P_{25}/25P_0$	$\Delta P_{20}/20P_0$	$\Delta P_{15}/15P_0$	$\Delta P_{10}/10P_0$	$\Delta P_5/5P_0$
At $P_0 = 31.6$ cm.	Methyl ether	0.0248	0.0267	0.0259	0.0248	0.0222
	Ethyl ether	.0284	.0293	.0303	.0313	.0307
	1:1 Mixture	.0224	.0231	.0234	.0236	.0230
At $P_0 = 10.0$ cm.	Methyl ether	0.0136	0.0134	0.0130	0.0125	0.0124
	Ethyl ether	.0178	.0180	.0179	.0175	.0169
	1:1 Mixture	.0125	.0128	.0130	.0128	.0129
At $P_0 = 3.16$ cm.	Methyl ether	0.0053	0.0054	0.0054	0.0050	0.0050
	Ethyl ether	.0108	.0106	.0102	.0110	.0113
	1:1 Mixture	.0074	.0075	.0075	.0078	.0086

It is desirable to determine the initial rate, if possible. This can probably be done best by plotting $(1/t)(\Delta P_t/P_0)$ against t and extrapolating

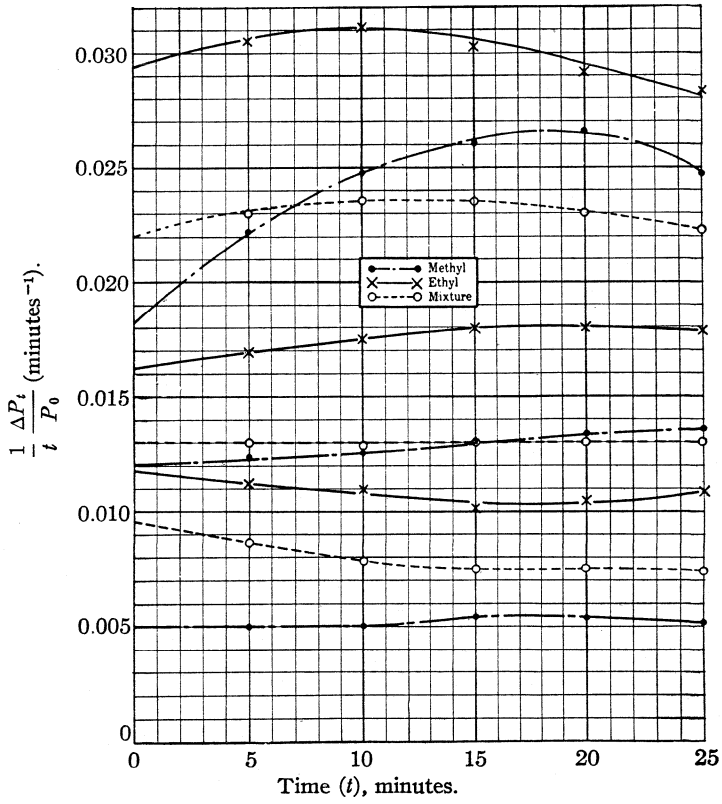

Fig. 2.—Extrapolation to initial rates.

back to $t = 0$; the intercept will be the value of k for the initial reaction, provided that this reaction results in doubling the pressure and that points have been obtained at values of t sufficiently small; the latter of these two requirements is the one more likely to be unfulfilled, but without analytical determination of the intermediates, nothing better can be done. Figure 2 shows plots of the kind described, made from the data of Table IV. It is at once apparent that the extrapolated initial rates for the 1:1 mixture are only slightly less than the averages of the rates for the separate ethers at the same pressure. At the higher pressures, as decomposition proceeds, the rate of pressure change for the mixture decreases with respect to that for the separate ethers, but at the lowest pressure this is not the case.

Table V shows the extrapolated initial rates for both ethers and for the 1:1 mixture, and also the rate calculated for the mixture assuming that each ether decomposes at the rate proper to the total pressure; the next column shows the effective pressure of the mixture, assuming that this is the same for both constituents; the final column gives the calculated efficiency of the ethers in cross activation, relative to that in activating themselves. This is calculated as follows. At 10-cm. pressure, for example, the effective pressure of ethyl ether (or methyl) is 8.32 cm., hence 5.00 cm. of methyl ether (or ethyl) is equivalent to 3.32 cm. of ethyl ether (or methyl); this is 66.4% efficient. At the lowest pressure, the errors become rather large, and but little weight is to be given the apparent increase in cross-activation efficiency.

TABLE V

EXTRAPOLATED VALUES OF $(1/t)(\Delta P_t/P_0)$

	$(1/t)(\Delta P_t/P_0)_{t=0}$, min.$^{-1}$					
Log P_0	Ethyl	Methyl	Average	Mixture	Log $P_{eff.}$	Cross activation efficiency, %
0.50	0.0118	0.0050	0.0084	0.0094	0.60	153
1.00	.0163	.0120	.0142	.0130	0.92	66
1.50	.0294	.0182	.0238	.0220	1.42	66

This rather elaborate treatment of the data would be unnecessary were it not for the discrepancy between the present results and those of Steacie; the final conclusion does not differ significantly from that reached by casual inspection of plots of direct experimental values of $\Delta P_t/P_0$ against log P_0, which is that the relative efficiency of cross collisions is between 0.4 and 0.70.

A number of experiments were made also with acetone–ethyl ether mixtures, at ratios of 1:1 and 2:1. It does not seem necessary to report these in detail. The acetone decomposes rather more slowly than the ether and presumably at a rate determined solely by its partial pressure; if this is the case, then acetone in acetone–ether mixtures is equivalent to from 80 to 120% of ether.

Discussion

The disagreement between the results reported by Steacie and those of the present work may easily be traced to the original experimental data.

Table VI gives a comparison of values of t_{25}, the time for 25% pressure increase, in both cases taken from smoothed curves, and referred to that for ethyl ether as 1.00, to eliminate temperature differences.

TABLE VI

	$\frac{t_{25}, \text{methyl}}{t_{25}, \text{ethyl}}$		$\frac{t_{25}, \text{mixture}}{t_{25}, \text{ethyl}}$	
Pressure, cm.	Steacie	Kassel	Steacie	Kassel
30	1.23	1.27	1.54	1.35
10	1.27	1.34	1.42	1.37

That is, in the present work methyl ether has been found to decompose slightly more slowly, and the 1:1 mixture rather faster than in that of Steacie, the rate for ethyl ether being assumed to be the same. No reason is evident why this should be so. In both investigations the experiments were performed in random order, and hence almost every systematic error was eliminated.

Summary

It has been found that mixtures of methyl and ethyl ether decompose significantly faster than the rate calculated from the partial pressures of the separate ethers. This result, which is in disagreement with a report made by Steacie, means that the transfer of internal energy between unlike ether molecules at collisions takes place about as readily as between like ether molecules; the exact value found is 66%, on which, however, not much confidence should be placed. A similar result is found for mixtures of acetone and ethyl ether.

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NOTE

The Standard Electrode Potentials of Silver–Silver Chloride and Calomel Electrodes and the Single Potentials of Calomel Electrodes

BY HUGH M. SPENCER

Carmody's[1] accurate data on the potentials of the cells H_2, HCl (xM), AgCl(s), Ag in quartz apparatus, when transformed into the form

$$\log \gamma + \text{const.} = \frac{E^\circ}{0.11831} + \log \gamma = -\frac{E}{0.11831} - \log m_\pm$$

superimpose beautifully on the curve of $\log \gamma$ *vs.* $m^{1/2}$, calculated by Randall and Young.[2] The constant obtained in this way is −1.8782, corresponding to

$$\text{Ag(s)} + \text{Cl}^- = \text{AgCl(s)} + E^-; \quad E^\circ_{298.1} = -0.2222_1 \text{ v.}$$

whereas Carmody's extrapolation of E' yielded −0.2223 v.

[1] W. R. Carmody, THIS JOURNAL, **54**, 188 (1932).

[2] M. Randall and L. F. Young, *ibid.*, **50**, 989 (1928).

Since comparable measurements of the hydrogen–calomel cell do not exist, the best value for the standard potential of the calomel electrode is to be had from measurements of the cell

$$\text{Ag (elect. crystals)} + \text{HgCl(s)} = \text{Hg(l)} + \text{AgCl(s)}$$

Randall and Young confirmed Gerke's[3] value, $E_{298.1} = 0.0455$ v., and found the same value when the silver–silver chloride electrodes were of the spiral type, also used by Carmody. This held for potassium chloride solutions and for hydrochloric acid solutions so long as the latter were free of oxygen. We may thus write

$$\text{Hg(l)} + \text{Cl}^- = \text{HgCl(s)} + E^-;\ E^\circ_{298.1} = -0.2677 \text{ v.}$$

From the "International Critical Tables," 1 Vol. M KCl at 18° has a density 1.04491 and is thus 7.135% KCl and 1.030_5 M. Also 0.1 Vol. M KCl at 18° has a density 1.0034 and is thus 0.743% KCl and 0.1004_1 M. These two solutions as well as 0.1 M KCl are used in reference calomel electrodes.

With the values of activity coefficients determined from freezing point measurements and corrected for the heats of dilution[4] the potentials listed in Table I result.

TABLE I

ELECTRODE POTENTIALS OF VARIOUS CALOMEL ELECTRODES

m	0.1	0.1004	1.0305
γ	0.7707	0.7704	0.6610
E	-0.3335_4	-0.333_{45}	-0.279_{56}

Since the potential of the "normal calomel electrode" by convention includes that of the liquid junction, KCl (1 Vol. M), KCl (0.1 M), which is −0.0004 v., its value is −0.2800 v. Attention is directed to the fact that the single potential of the 0.1 M KCl or 0.1 Vol. M KCl calomel electrode plus that of the cell

$$\text{Hg, HgCl(s)KCl(1 Vol. } M\text{), KCl(0.1 Vol. } M\text{)HgCl(s) Hg}$$
$$E_{298.1} = 0.0529 \text{ v.}$$

or −0.2806 v. does not agree with the value −0.2800 v.

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COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
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PUBLISHED SEPTEMBER 5, 1932

[3] R. H. Gerke, THIS JOURNAL, **44**, 1684 (1922).

[4] H. M. Spencer, *ibid.*, **54** (1932).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

STUDIES IN THE KETONE SUGAR SERIES. I. A NOVEL FORM OF STEREOISOMERISM IN THE SUGAR GROUP. THE ACETYL AND HALOGENO-ACETYL DERIVATIVES OF TURANOSE[1]

BY EUGENE PACSU

RECEIVED MARCH 10, 1932 PUBLISHED SEPTEMBER 5, 1932

The experimental investigations which led to the firm establishment of the present views in sugar chemistry have been carried out almost entirely with the aldehyde sugars and comparatively little work has been done with the ketone sugars. This is undoubtedly due to the fact that only a few ketoses are known in comparison with the large number of aldoses that are recognized. A review of the literature reveals that only one of the eight crystalline ketoses known at the present day, namely, *d*-fructose, has been submitted to a somewhat detailed investigation. Almost nothing is known of the derivatives of these ketoses except fructose, from which sugar, among others, two crystalline pentaacetates, methylfructosides, chloroacetyl compounds and tetraacetylfructosides, all designated as α,β-stereoisomers, have been prepared. Striking differences in the behavior of some of these fructose derivatives from the corresponding compounds of the aldoses prompted me to undertake the preparation of the unknown derivatives of some of the available ketoses in order to obtain experimental evidence which would justify the extension to the ketone sugars of the general views accepted in the aldose series. This paper represents the first in a series of investigations which is being conducted in this Laboratory and it deals with the derivatives of crystalline turanose.

This very rare ketone sugar is the first known true isomer of sucrose and its definite structure as 5-glucosido-fructose, one of the possibilities suggested by Zemplén,[2] has been established by the present author.[3] Since its structure excludes the possibility of a 2,5-ring formation in the fructose

[1] This investigation is a continuation of the studies on turanose which began with the preparation of this disaccharide in pure crystalline condition for the first time [C. S. Hudson and E. Pacsu, *Science*, **69**, 278 (1929); THIS JOURNAL, **52**, 2519 (1930)]. Dr. Hudson joins me in thanking Mr. F. P. Phelps, of the Bureau of Standards, for preparing the microphotograph of turanose crystals that was published in the latter article. The considerable quantities of turanose which were used in these investigations were prepared from a stock of several kilograms of melezitose which Dr. C. S. Hudson and Dr. H. S. Isbell prepared at the Bureau of Standards in 1928 from a large amount of honeydew honey kindly supplied by the Office of Bee Culture Investigations, U. S. Department of Agriculture; grateful acknowledgment is made of the aid from these sources. Some of the turanose derivatives now to be described were prepared in 1929 while the author was a fellow of the International Education Board, at the National Institute of Health, Washington, D. C.

[2] G. Zemplén and G. Braun, *Ber.*, **59**, 2230 (1926); Zemplén, *ibid.*, **59**, 2539 (1926).

[3] E. Pacsu, THIS JOURNAL, **53**, 3099 (1931).

part, it was hoped that turanose would yield derivatives the study of which would render easier the correct interpretation of the anomalous behavior of the corresponding fructose derivatives.

Being a disaccharide with a free OH group at the potentially reducing carbon atom 2, turanose would be expected to yield, according to the generally accepted principles in sugar chemistry, two stereoisomeric octaacetates on acetylation. Experiments showed, however, that on acetylation with acetic anhydride and zinc chloride at room temperature, turanose gave rise to three beautiful crystalline acetates, each of them containing eight acetyl radicals in its molecule. The three modifications can easily be separated on the basis of their different solubility in certain solvents. The first octaacetate, being almost insoluble in acetic anhydride, crystallizes from that medium during its formation, in very small needles, and can be removed by filtration. This substance, which is the starting material for the preparation of the majority of the other derivatives of turanose, melts at 216–217° and, on account of its low rotation, $[\alpha]_D^{20}$ +20.5° in chloroform solution, was believed to represent the beta isomer of octaacetylturanose with a normal 2,6-ring structure. From the acetic anhydride solution a mixture of a second and third octaacetylturanose was obtained. They were easily separated by cold alcohol, which dissolves readily the third octaacetate, leaving undissolved the second isomer. On recrystallization from hot absolute alcohol the second octaacetate was obtained in well-developed small prisms, melting at 158°. Judging from its high rotation, $[\alpha]_D^{20}$ +107° in chloroform solution, and from other properties, it is safe to assume that this substance represents the α-modification of octaacetylturanose with a normal 2,6-ring structure. The third octaacetyl derivative of turanose was isolated from the original alcoholic mother liquor of the second isomer. This substance melts at 96°, which appears to be unusually low in comparison with the melting points of the first two isomers, and its specific rotation, $[\alpha]_D^{20}$+126.2° in chloroform solution, is only slightly higher than that of the second variety. Its solubility in alcohol at room temperature and even in ether, from which it can be isolated on cooling in beautifully developed large hexagonal prisms, renders its separation from the other isomers very easy.

From the theoretical standpoint the existence of three octaacetyl derivatives of turanose is noteworthy because, while the first two of them may be assigned the usual stereoisomeric structures, the existence of a third isomer must be accounted for on other grounds. It could have been assumed that not possessing a normal primary ring, the substance belongs to the so-called "gamma" sugars. However, the structure of turanose excludes the possibility of a 2,5- or butylene oxide ring characteristic of the gamma sugars, since at carbon atom 5 of the fructose part occurs the disaccharide linking in the molecule. The assumption of a propylene oxide ring involving

carbon atoms 2 and 4, or still more that of an ethylene oxide ring attached at positions 2 and 1, or 2 and 3, appears to be unwarranted and very improbable. On the accepted principles of stereoisomerism it is, therefore, possible to accommodate only two of these isomers, namely, the first and second octaacetates. In considering the possible structure of the third isomer it was first necessary to study its behavior toward different reagents. It was surprising to find this substance to be very unstable to alkali and potassium permanganate. On the addition of a few drops of dilute sodium hydroxide solution, its colorless acetone solution immediately turns deep yellow. On adding dilute sulfuric acid the color disappears and then the solution reduces very strongly potassium permanganate solution. Neither of the first two isomers shows such behavior when submitted to the same test. The properties of the third octaacetate are, moreover, sharply distinctive in that it does not react with hydrogen bromide dissolved in glacial acetic acid, unchanged starting material being obtained even after standing for several hours at room temperature with that reagent. The unique behavior associated with the third octaacetylturanose seems to point irresistibly to the presence of a free ketone group in the molecule. Indeed, theoretical considerations and direct experimental evidences to be discussed in Part III of this series will show that the third octaacetylturanose is a derivative of the open-chain fructose, and should be named octaacetyl-*keto*-turanose. The same is true, moreover, of the well-known "α-fructose pentaacetate," generally regarded as the stereoisomeric modification of the β-pentaacetylfructose with a pyranoid ring structure.[3a]

By the recognition of this novel form of structure isomerism in the ketone sugar group it became possible to explain satisfactorily the existence of the three turanose octaacetates. However, manifestation of a sharp distinction between the behavior of the halogeno-acetyl derivatives of the first and of the second turanose octaacetate on the one hand, and between the properties of these halogenated compounds and those of the well-known β-halogeno-acetylfructoses on the other, soon aroused suspicion whether the first two octaacetylturanoses really constitute a true α,β-stereoisomeric pair. A striking solution of the problem came in an unexpected way by the discovery of a fourth crystalline octaacetate of turanose which, moreover, led to the recognition of a novel type of stereoisomerism in the sugar group. Since the halogeno-acetyl derivatives of turanose have an important bearing on the development of the present problem, it is necessary first to compare their properties with those of the known halogeno-acetylfructoses.

Starting from the chloroform solution of the first octaacetylturanose and applying titanium tetrachloride according to the method recently published by the present author,[4] it was possible to prepare a crystalline chloroacetyl-

[3a] E. Pacsu and F. V. Rich, THIS JOURNAL, **54**, 1697 (1932).

[4] E. Pacsu, *Ber.*, **61**, 1508 (1928).

turanose with m. p. 165° and $[\alpha]_D^{20}$ −0.44°. The crystalline bromoacetyl derivative with m. p. 133–134° and $[\alpha]_D^{20}$ −30.5° was obtained from the first acetate dissolved in chloroform and a 40% solution of hydrogen bromide in glacial acetic acid. On mixing the ingredients the formation of the bromoacetylturanose occurs almost instantaneously, strongly resembling an ionic reaction. The same is true of the change taking place in the chloroform solution of the first octaacetate on the addition of a 20% solution of hydrogen iodide in glacial acetic acid and yielding crystalline iodoacetylturanose with m. p. 105° and $[\alpha]_D^{20}$ −54°. The bromoacetylturanose was as a rule prepared from the first octaacetate by the above method. However, the same compound can be obtained in satisfactory yield from turanose itself when the latter is allowed to stand for several hours at room temperature with acetic anhydride containing free bromine. This reaction was originally carried out with the purpose of studying the catalytic action of bromine on the acetylation of turanose and it does not seem to have been observed before in the preparation of other bromoacetyl sugars.

The exceptionally easy and rapid formation of the halogeno-acetyl derivatives of turanose and the mobility displayed by their halogen atom in different reactions distinguish these substances markedly from the corresponding derivatives of the aldehyde sugars. The difference is by no means unexpected if it be observed that the former compounds contain a tertiary bound halogen atom which is known to be more reactive than a secondary bound halogen present in the halogeno-acetyl derivatives of the aldehyde sugars. What is really surprising is the relatively great stability in the solid state of the halogeno derivatives of the first octaacetylturanose[5] in comparison with the β-chloro- and β-bromoacetylfructose, both of which are known to undergo rapid decomposition during one day even if kept in a desiccator. Since the rotation of the halogeno-acetylturanoses increases in the levo direction when we pass from the chloro- to the iodo derivative, these substances must belong to the β-series. Under such circumstances it is incomprehensible why, for example, the reactive ≡C—Br group causing the instability of the β-bromoacetylfructose should change its character completely and lend stability to the bromoacetylturanose, which structurally differs from the former compound only in that it contains an acetylated glucosyl residue at carbon atom 5 instead of an acetyl group.

In order to throw more light upon this problem I undertook the preparation of the halogeno-acetyl derivatives of the second or α-octaacetylltura-

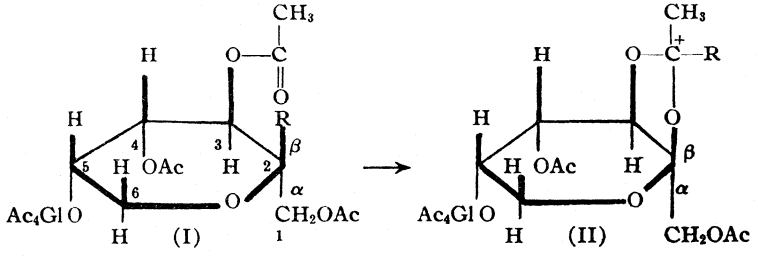
[5] The most stable of the three halogeno-acetylturanoses is the chloro compound, a sample of the crystals being unchanged after a year's standing in a loosely stoppered bottle. The bromo derivative is somewhat less stable as it decomposed to a black mass after standing for three months under the same conditions. The least stability is shown by the iodoacetylturanose, which must be stored in a vacuum desiccator over soda lime and phosphorus pentoxide.

nose with a normal 2,6-ring structure. Both the chloro- and the bromo-acetyl derivative of that octaacetate form as rapidly as the analogous compounds of the first octaacetate, but unlike the latter they are soluble in ether and cannot be isolated except in a sirupy form. Either sirup soon began to give off fumes and turned into a black tar with decomposition. Since the rotation increases in the dextro direction when we pass from the chloro compound ($[\alpha]_D^{20}$ +93° in chloroform solution) to the bromo derivative ($[\alpha]_D^{20}$ +117° in chloroform solution), these substances must belong to the α-series. The obvious similarity in the properties of the α-halogeno-acetylturanoses to the β-halogeno-acetylfructoses on the one hand, and the dissimilarity to the stable halogeno-acetylturanoses on the other, leave no element of doubt in the conclusion that these substances cannot represent a true α,β-stereoisomeric pair. Accordingly, the stable halogeno-acetylturanoses must differ *structurally* from the unstable α-isomers, the latter substances undoubtedly possessing the same reactive tertiary $\equiv$C—Hlg grouping only in a reversed configuration as the β-halogeno-acetylfructoses. However, this difference must be of another kind from that which was recognized in the course of this work between the chloroacetyl fructose and the substance known in the literature as its α-stereoisomer. In Part III of this series it will be shown that the "α-chloroacetylfructose" represents an acetylated derivative of the open-chain fructose containing a firmly bound primary chlorine atom at carbon atom 6 and thus it has nothing in common in structure with the true halogeno-acetyl sugars.[3a]

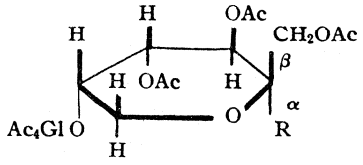
The final solution of the problem was made possible by the discovery of a fourth crystalline octaacetylturanose. Replacing the bromine atom with acetoxyl residue by silver acetate in the stable bromoacetylturanose dissolved in acetic anhydride, it was found that a mixture of two octaacetates had formed instead of one octaacetate as predicted by analogous reactions in the aldose series. Had the stable bromoacetylturanose the usual structure ascribed to the true halogeno-acetyl sugars, the octaacetate expected must have been the first (supposed β-) octaacetylturanose if no Walden inversion accompanied the reaction or the α-octaacetylturanose if such a change would have taken place. The mixture actually obtained was easily separated from hot alcohol, yielding about equal amounts of the first octaacetylturanose (m. p. 215°, $[\alpha]_D^{20}$ +20.5°) and a new isomer with m. p. 195° and $[\alpha]_D^{20}$ +103° in chloroform solution. Since, on treatment with hydrogen bromide dissolved in glacial acetic acid, this fourth octaacetylturanose like the first isomer gave rise in practically quantitative yield to the original stable bromoacetylturanose, it became evident that on the replacement of the bromine atom with the acetoxyl residue of the latter compound racemization occurred on the carbon atom to which the bromine atom was attached. Obviously, this particular carbon atom cannot be the constituent of the potential ketone group of the sugar, first, because on the

replacement of the halogen atom of the true halogeno-acetyl sugars with acetoxyl group the carbon atom to which the halogen atom is attached changes its configuration completely (Walden inversion) but never partially; second, because if such an unusual process would have taken place the second product must have been the α-octaacetylturanose. It is, therefore, necessary to find a structural formula which would account for the strange behavior of the stable halogeno-acetylturanoses and explain their close relationship to the first and fourth octaacetates.

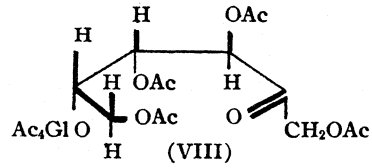
Such a formula is possible if the substances be regarded as derivatives of the orthoacetic acid. Inspection of the model in perspective of any acetylated turanose with substituent R at the potential ketone group (I) serves to illustrate that the 3-acetyl group can become intimately linked with the carbon atom 2 and give an orthoacetic acid derivative (II) *provided the substituent R on the latter carbon atom has a β-configuration.*

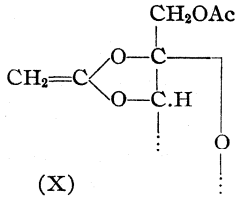


III, R = *l*-Hlg
IV, R = *l*-O.OC.CH$_3$
V, R = *d*-O.OC.CH$_3$
IX, R = *d,l*-C_5H_5NBr-



VI, R = O·OC·CH$_3$
VII, R = Hlg





The occurrence of this type of isomerism was first observed by Freudenberg[6] on the so-called "third chloroacetylmaltose" and almost simul-

[6] K. Freudenberg, *Naturwissenschaften*, **18**, 393 (1930); K. Freudenberg and H. Scholz, *Ber.*, **63**, 1969 (1930).

taneously by Bott, Haworth and Hirst[7] on both the "γ"-variety of triacetylmethylrhamnoside of Fischer[8] and tetraacetylmethylmannoside of Dale.[9]

In the recognition of this interesting isomerism of the turanose derivatives I wish to draw attention to an important factor which apparently has remained unobserved by the above investigators, namely, that the carbonyl carbon atom of the 3-acetoxyl residue becomes asymmetric during the transformation, thus creating a novel form of stereoisomerism of such type of compounds. In formula (II) the carbon atom marked with an asterisk is the central atom of the orthoacetic acid which became asymmetric; therefore, all compounds having this type of structural formula can exist in *d*- and *l*-forms according to the position of substituent R around this carbon atom. If R represents a strongly polar substituent like a halogen, only one form may exist but on replacement of the halogen by a less negative group racemization may occur on this carbon atom and two diastereomers can be obtained. Evidently, such racemization takes place when the halogen of the stable halogeno-acetylturanoses is replaced by the acetoxyl residue, giving rise to two different octaacetates, which on treatment with hydrogen halides will give back the same halogeno-acetyl compounds. Since the latter substances are the derivatives of the orthoacetyl halides, CH_3-$C^+(OH)_2$.Hlg, and the first and fourth octaacetates those of the semiorthoacetic anhydride, $CH_3C^+(OH)_2\,OCOCH_3$, with C^+ becoming asymmetric on ester formation with the sugar, the "stable halogeno-acetylturanoses" should be designated as hexaacetyl-β-turanose <2,6>-2,3-*l*-orthoacetyl halides (III), and the "first" and "fourth octaacetates" as hexaacetyl-β-turanose <2,6>-2,3-*l*-semiorthoacetic anhydride (IV) and *d*-semiorthoacetic anhydride (V), respectively. The actual configuration of the substituents around the new asymmetric carbon atom, of course, is not known, the designation of *l* and *d* being arbitrary and based only on the relative values of the specific rotations.

Inspection of model (I) shows that if substituent R around the carbon atom 2 occupies the α-configuration, there is no possibility for the formation of orthoacetic acid derivatives. Accordingly, the second octaacetate has the regular structure of an α-octaacetylturanose (VI) and the halogeno compounds derived from this substance are represented by formula (VII). The "third octaacetylturanose," as has been stated previously, is a derivative of the open-chain turanose (*keto*-turanose) having the structural formula of (VIII).

From the formula (VII) it is seen that on account of the presence of a tertiary bound halogen at the potential ketone carbon atom the α-halogeno-

[7] H. G. Bott, W. N. Haworth and E. L. Hirst, *J. Chem. Soc.*, 1395 (1930).

[8] E. Fischer, M. Bergmann and A. Rabe, *Ber.*, **53**, 2362 (1920).

[9] J. K. Dale, THIS JOURNAL, **46**, 1046 (1924).

acetylturanoses must be very unstable compounds. Furthermore, one can predict that on replacement of their halogen by the acetoxyl residue these substances will give rise either to α-octaacetate (VI) if no Walden inversion accompanies the change, or to a mixture of the "first" (IV) and "fourth octaacetate" (V) if such an inversion takes place. Actually, as experiment shows, the first case happens and the substance formed proves to be pure α-octaacetylturanose (VI).

Additional evidence regarding the correctness of formula (III) can be obtained if these substances are kept standing with dry pyridine for one day at room temperature. During this time the rotation of a pyridine solution of the bromo compound changed from $\alpha_D - 3.08°$ to $\alpha_D + 6.32°$. The change in rotation is due to a complicated reaction occurring between the substance and pyridine, yielding a large amount of a water-soluble quaternary pyridinium bromide salt. This salt is very likely a mixture of two diastereomers differing in the configuration of the groups around the carbon atom marked with an asterisk in formula (IX). Besides this main reaction another side change occurs in the pyridine solution, since it was possible on careful addition of ether to isolate a small amount of crystalline pyridine hydrobromide. The formation of that substance can only be explained if it be assumed that one of the hydrogen atoms of the methyl group of the orthoacetyl radical and the bromine atom of the molecule split out by the action of pyridine, giving rise to a ketene acetale, an unsaturated compound illustrated in formula (X). The formation of a similar ketene acetale was first observed by Freudenberg[10] from the "third chloroacetylmaltose" and pyridine. It can be detected by the aid of an acetone solution of potassium permanganate, which will be instantaneously reduced on mixing with the aged pyridine solution of the substance, thus indicating the presence of an unsaturated compound. This test is entirely negative if carried out with a freshly prepared pyridine solution. The actual isolation of this unsaturated compound appears to be difficult. It forms only in a small quantity since it is the product of a side reaction.

Further evidence in support of the correctness of the structural formulas suggested in this paper will be given in Part II of this series dealing with the methylglycosidic derivatives of turanose. Finally, it is to be noted that among the isomeric substances obtained in the course of this investigation there are no two substances which would constitute a real α,β-stereoisomeric pair. The four octaacetates represent three different types of structure isomerism and the halogeno compounds belong to two different classes. On account of these structural differences no calculation is permissible to test the validity of the principle of optical superposition as applied by Hudson in sugar chemistry.

[10] K. Freudenberg and H. Scholz, *Ber.*, **63**, 1969 (1930).

Experimental Part

Acetylation of Turanose. Preparation of the First (IV), Second (VI) and Third (VIII) Octaacetyl Derivatives.—Five grams of fused zinc chloride was dissolved in 300 g. of acetic anhydride and 50 g. of crystalline turanose (m. p. 157°; $[\alpha]_D^{22}$ +22.0° ⟶ 75.3° in water) was added to the solution. The mixture was kept at room temperature with occasional shaking until the sugar with a rise of temperature to 60–70° went into solution, which required about three hours. On twenty-four hours' standing at room temperature the liquid deposited a mass of fine needles which were filtered off and washed first with 20 cc. of acetic anhydride and finally with ether. The ether washings were rejected. The substance which represents the first octaacetylturanose (IV) was dissolved in 100 cc. of chloroform and filtered from a slight amount of unchanged sugar. On addition of ether to the clear filtrate, crystallization took place immediately. The crystals were triturated with 150 cc. of boiling alcohol, filtered while hot, dissolved in chloroform and precipitated from that solution by ether; yield, 21 g., or about 21% of the theoretical; m. p. 216–217°, $[\alpha]_D^{20}$ 20.5° (0.8878 g. in 25 cc. of chloroform solution rotated 1.455° to the right in a 2-dm. tube). The substance is readily soluble in chloroform and acetone, but only slightly in hot alcohol, and insoluble in ether.

In an acetyl estimation made by the method of Kunz,[11] 0.3 g. was dissolved in 50 cc. of pure acetone to which 60 cc. of 0.1 *N* sodium hydroxide was subsequently added. The acetylated sugar neutralized 35.3 cc. of decinormal alkali, in excellent agreement with the calculated value of 35.4 cc.

After the removal of the first octaacetate (IV) the original acetic anhydride solution was kept at room temperature for two more days, then it was poured into two liters of ice water. The sirup which was precipitated soon turned into a solid mass. This was filtered off, and the filtrate neutralized with solid sodium bicarbonate. The gummy precipitate so obtained was united with the first crop, then washed thoroughly with water. This raw material is a mixture of two different octaacetates. For separation the substance was treated with 150–200 cc. of cold 95% alcohol, which left the second octaacetylturanose (VI) undissolved while taking up the third isomer (VIII). After filtration the second octaacetate was dissolved in 250 cc. of hot 95% alcohol, the cloudy solution filtered through activated carbon and the filtrate kept at room temperature until the separation of the well-developed small prisms was complete. A second crystallization was accomplished by adding ether to the concentrated chloroform solution of the substance; yield, 28 g., or about 28% of the theoretical. After another recrystallization from hot alcohol the crystals melted at 158° and showed $[\alpha]_D^{20}$ 107.0°, $[\alpha]_C^{20}$ 85.4°, and $[\alpha]_{HgI}^{20}$ 125.75°, respectively (0.2137 g. of substance, 25 cc. of solution in chloroform, 2-dm. tube; rotation 1.83, 1.46 and 2.15° to the right, respectively). Further recrystallizations caused no significant change in these values of the specific rotation. The substance is soluble in chloroform, acetone and hot alcohol, insoluble in ether.

An acetyl estimation was carried out by the method previously indicated; 0.5 g. of the substance required 58.6 cc. of 0.1 *N* sodium hydroxide whereas the value calculated for octaacetylturanose is 58.9 cc.

The third octaacetate of turanose (VIII) was isolated from the original alcoholic extract of the mixture of the second and third isomers. The solution was evaporated under reduced pressure to a sirup which was dissolved in chloroform, washed with a dilute aqueous solution of sodium bicarbonate, then with water, dried with calcium chloride and concentrated under reduced pressure to a thin sirup. On the addition of ether the third octaacetate crystallized in well-developed large hexagonal prisms from the ice cold solution; yield 34.3 g., or about 34% of the theoretical. After a second recrystallization

[11] A. Kunz and C. S. Hudson, THIS JOURNAL, **48**, 1982 (1926).

from chloroform and ether the substance melted at 96° and showed $[\alpha]_D^{20}$ 126.2°, $[\alpha]_C^{20}$ 98.14° and $[\alpha]_{HgI}^{20}$ 151.65°, respectively (1.5067 g. in 25 cc. of chloroform solution rotated in a 2-dm. tube 15.21°, 11.83° and 18.28° to the right, respectively). The substance is readily soluble in chloroform, acetone and alcohol at room temperature, and in warm ether.

In an acetyl estimation carried out by Kunz's method at −10°, 0.4 g. was equivalent to 46.9 cc. of decinormal alkali, the reaction time being thirty minutes, in comparison with 47.17 cc. calculated for octaacetylturanose.

For studying the behavior of the three isomer octaacetates to alkali and potassium permanganate, about 0.1 g. of the three substances was dissolved, each in 15 cc. of pure acetone, and 1 cc. of dilute alkali was added to the samples. The solution of the third octaacetate (VIII) developed a deep yellow color whereas that of the first (IV) and of the second (VI) isomer remained colorless. After two minutes the samples were mixed with a slight excess of dilute sulfuric acid, whereupon the color of the third isomer disappeared. Then, on addition of 0.5 cc. of a potassium permanganate solution to each sample, the solution of the first and second octaacetates remained pink for about ten minutes, while the third solution lost its color immediately and reduced about 10 cc. of the same permanganate solution during that time.

The Halogeno Derivatives (III) of the First Octaacetate (IV) of Turanose. (a) Preparation of the Chloro Derivative (III, R = Cl).—According to the general method of the author,[12] a solution of 2.8 g. of titanium tetrachloride in absolute chloroform[13] was added to a solution of 6.8 g. of the first octaacetate in 80 g. of the same solvent at room temperature. A lemon yellow amorphous halochromic compound immediately separated but rapidly redissolved on shaking. The solution was gently refluxed for thirty-five minutes, after which the grayish-brown liquid was cooled, washed twice with ice water, once with a dilute sodium bicarbonate solution and then washed again with ice water. It was dried with calcium chloride, decolorized with activated carbon and evaporated under reduced pressure to about 25 cc. On the addition of ether crystallization took place rapidly; yield, 5.8 g. One recrystallization from chloroform by the addition of ether was sufficient for purification to constant rotation, which was $[\alpha]_D^{20}$ −0.44° (1.4748 g. of substance in 25 cc. chloroform solution rotated 0.052° to the left in a 2-dm. tube). The chlorine percentage was found to be 5.18 in comparison with 5.4 calculated for chloroacetylturanose (1.027 g. of substance yielded 0.2150 g. of silver chloride). The substance melted with decomposition at 165° to a red liquid.

(b) **Preparation of the Bromo Derivative (III, R = Br).**—(1) Thirty grams of the first octaacetate (IV) was dissolved in 100 cc. of chloroform and the solution was mixed with 130 cc. of a 40% solution of hydrogen bromide in glacial acetic acid. Five minutes after the mixing of the ingredients the light yellow liquid showed the constant rotation of about $[\alpha]_D$ −30°, thus indicating a rapid formation of the bromo compound. After the usual treatment with ice water, potassium bicarbonate solution, etc., the chloroform solution was evaporated under reduced pressure to a thin sirup. On the addition of ether crystallization took place immediately; yield, 29.3 g. or 95%. Recrystallization from chloroform by the addition of ether did not change the rotation, which was $[\alpha]_D^{20}$ −30.5° (1.2978 g. in 25 cc. of chloroform solution gave a reading of 3.18° to the left in a 2-dm. tube). The bromine percentage was found to be 11.28 in comparison with 11.43 calculated for bromoacetylturanose (0.8893 g. of substance yielded 0.2357 g. of silver bromide). The melting point was 133–134° with decomposition.

(2) Five grams of crystalline turanose was added to 40 cc. of cold acetic anhydride

[12] E. Pacsu, *Ber.*, **61**, 1508 (1928).

[13] For preparation of the chloroform, see E. Pacsu, THIS JOURNAL, **52**, 2563 (1930), Note 13.

containing 1 cc. of bromine. In about thirty minutes the sugar went into solution with evolution of heat. The light yellow solution was kept at room temperature for sixteen hours. During this time its color changed to deep violet. On pouring the solution into ice water a viscous cake separated and the color disappeared. The substance was washed with water, then triturated with cold ether, filtered, dissolved in chloroform and dried with calcium chloride. On addition of ether brilliant needles separated; yield, 3.2 g., or 31%. After one recrystallization from chloroform and ether the crystals showed $[\alpha]_D^{20}$ −29.5° and melted at 133°.

The reaction taking place between the substance and pyridine has been discussed in the theoretical part of this paper.

(c) **Preparation of the Iodo Derivative (III, R = I).**—The solution of 5 g. of the first octaacetate (IV) in 30 cc. of chloroform was mixed with 20 cc. of a 20% solution of hydrogen iodide in glacial acetic acid. The liquid was immediately poured into ice water, washed quickly with ice water and dried with anhydrous sodium sulfate. On addition of ether colorless needles separated from the ice cold solution, yield, 3.2 g., or about 58%. The specific rotation was found to be $[\alpha]_D^{20}$ −54.2° (0.9728 g. in 25 cc. of chloroform solution rotated 4.25° to the left in a 2-dm. tube). The iodine percentage was found to be 16.45 in comparison with 17.01 calculated for iodoacetylturanose (0.3881 g. of substance yielded 0.1181 g. of silver iodide). The melting point was 105–106° with decomposition. Recrystallization from U. S. P. chloroform and ether produced a considerable loss of material. This is due to the reactivity of the substance to alcohol present in the former solvent. One sample after the third recrystallization showed $[\alpha]_D^{20}$ −9.3° and contained only 10.2% of iodine.

The Halogeno Derivatives (VII) of the Second Octaacetate (VI) of Turanose. (a) **Preparation of the Chloro Derivative (VII, R = Cl).**—The same procedure was used which has been described for the preparation of the chloro derivative (III, R = Cl) of the first octaacetate. The substance obtained was a sticky sirup readily soluble in ether. On addition of petroleum ether to its ether solution no crystallization took place, but the compound was precipitated as a sirup showing $[\alpha]_D^{20}$ 92.9° (0.5262 g. of substance in 25 cc. of chloroform solution rotated 3.9° to the right in a 2-dm. tube). The chlorine percentage was found to be 4.92 in comparison with 5.4 calculated for chloroacetylturanose (0.8360 g. of substance yielded 0.1750 g. of silver chloride). Within a few hours the fuming sirup turned into a black tar with decomposition.

(b) **Preparation of the Bromo Derivative (VII, R = Br).**—The substance was prepared in a manner similar to the preparation of the bromo derivative (III, R = Br) of the first octaacetate. The compound formed was a very unstable, ether-soluble sirup having the specific rotation of $[\alpha]_D^{20}$ 117.4° (1.1076 g. of substance in 25 cc. of chloroform solution rotated 10.41° to the right in a 2-dm. tube). The bromine content was 10.2% in comparison with 11.43 calculated for bromoacetylturanose.

For the replacement of the bromine atom by the acetoxyl residue 4 g. of the α-bromoacetylturanose was dissolved in 20 cc. of acetic anhydride and the solution was shaken for ten minutes at room temperature with 4 g. of silver acetate. After filtration the acetic anhydride solution was worked up in the usual way; yield, 3 g. of crystalline α-octaacetate (VI), m. p. 157–158°, $[\alpha]_D^{20}$ 106.4°.

Preparation of the Fourth (V) Octaacetyl Derivative of Turanose.—Ten grams of crystalline bromoacetylturanose (III, R = Br) was dissolved in 50 cc. of acetic anhydride, 3.6 g. of silver acetate was added and the mixture was heated for ten minutes on the water-bath. After the addition of charcoal the milky liquid became clear. It was filtered and the solution was kept for twelve hours in the ice box. During this time the first octaacetate (IV) of turanose crystallized from the solution in the form of small needles, which were filtered and purified as previously described; yield, 2.8 g. The substance

showed the correct specific rotation of $[\alpha]_D^{20}$ 20.5° and m. p. 216–217°. After the removal of the first octaacetate the acetic anhydride solution was poured into ice water. The sirup which was precipitated turned very soon into a crystalline mass. It was filtered off, washed with water and dissolved in 200 cc. of hot 95% alcohol, from which it crystallized on cooling in brilliant prismatic needles; yield, 3.8 g. After one recrystallization from alcohol the substance, which represents the fourth octaacetate of turanose, melted at 194–195° and showed $[\alpha]_D^{20}$ 103.16° in chloroform (0.7828 g. of substance, 25 cc. of solution in chloroform, a 2-dm. tube; rotation, 6.46° to the right). Subsequent recrystallization from chloroform by the addition of ether and recrystallization of the substance thus obtained from alcohol did not change the rotation.

In an acetyl estimation, carried out by Kunz's method, 0.3117 g. of the substance required 36.3 cc. of decinormal alkali, whereas the value calculated for octaacetylturanose is 36.78 cc. The substance is soluble in chloroform, acetone and hot alcohol, insoluble in ether.

The chemical properties of the fourth octaacetate were found to be identical with those of the first isomer (IV). Like the latter substance, the new isomer displayed in acetone solution no coloration with dilute alkali, and, similarly, no reduction took place on subsequent addition of potassium permanganate to the acidified solution. Addition of 3 cc. of a 40% solution of hydrogen bromide in glacial acetic acid to the chloroform solution of 0.5 g. of the fourth octaacetate resulted in the rapid formation of the stable bromoacetylturanose (III, R = Br); yield, 0.4 g.; m. p. 133° and $[\alpha]_D^{20}$ −29.3°.

Summary

1. Instead of two isomerides required by the theory of oxo-cyclo desmotropy of the reducing sugars, three octaacetyl derivatives have been obtained on acetylation of crystalline turanose with acetic anhydride and zinc chloride at room temperature. It has been found that each of the three octaacetates represents a different type of structure isomerism.

2. From the properties of the third octaacetate (VIII), the conclusion has been drawn that this substance possesses an open-chain structure with a free ketone group in the molecule.

3. The second octaacetate (VI) has been assigned the regular structure of an α-octaacetylturanose with a normal 2,6 primary ring in the molecule.

4. The first octaacetate (IV) has been found to be the derivative of the semiorthoacetic anhydride. Attention is directed to the fact that all sugar derivatives which represent the latter type of structure isomerism contain a new asymmetric carbon atom in the molecule and can, therefore, exist in two diastereomeric forms. This novel form of stereoisomerism in sugar chemistry has been given strong support by the discovery of a fourth octaacetylturanose (V), which represents the second of these possible diastereomers.

5. The stable, crystalline halogeno compounds (III) obtainable from either the first or fourth octaacetate have been found to be the derivatives of the orthoacetyl halides. In support of the correctness of this conclusion stands the observed formation of a ketene acetale (X), an unsaturated compound, from the crystalline bromoacetylturanose (III, R = Br) and pyridine.

6. The unstable, sirupy halogeno compounds obtained from the second octaacetate have the regular structures of the α-halogeno-acetylturanoses (VII). Inasmuch as the properties of these substances are extremely different from those of the "α-chloroacetylfructose," it has been concluded that the latter substance cannot be the stereoisomer of the unstable β-chloroacetylfructose.

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[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS, WELLCOME AND COMPANY]

HYDROXY- AND DIHYDROXYPHENYLETHYLMETHYLAMINES AND THEIR ETHERS

BY JOHANNES S. BUCK

RECEIVED MARCH 28, 1932 PUBLISHED SEPTEMBER 5, 1932

In an earlier paper[1] the synthesis of Epinine, 3,4-dihydroxyphenylethylmethylamine, was described. This, with two other members of the same series, has been examined pharmacologically.[2] Owing to their pressor activity, it was decided to attempt the synthesis of the remaining members of the series and to carry out a pharmacological examination of these. The compounds recorded up to the present are the unsubstituted amine, the 4-hydroxyamine and the 3,4-dihydroxyamine. Those so far not described are the 2-hydroxy, 3-hydroxy, and the 2,3-, 2,5-, 2,4-, 3,5- and the 2,6-dihydroxyphenylethylmethylamines. Of these, all but the three latter have been synthesized and are described, together with their intermediates, in the present paper. The synthesis of the 2,4-dihydroxy compound broke down at the last stage, the demethylation proceeding abnormally. This reaction will form the subject of another communication. The syntheses of the remaining two members of the series, the 3,5- and 2,6-dihydroxyamines, have not been carried out, the first owing to lack of starting material, and the second owing to difficulties caused by the powerful steric hindrance of the 2,6-groups. It is hoped to complete the series in the future. The pharmacological action will be described in another place.

Experimental

The preparation of the hydroxyphenylethylmethylamines was carried out in all cases by a series of reactions similar to that used in the synthesis of epinine.[1]

$$(OMe)RCHO \longrightarrow (OMe)RCH{=}CHCOOH \longrightarrow (OMe)RCH_2CH_2COOH \longrightarrow (OMe)RCH_2CH_2CONH_2 \longrightarrow (OMe)RCH_2CH_2NH_2 \longrightarrow (OMe)RCH_2CH_2N{=}CHC_6H_5 \longrightarrow (OMe)RCH_2CH_2N(MeI){=}CHC_6H_5 \longrightarrow (OMe)RCH_2CH_2NHMe\cdot HI \longrightarrow (OMe)RCH_2CH_2NHMe \longrightarrow (OH)RCH_2CH_2NHMe\cdot HCl$$

[1] Buck, THIS JOURNAL, **52**, 4119 (1930).

[2] Barger and Dale, *J. Physiol.*, **41**, 19 (1910).

The cinnamic acid in each case was made by the well-known Knoevenagel method, by condensation of the aldehyde with malonic acid in the presence of pyridine, piperidine being used as catalyst. On reduction with 4% sodium amalgam (excess = 4H being used), the corresponding phenylpropionic acid was produced, usually in very good yield. From the acid, the amide was made by heating in a stream of ammonia at 220–230° for two hours, the liquors, after removal of the first crop from benzene, being evaporated and the treatment repeated. Conversion to the phenylethylamine was carried out by a Hofmann reaction, the theoretical amount of sodium hypochlorite being used. Monomethylation of the phenylethylamine was done by the elegant Decker method,[3] except that the reaction mixture was heated for eighteen hours at 37° in place of the higher temperatures used by Decker. The Schiff bases and the methyl iodide addition products were used directly, the first being thick sirups and the second being too unstable to manipulate. Subsequent O-demethylation was carried out in one of two ways, either by heating with hydriodic acid (52% colorless, sp. gr. 1.7) at the boiling point, removal of excess of acid and conversion to the chloride by means of silver chloride, or by demethylating the free amine by concentrated hydrochloric acid at 180°. In the latter case the amine

INTERMEDIATES, PREVIOUSLY PREPARED AND DESCRIBED

Compound	Yield, %	Lit. refs.	Compound	Yield, %	Lit. refs.
o-Methoxycinnamic acid[a,b]	95	4	2,3-Dimethoxyphenylpropionic acid	..	11
o-Methoxyphenylpropionic acid	87	5, 6	2,3-Dimethoxyphenylpropionamide[b,e]	84	11
m-Methoxybenzaldehyde[b,c,d]	83	8	2,4-Dimethoxybenzaldehyde[d]	..	12, 8
m-Methoxycinnamic acid	..	9	*Trans*-2,4-dimethoxycinnamic acid[a,b]	97	13
m-Methoxyphenylpropionic acid	..	10	2,4-Dimethoxyphenylpropionic acid	89	14
m-Methoxyphenylpropionamide[b,e,f]	86	10	2,5-Dimethoxybenzaldehyde	37	15
2,3-Dimethoxybenzaldehyde	..	8	2,5-Dimethoxycinnamic acid[a,b]	95	15
2,3-Dimethoxycinnamic acid	..	11			

[3] Decker, *Ann.*, **395**, 390 (1913).

[4] Perkin, *J. Chem. Soc.*, **31**, 414 (1877).

[5] Perkin, *ibid.*, **39**, 415 (1881).

[6] Tiemann and Ludwig, *Ber.*, **15**, 2043 (1882).

[7] Mentioned but not described by Shoesmith and Connor, *J. Chem. Soc.*, 2230 (1927).

[8] Douetteau, *Bull. soc. chim.*, [iv] **9**, 932 (1911).

[9] Chakravarti, Haworth and Perkin, *J. Chem. Soc.*, 2265 (1927).

[10] Helfer, *Helv. Chim. Acta*, **7**, 945 (1924).

[11] Haworth, *J. Chem. Soc.*, 2281 (1927).

[12] Adams and Levine, THIS JOURNAL, **45**, 2373 (1923).

[13] Perkin and Schiess, *J. Chem. Soc.*, **85**, 159 (1904).

[14] Will, *Ber.*, **16**, 2106 (1883).

[15] Kauffmann and Burr, *ibid.*, **40**, 2352 (1907).

NEW INTERMEDIATES

Compound	Cryst. form	Sol. in	Yield, %	M. p., °C.	Analyses Found, % C	H
o-Methoxyphenylpropionamide[7,a]	Prisms	Bz, EtOH, Et_2O	73	110	66.61	7.23
2,4-Dimethoxyphenylpropionamide[e]	Prisms	Bz, EtOH, Et_2O	71	113	63.23	7.35
2,5-Dimethoxyphenylpropionamide[e]	Needles	EtOH	85	111	63.24	6.99
2,5-Dimethoxyphenylpropionic acid[g]	Poor prisms	EtOH	94	101	63.02	6.49

[a] Malonic acid method of preparation. [b] Method differs from that in literature. [c] B. p. 122° (22 mm.). [d] Method of Ref. 8 adapted to present compound. [e] Ammonia method of preparation. [f] Purification difficult, b. p. 180–205° (1 mm.). [g] Sodium amalgam method of preparation.

hydrochloride was obtained directly. Repeated efforts failed to give the 2,4-dihydroxyamine, the reaction taking another course and giving products of a different type.

β-Phenylethylamines.—The amines are all colorless, somewhat viscous liquids, which rapidly absorb carbon dioxide from the air, forming solid carbonates. With the exception of the 2,3-compound, which is miscible with water, they are rather slightly soluble in water, giving strongly alkaline solutions. They are miscible with alcohol, benzene and ether. The odors are much fainter than would be expected. The mediocre yields in some cases are doubtless due to nuclear halogenation, a not infrequent accompaniment to the Hofmann reaction.

Amine	Odor	B. p., °C.,	mm.	n_D^{25}	d_4^{25}	M_D	Formula	Analyses Calcd. C	H	Found C	H	Yield, %
2-Methoxy	Musty, amine	117	9	1.5391	1.0408	45.49[a]	$C_9H_{13}ON$	71.48	8.66	71.70	8.88	65
3-Methoxy[c]	Musty, sweet	118	6	1.5370	1.0385	45.44[a]	$C_9H_{13}ON$	71.48	8.66	71.43	8.75	33
2,3-Di-methoxy	Slight amine	138	8	1.5348	1.0839	52.01[b]	$C_{10}H_{15}O_2N$	66.25	8.33	65.94	8.53	79
2,4-Di-methoxy	Faint amine	140	1	1.5402	1.0915	52.08[b]	$C_{10}H_{15}O_2N$	66.25	8.33	66.33	8.41	31
2,5-Di-methoxy	Faint ester	150	8	1.5399	1.0889	52.18[b]	$C_{10}H_{15}O_2N$	66.25	8.33	65.94	8.40	63

[a] Calcd. (Brühl), 45.42. [b] Calcd. (Brühl), 51.73. [c] Helfer[10] uses hypobromite.

β-Phenylethylmethylamines.—The amines were prepared by adding excess of 30% potassium hydroxide solution to the aqueous solution of the hydriodide. The resulting oil was extracted with ether, dried over solid potassium hydroxide, and distilled under reduced pressure. Small amounts of white crystalline material usually separate during the ether extraction. The amines form colorless, viscous liquids, slightly soluble in water, with the exception of the 2,3-compound, which is more soluble. The aqueous solutions are strongly alkaline. The amines do not form solid carbonates in the air.

Amine	Odor	B. p., °C.	Mm.	n_D^{25}	d_4^{25}	M_D	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
2-Methoxy	Strong amine	115	9	1.5249	1.0043	50.38[a]	$C_{10}H_{15}ON$	72.68	9.16	73.04	9.21
3-Methoxy	Strong amine	118	7	1.5225	0.9999	50.40[a]	$C_{10}H_{15}ON$	72.68	9.16	72.83	8.99
2,3-Dimethoxy	Faint amine	136	6	1.5218	1.0471	56.82[b]	$C_{11}H_{17}O_2N$	67.64	8.78	68.02	9.01
2,4-Dimethoxy	Faint, musty	136	4	1.5283	1.0534	57.07[b]	$C_{11}H_{17}O_2N$	67.64	8.78	67.82	8.87
2,5-Dimethoxy	Pract. odorless	155	8	1.5278	1.0545	56.96[b]	$C_{11}H_{17}O_2N$	67.64	8.78	68.01	8.57

[a] Calcd. (Brühl), 50.23. [b] Calcd. (Brühl), 56.51.

β-Phenylethylmethylamines—Hydriodides.—With the exception of the 2,4-compound, which could not be crystallized, the hydriodides were recrystallized from alcohol–ether mixture. They are all white when pure, and are very soluble in water and in alcohol. The hydriodides show marked supercooling and are difficult to crystallize.

Hydriodide	Appearance	M. p., °C.	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H	Yield,[a] %
2-Methoxy	Glittering rounded prisms	101	$C_{10}H_{16}ONI$	40.95	5.50	41.16	5.62	76
3-Methoxy	Glittering tiny rect. plates	108	$C_{10}H_{16}ONI$	40.95	5.50	41.27	5.26	52
2,3-Dimethoxy	Glittering prisms	90	$C_{11}H_{18}O_2NI$	40.86	5.62	41.01	5.60	82
2,4-Dimethoxy	Uncrystallizable sirup	...	.....	...	..	...	..	[b]
2,5-Dimethoxy	Pearly plates	137	$C_{11}H_{18}O_2NI$	40.86	5.62	41.00	5.62	92

[a] The yields are given for unrecrystallized hydriodide. [b] Weighed as amine, 47% over both stages.

β-Phenylethylmethylamines—Hydrochlorides.—The hydrochlorides were prepared either by passing hydrogen chloride into an ether solution of the pure amine, or by the action of silver chloride on the hydriodide. They form bulky, pure white masses of micro crystals. Alcohol–ether mixture is the best solvent for recrystallization, as the hydrochlorides are all very soluble in cold water and in cold alcohol, but sparingly soluble in ether.

Hydrochloride	Appearance[a]	M. p., °C.	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
2-Methoxy	Mesh of long thin plates	119	$C_{10}H_{16}ONCl$	59.52	8.00	59.31	8.05
3-Methoxy	Tiny rhombic plates	119	$C_{10}H_{16}ONCl$	59.52	8.00	59.48	8.08
2,3-Dimethoxy	Mesh of long thin plates	117	$C_{11}H_{18}O_2NCl$	56.99	7.83	57.11	7.80
2,4-Dimethoxy	Mesh of flat needle-prisms	145	$C_{11}H_{18}O_2NCl$	56.99	7.83	56.91	8.20
2,5-Dimethoxy	Mass of tiny needles	110	$C_{11}H_{18}O_2NCl$	56.99	7.83	56.80	7.60

[a] Under microscope, from alcohol.

Hydroxyphenylethylmethylamines—Hydrochlorides.—The hydrochlorides all form white crystals, very soluble in water, alcohol, acetic acid and concd. hydrochloric acid. They are very difficult to obtain in a crystalline form, the 3-hydroxy compound being particularly so. When pure, however, they are quite stable. No bases could be isolated on account of their solubility and instability. The dihydroxy compounds are powerful reduc-

ing agents. Alcohol–ether or acetone–ether mixtures are the best solvents for crystallizing the salts, as they are sparingly soluble in ether.

No.	Hydrochloride	Appearance	$FeCl_3$	Ammon. $AgNO_3$	Excess NaOH
1	2-Hydroxy	Thin, pearly plates	Dull violet	No redn.	Colorless, stable
2	3-Hydroxy	Glittering plates	Pale violet	No redn.	Colorless, stable
3	2,3-Dihydroxy	Stars of prisms	Dull green	Reduced in cold	Rapidly blackens
4	2,5-Dihydroxy	Felted tiny plates	Transient pale green	Reduced in cold	Rapidly blackens

No.	Hydrochloride	M. p., °C.	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
1	2-Hydroxy	148	$C_9H_{14}ONCl$	57.63	7.53	57.98	7.49
2	3-Hydroxy	89	$C_9H_{14}ONCl$	57.63	7.53	57.43	7.60
3	2,3-Dihydroxy	149	$C_9H_{14}O_2NCl$	53.05	6.93	53.30	6.72
4	2,5-Dihydroxy	128	$C_9H_{14}O_2NCl$	53.05	6.93	53.23	7.01

The analyses given in this paper are all micro-analyses (Pregl). The author is indebted to Mr. W. S. Ide for these.

Summary

The paper describes the synthesis of four of the seven previously unknown hydroxy- and dihydroxyphenylethylmethylamines. The synthesis of one of the remaining three broke down at the last stage. It has not been possible to obtain starting material to attempt the syntheses of the other two.

TUCKAHOE, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

THE HALOFORM REACTION. VI. ALPHA-HALOGEN DERIVATIVES OF HINDERED KETONES

BY C. HAROLD FISHER, HAROLD R. SNYDER AND REYNOLD C. FUSON

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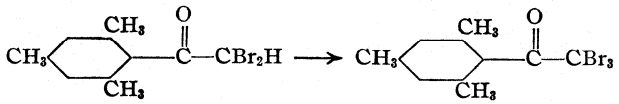
The study of the halogenation phase of the haloform reaction has now been extended to types other than methyl ketones, and it has been found that the replacement of α-hydrogen by halogen is a fairly general reaction between hindered ketones and hypohalite solutions. This investigation has also included a study of certain unusual reactions which are apparently general for this type of compound. These reactions are (1) cleavage by alkali, (2) the dehalogenation by phenol and (3) dehalogenation by the Grignard reagent. These several phases of the work will be discussed under separate headings.

The Halogenation.—From the previous work[1] in this series it appears that the hindered methyl ketones are generally converted directly into the corresponding trihalomethyl compounds. In no case has the mono- or the di-halomethyl derivative been isolated as an intermediate.

[1] (a) Fuson and Walker, THIS JOURNAL, **52**, 3269 (1930); (b) Gray, Walker and Fuson, *ibid.*, **53**, 3494 (1931); (c) Fuson, Farlow and Stehman, *ibid.*, **53**, 4097 (1931); (d) Fuson, Lewis and Du Puis, *ibid.*, **54**, 1114 (1932).

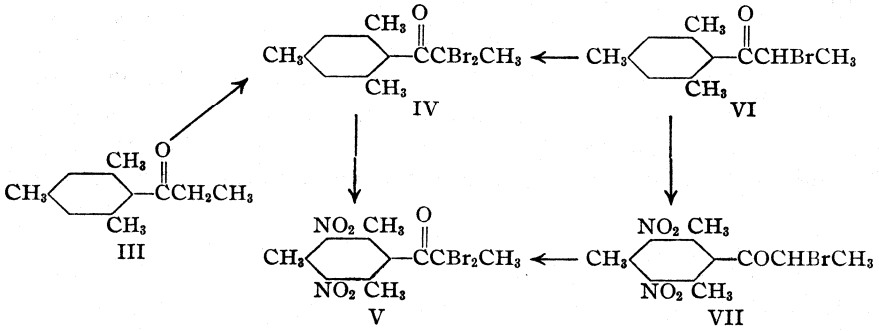
On the other hand, α-bromoacetylmesitylene, α-chloroacetylmesitylene and di-(α-chloroacetyl)-mesitylene have been converted into the corresponding trihalomethyl ketone. It remained to try the dihalomethyl ketones to see if they likewise would yield the fully halogenated derivatives.



I II

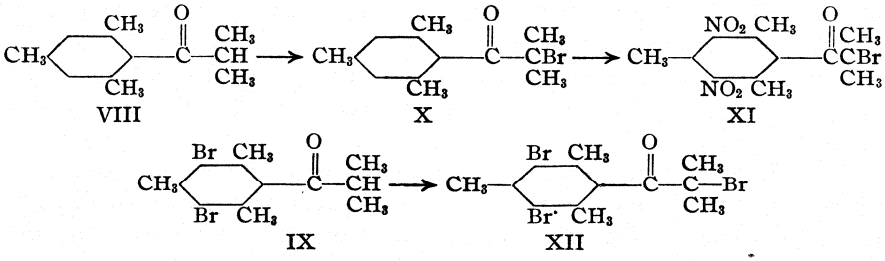
When α,α-dibromoacetylmesitylene (I) was treated with a solution of sodium hypobromite it was, in fact, converted into the corresponding tribromo derivative, tribromoacetylmesitylene (II).

The halogenation of propionylmesitylene (III) was next studied.



III IV V VI VII

The product in this case was α,α-dibromopropionylmesitylene (IV) isolated in the form of its dinitro derivative, α,α-dibromo-3,5-dinitropropionylmesitylene (V). As might be expected from the foregoing work, α-bromopropionylmesitylene (VI) when treated with a solution of sodium hypobromite gave α,α-dibromopropionylmesitylene, which was also identified by means of the dinitro derivative (V). Also α-bromo-3,5-dinitropropionylmesitylene (VII) was converted directly into α,α-dibromo-3,5-dinitropropionylmesitylene (V) by treatment with a hypobromite solution.

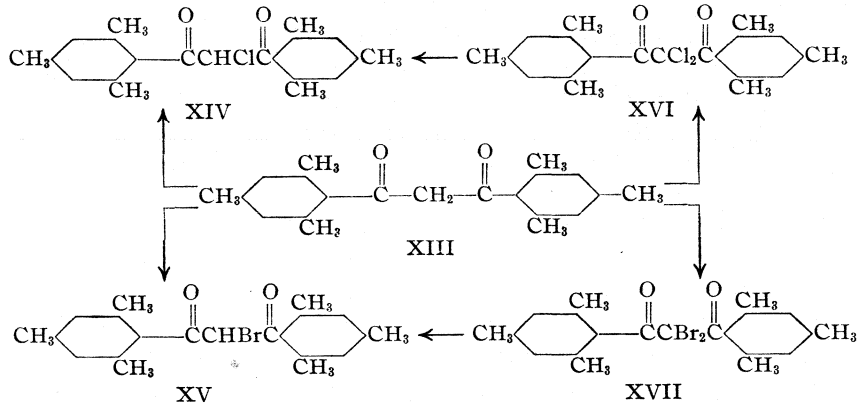


VIII X XI IX XII

In a similar fashion isobutyrylmesitylene (VIII) and 3,5-dibromoisobutyrylmesitylene (IX) gave α-bromoisobutyrylmesitylene (X) (which was identified by its solid dinitro derivative (XI)) and α,3,5-tribromoiso-

butyrylmesitylene (XII), respectively. The α-bromo-3,5-dinitroisobutyrylmesitylene (XI) was also prepared by direct bromination of the corresponding dinitro compound.[2] When a very pure sample of the dinitro compound was treated with a solution of sodium hypobromite, the bromo derivative obtained melted at 125–126°. The melting point (117.8–118.5°) reported earlier for this compound is, therefore, to be corrected.[3]

Of unusual interest is the case of the 1,3-diketones. In this work di-(β-isoduryloyl)-methane (XIII) was used. Although direct halogenation by use of chlorine and bromine gave only the corresponding monohalogen derivatives, (XIV) and (XV), the original diketone was converted into the dihalogen derivatives (XVI) and (XVII) by the action of solutions of alkali hypohalites.



The Action of Alkali.—The cleavage of trichloroacetylmesitylene by hot, concentrated solutions of alkali has been carried out by Houben and Fischer.[4] Tribromoacetylmesitylene was found to undergo cleavage only with great difficulty and in small yields. When di-(β-isoduryloyl)-dichloromethane (XVI) and di-(β-isoduryloyl)-dibromomethane (XVII) were treated with strong solutions of alkali, they did not undergo cleavage but dehalogenation, giving the corresponding monohalogen derivatives (XIV) and (XV).

Dehalogenation by the Action of Phenol.—The dehalogenating action of phenol on certain α-halo ketones has been reported by Löwenbein and Schuster,[5] and by Koelsch.[6] A similar study was made of the halogenating action of two of the polyhalogen ketones which have been obtained in this

[2] Maxwell and Adams, THIS JOURNAL, **52**, 2959 (1930).

[3] Fisher, Oakwood and Fuson, *ibid.*, **52**, 5039 (1930).

[4] Houben and Fischer, *Ber.*, **63B**, 2459 (1930).

[5] Löwenbein and Schuster, *Ann.*, **481**, 106 (1930); also Schuster, *Ber.*, **63**, 2397 (1930).

[6] Koelsch, THIS JOURNAL, **53**, 1147 (1931).

investigation. It was found that tribromoacetylmesitylene reacted with phenol to give dibromoacetylmesitylene and *p*-bromophenol: $C_9H_{11}COCBr_3 + C_6H_5OH \longrightarrow C_9H_{11}COCHBr_2 + p\text{-}BrC_6H_4OH$. In a similar manner di-(β-isoduryloyl)-dibromomethane reacted with phenol to yield the corresponding monobromo diketone.

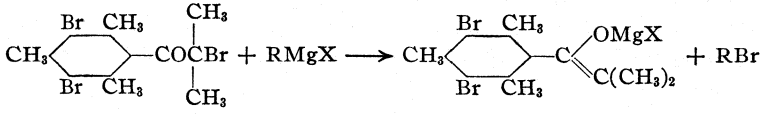
Dehalogenation by the Action of the Grignard Reagent.—The reaction of the Grignard reagent on α-halo ketones, which has been studied by Kohler and others,[7] also represents a process apparently peculiar to halogen derivatives of this type. The trihalomethyl ketones are transformed into the corresponding dihalomethyl compounds under the influence of this reagent. Tribromoacetylmesitylene and trichloroacetylmesitylene were converted in this way into dibromoacetylmesitylene and dichloroacetylmesitylene, respectively.

In a similar manner, di-(β-isoduryloyl)-dichloromethane and di-(β-isoduryloyl)-dibromomethane were converted, respectively, into di-(β-isoduryloyl)-chloromethane and di-(β-isoduryloyl)-bromomethane.

The Grignard reagent caused dehalogenation also in the case of α,α-dibromoacetylmesitylene; α-bromoacetylmesitylene was the product formed in the reaction.

The action of the Grignard reagent on α-chloroacetylmesitylene was tried but the original compound was recovered unchanged. On the other hand, α-bromoacetylmesitylene was converted into acetomesitylene by this treatment. The acetomesitylene was identified by converting it into its dinitro derivative, a solid melting at 138–139°.

The case most carefully studied was that of α,3,5-tribromoisobutyrylmesitylene. This ketone was treated with *n*-butylmagnesium bromide, *n*-amylmagnesium chloride, phenylmagnesium bromide and *p*-tolylmagnesium bromide. In all cases the products were 3,5-dibromoisobutyrylmesitylene and the alkyl or aryl bromide corresponding to the Grignard reagent used. The equation is



Analyses of the Grignard solutions used showed alkyl or aryl bromides to be absent, thus indicating that the bromide obtained in each case was a product of the reaction.[8]

[7] Malmgren, *Ber.*, **36**, 2626 (1903); Kohler and Johnstin, *Am. Chem. J.*, **33**, 39 (1905); Kohler, Richtmyer and Hester, THIS JOURNAL, **53**, 207 (1931); Kohler and Erickson, *ibid.*, **53**, 2301 (1931); see also Umnova, *J. Russ., Phys.-Chem. Soc.*, **45**, 881 (1913); Löwenbein and Schuster, *Ann.*, **481**, 106 (1930); and Fisher, Oakwood and Fuson, THIS JOURNAL, **52**, 5036 (1930).

[8] Since this work was finished a similar result has been reported by Kohler and Tishler [THIS JOURNAL, **54**, 1594 (1932)].

Experimental

α,α,α-Tribromoacetylmesitylene (II).—The method of Fuson and Walker[1a] was used to convert the dibromomethyl to the tribromomethyl ketone. One gram of α,α-dibromoacetylmesitylene was mechanically shaken with a dilute solution of sodium hypobromite (15 g. of bromine and 15 g. of sodium hydroxide in 150 cc. of water) for fifty-two hours. The product was filtered, dissolved in hot alcohol and the insoluble material was separated by filtration. The crystals obtained when the solution was cooled were recrystallized from alcohol. The product (amounting to 0.8 g.) melted at 66–68° and was shown to be the known tribromomethyl ketone by the fact that a mixture of the two showed no lowering of the melting point. A mixture of the product and the starting material melted at 50–60°.

α-Bromopropionylmesitylene (VI).[9]—To 85 g. (0.5 mole) of α-bromopropionyl chloride, 60 g. (0.5 mole) of mesitylene, and 340 g. of carbon disulfide contained in a three-necked flask equipped with a reflux condenser and an air-propelled stirrer, and surrounded by an ice–salt mixture, was added 80 g. of aluminum chloride in 10-g. portions at intervals of ten minutes. The stirring was continued for one and one-half hours and the carbon disulfide was then distilled. After the addition of ice and hydrochloric acid, the product was extracted with ether, the ether washed with sodium hydroxide solution, then with water and dried over magnesium sulfate. After removal of the ether the residue was distilled. The fraction which distilled at 169–178° at 31 mm. was redistilled, 70 g. (55.5% of the theoretical) being obtained at 174–176° under the same pressure.

Anal. Calcd. for $C_{12}H_{15}OBr$: Br, 31.4. Found: Br, 31.6.

α-Bromo-3,5-dinitropropionylmesitylene (VII).—A mixture of 20 g. each of concentrated sulfuric acid and nitric acid was added to 5 g. of α-bromopropionylmesitylene. The mixture was kept cold and allowed to stand for fifteen minutes, during which time a solid formed. Water was added, the product filtered, washed with water and dissolved in 100 cc. of hot alcohol. When the solution was allowed to cool, cotton-like needles were formed which, after several recrystallizations from alcohol, melted at 148.5–149°.

Anal. Calcd. for $C_{12}H_{13}O_5N_2Br$: N, 8.1. Found: N, 8.1.

α,α-Dibromo-3,5-dinitropropionylmesitylene (V).—Three grams of propionylmesitylene was brominated with a solution of sodium hypobromite consisting of 300 g. of water, 30 g. of sodium hydroxide and 30 g. of bromine. The viscous oil remaining at the bottom of the flask was extracted with ether. The oil remaining after the removal of the ether was poured slowly into ice-cold, fuming nitric acid, and the nitric acid mixture was then poured into cold water. The solid product was filtered and recrystallized from alcohol. The melting point was 99–99.5°.

Anal. Calcd. for $C_{12}H_{12}O_5N_2Br_2$: N, 6.6. Found: N, 6.6.

α,α-Dibromo-3,5-dinitropropionylmesitylene (V).—(Second Method). Three grams of α-bromopropionylmesitylene was stirred for three days with a solution (300 g. of water, 30 g. of sodium hydroxide and 30 g. of bromine) of sodium hypobromite. The dense, viscous oil which formed was extracted with ether, and the ether solution was dried over magnesium sulfate. The oil remaining after removal of the ether was nitrated with a solution of equal parts of concentrated nitric and sulfuric acids. The solid which precipitated when the nitration mixture was added to water was filtered, washed with water and recrystallized several times from alcohol. The needle-like crystalline material melted at 98–99.5° and was shown by the mixed melting point method to be α,α-dibromo-3,5-dinitropropionylmesitylene.

[9] The preparation and nitration of this compound were carried out by Mr. R. C. Waymire.

α,α-Dibromo-3,5-dinitropropionylmesitylene (V).—(Third Method). α-Bromo-3,5-dinitropropionylmesitylene (0.6 g.) was brominated with a sodium hypobromite solution (150 cc. of water, 15 g. of sodium hydroxide and 15 g. of bromine). After the reaction mixture had been stirred vigorously for thirty-six hours, the melting point of the crude product was 84–104°. The reaction mixture was stirred for four days. After being filtered, washed and recrystallized twice from aqueous alcohol, the product melted at 97–100°. The amount obtained was 0.4 g. After one more recrystallization the melting point was 97–98°. The mixed melting point with α,α-dibromo-3,5-dinitropropionylmesitylene was 98–99°.

α-Bromo-3,5-dinitroisobutyrylmesitylene (XI). (By Bromination with Sodium Hypobromite.)—Three grams of isobutyrylmesitylene was brominated with a solution of sodium hypobromite consisting of 300 g. of water, 30 g. of sodium hydroxide and 30 g. of bromine. The viscous oil remaining at the bottom of the flask was extracted with ether. The oil remaining after the removal of the ether was poured slowly into a mixture of equal parts of concentrated sulfuric and nitric acids. The reaction mixture was then poured into cold water. The solid which precipitated was crystallized once from alcohol. In this way was obtained 3.1 g. of crystals melting at 117–120°. The melting point, 124.5–125.5°, finally obtained after several recrystallizations, was not lowered when the product was mixed with a known sample of α-bromo-3,5-dinitroisobutyrylmesitylene, melting at 125–126°.

α-Bromo-3,5-dinitroisobutyrylmesitylene (XI). (By Bromination of 3,5-Dinitroisobutyrylmesitylene.)—A pyridine solution (1.6 g. of ketone, 20 cc. of pyridine) of the dinitro ketone was added to a hypobromite solution made from 9.5 cc. of bromine, 30 g. of sodium hydroxide and 280 cc. of water, and stirred for thirty-six hours. The solid which was in the bottom of the reaction mixture was filtered and, after several recrystallizations from alcohol, found to melt at 125–126°. The melting point was not lowered when mixed with the product obtained on nitrating the hypobromite bromination product of isobutyrylmesitylene, which melted at 124.5–125.5°.

α,3,5-Tribromoisobutyrylmesitylene (XII).—Thirty grams of bromine was added slowly and with shaking to a cold solution of 30 g. of sodium hydroxide in 250 cc. of water. To this solution was then added 3 g. of 3,5-dibromoisobutyrylmesitylene dissolved in 50 cc. of pyridine. The reaction mixture was stirred vigorously for three hours, after which a small sample of the finely divided solid was removed from the flask and found to melt, without recrystallization, at 96–103°. This indicated that most of the starting material (m. p. 70–71°) had been converted to the desired product (m. p. 106–107°). After being stirred for twenty-four hours longer, the reaction mixture was filtered, and the solid extracted with hot alcohol. The alcohol on cooling deposited 3.5 g. of colorless crystals melting at 104–106°. A mixed melting point with α,3,5-tribromoisobutyrylmesitylene showed no depression.

Di-(β-isoduryloyl)-methane (XIII).—The compound was prepared from mesitylene and malonyl chloride by the method of Béhal and Auger.[10] The yields were variable, amounting in some cases to as much as 70% of the theoretical.

Di-(β-isoduryloyl)-bromomethane (XV). (a) By the Use of Bromine.—A dilute solution of bromine was prepared by adding carbon disulfide to 10 g. of bromine until a volume of 250 cc. was reached. Five grams of di-(β-isoduryloyl)-methane was dissolved in 50 cc. of carbon disulfide and to this solution through a buret 130 cc. of the bromine solution was added slowly and with shaking. The solution remained colorless until about one-third of the bromine solution had been added, after which it developed the reddish color of bromine. After the addition was complete, the solution was warmed and stirred for four hours, the color, however, persisting. The solvent was removed

[10] Béhal and Auger, *Bull. soc. chim.*, [3] **9**, 702 (1893).

by distillation under reduced pressure and the residue was crystallized from alcohol. It formed colorless needles which melted at 163.5–164°.

Anal. Calcd. for $C_{21}H_{23}O_2Br$: Br, 20.6. Found: Br, 20.5.

(b) **By the Use of Sodium Hypobromite.**—Fifteen grams of bromine was dissolved in an ice-cold solution of 15 g. of sodium hydroxide in 150 cc. of water. One gram of finely ground di-(β-isoduryloyl)-methane was placed with this solution in a 250-cc. round-bottomed flask and the mixture was left on a mechanical shaker for ten days. The solid material was filtered and dissolved in alcohol. From this solution there separated on standing a few needle-like, colorless crystals which melted at 161.5–162.5° and which were shown by the mixed melting point method to be identical with the monobromo derivative obtained above.

Di-(β-isoduryloyl)-chloromethane (XIV).—Ten cc. of carbon tetrachloride in a 250-cc. Erlenmeyer flask was cooled to 0° in an ice-bath and saturated with chlorine by passing a slow stream of the gas into the liquid, the temperature being kept at 0°. Twenty cc. of carbon tetrachloride containing 7.7 g. of di-(β-isoduryloyl)-methane was then added to this solution and the flask was kept in the ice-bath for an hour longer. Hydrogen chloride was slowly evolved. The solution was allowed to stand at room temperature for an hour and was boiled for ten minutes. After the solvent was evaporated, the residue was recrystallized several times from alcohol. The monochloro compound melted at 157.5–158°; the yield was 45% of the theoretical.

Anal. Calcd. for $C_{21}H_{23}O_2Cl$: Cl, 10.4. Found: Cl, 10.7.

Di-(β-isoduryloyl)-dibromomethane (XVII).—A sodium hypobromite solution was prepared by using 112.5 g. of sodium hydroxide, 112.5 g. of bromine and 1125 cc. of water. To this solution in a 2-liter flask was added 7.5 g. of finely ground di-(β-isoduryloyl)-methane. After the mixture had been shaken for sixty hours, the solid material was filtered and recrystallized from alcohol. In this way was obtained 7.5 g. of the dibromo compound in the form of thick colorless needles melting at 136–136.5°.

Anal. Calcd. for $C_{21}H_{22}O_2Br_2$: Br, 34.3. Found: Br, 34.0.

Di-(β-isoduryloyl)-dichloromethane (XVI).—A solution of sodium hypochlorite was prepared by passing chlorine into a cold solution of 12.5 g. of sodium hydroxide in 150 cc. of water until the greenish color of free chlorine appeared. Then another 2.5 g. of sodium hydroxide was added. To this solution in a 250-cc. flask was added 2 g. of finely ground di-(β-isoduryolyl)-methane and the mixture was shaken for five days. The solid material was filtered and purified by recrystallization from alcohol. It melted at 104.104.5°; the yield was 83% of the theoretical.

Anal. Calcd. for $C_{21}H_{22}O_2Cl_2$: Cl, 18.8. Found: Cl, 18.6.

The Action of Alkali on α,α,α-Tribromoacetylmesitylene.—Five grams of the tribromo ketone was boiled for a few hours with a large excess of 40% aqueous sodium hydroxide. The reaction mixture was decanted from resinous material and acidified. The acid-insoluble portion yielded 0.2 g. of crystals which were shown by the method of mixed melting points to be β-isodurylic acid.

The Action of Alcoholic Sodium Hydroxide on Di-(β-isoduryloyl)-dibromomethane.—Two grams of finely powdered di-(β-isoduryloyl)-dibromomethane was added to a solution of 25 g. of sodium hydroxide in 20 cc. of water and 30 cc. of methyl alcohol. The resulting solution was heated on a steam cone overnight. Addition of dilute hydrochloric acid precipitated a solid which, after three recrystallizations from alcohol, melted at 160–162°. A mixed melting point showed it to be the monobromo derivative of di-(β-isoduryloyl)-methane. The yield was 41% of the theoretical.

The Action of Alcoholic Sodium Hydroxide on Di-(β-isoduryloyl)-dichloromethane.—Using the above procedure with 2 g. of the dichloro diketone, 1 g. of di-(β-iso-

duryloyl)-chloromethane was obtained. It was identified by a mixed melting point determination with an authentic specimen. The yield was 54% of the theoretical.

The Action of Phenol on α,α,α-Tribromoacetylmesitylene.—Ten grams of α,α,α-tribromoacetylmesitylene and 2.35 g. of phenol were heated together at 100° for three hours. The heavy brown oil which resulted was shaken with 100 cc. of 5% sodium hydroxide solution until a solid formed. This solid when recrystallized from alcohol melted at 69–71° and by means of a mixed melting point determination was identified as α,α-dibromoacetylmesitylene. The yield was 60% of the theoretical.

In a second run a 60% yield of *p*-bromophenol was obtained and identified by the mixed melting point method. However, in this run only a small amount of α,α-dibromoacetylmesitylene was isolated.

The Action of Phenol on Di-(β-isoduryloyl)-dibromomethane.—A mixture of 2.3 g. of the dibromo diketone and 0.5 g. of phenol was heated at 100° for three hours. Extraction with a 10% sodium hydroxide solution left an amorphous residue. This solid after recrystallization from alcohol melted at 160–162° and was identified by a mixed melting point as di-(β-isoduryloyl)-bromomethane. The yield was 47% of the theoretical.

The Action of Grignard Reagents on α-Haloalkyl Mesityl Ketones.—In each case an ether solution of the α-halo ketone was added dropwise from a separatory funnel to the Grignard reagent (1.5 moles) contained in a three-necked flask equipped with a mercury-sealed stirrer and a reflux condenser. Gentle refluxing occurred during the addition, and a colorless, finely-divided solid precipitated. The stirring was continued for an hour after the addition. The Grignard complex was decomposed with dilute hydrochloric acid. The ether layer was washed with a sodium bicarbonate solution and water, and then was dried over magnesium sulfate. The ether was removed either by distillation from a steam cone or by evaporation in a current of air. The isolation of the products is described below.

(a) **Ethylmagnesium Bromide with α,α,α-Tribromoacetylmesitylene.**—Removal of the ether left large, square, crystalline plates. After one crystallization from 85% methyl alcohol there was obtained 5.5 g. (68.7% of the theoretical) of the colorless, crystalline dibromomethyl ketone. A mixture of the product and the starting material melted at 43–55°. The pure product melted at 73–74°.

Anal. Calcd. for $C_{11}H_{12}OBr_2$: Br, 50.0. Found: Br, 49.8.

(b) **Ethylmagnesium Bromide with α,α-Dibromoacetylmesitylene.**—The residue was crystallized from petroleum ether. The crystals which resulted melted at 56–57.5°, and amounted to 2.7 g., or 56.2% of the theoretical. The substance was shown to be α-bromoacetylmesitylene by the mixed melting point method.

(c) **Ethylmagnesium Bromide with α-Bromoacetylmesitylene.**—Nearly all of the residue, a light brown oil, distilled at 79–83° at 2 mm. The yield was 5.3 g., or 65.4% of the theoretical. Part of the product was nitrated with equal parts of cold, concentrated sulfuric and nitric acids. After several recrystallizations from alcohol, the resulting product melted at 137–138.5°. A mixture of an authentic sample of 3,5-dinitroacetylmesitylene (m. p. 138–139°) and the product melted at 138–139°.

(d) **Phenylmagnesium Bromide with α,α,α-Trichloroacetylmesitylene.**—The residue was high-boiling and crystallized in the receiver. After recrystallization from petroleum ether, it melted at 71–72°. An analysis showed it to be α,α-dichloroacetylmesitylene. The yield was 46% of the theoretical.

Anal. Calcd. for $C_{11}H_{12}Cl_2O$: Cl, 30.7. Found: Cl, 30.6.

(e) **Ethylmagnesium Bromide with α-Chloroacetylmesitylene.**—The residue was a colorless, crystalline solid melting at 66–67°. This was found to be α-chloroacetylmesitylene by the mixed melting point method. The compound was almost quantitatively recovered.

(f) ***n*-Butylmagnesium Bromide with α,3,5-Tribromoisobutyrylmesitylene.**—By distillation at atmospheric pressure the residue was separated into two fractions. Redistillation of the low boiling portion yielded 7.9 g. of *n*-butyl bromide (57.6% of the theoretical) boiling at 100–105°. The mercuric bromide of this oil was prepared and found to melt at 129.5–130.5°. The melting point of *n*-butylmercuric bromide is given as 129°.[11]

The residue remaining after the low boiling portion had been distilled from the reaction product was distilled at 3 mm. pressure. Most of it (29.5 g.) came over at 168–176°, and after solidification melted at 62–65°. After recrystallization from methanol there remained 26.5 g. (75% of the theoretical) melting at 69–70.5°. A mixed melting point with 3,5-dibromoisobutyrylmesitylene showed no depression.

(g) ***n*-Amylmagnesium Chloride with α,3,5-Tribromoisobutyrylmesitylene.**—The lower boiling portion of the residue was distilled with a water pump. (The residue of this distillation was saved for subsequent treatment.) The low boiling portion was redistilled at atmospheric pressure. As the first fraction, 7 g. was obtained at 120–130°; the second fraction distilled at 130–165° and amounted to 4.7 g. The second fraction was redistilled, and the portion distilling at 120–130° was added to the corresponding fraction of the first distillation. The total amount obtained at 120–130° was 9.6 g., or 63.5% of the theoretical. This oil was shown to be *n*-amyl bromide by preparing the mercuric bromide derivative, which melted at 123.5–124.5° after several recrystallizations from alcohol. The melting point of *n*-amylmercuric bromide has been given as 122°,[11] and as 127°.[12]

The residue from the water pump distillation was distilled at 3 mm. pressure. Most of it (31 g.) came over at 180–190°, and solidified on cooling. After several recrystallizations from methanol, there remained 28.5 g. (81.8% of the theoretical) which melted at 69.5–70.8°. This substance was shown to be 3,5-dibromoisobutyrylmesitylene by the mixed melting point method.

(h) **Phenylmagnesium Bromide with α,3,5-Tribromoisobutyrylmesitylene.**—The residue, a clear oil, was distilled at 3 mm. pressure. The lower boiling fraction was reserved for a later distillation at atmospheric pressure. The second fraction came over at 175–188°, and solidified on cooling. After several recrystallizations from methanol, there was 22.9 g. (65.8% of the theoretical) melting at 68–69°. By the method of mixed melting points this was shown to be 3,5-dibromoisobutyrylmesitylene.

The lower boiling fraction was redistilled at atmospheric pressure. Between 151 and 160° there was collected 11.3 g. (72% of the theoretical) of a clear liquid. Nitration of 3 cc. of this liquid yielded *p*-nitrobromobenzene, melting at 125–126°, which was identified by the mixed melting point method.

(i) ***p*-Tolylmagnesium Bromide with α,3,5-Tribromoisobutyrylmesitylene.**—The residue was a slightly brown, viscous oil. The solid which appeared on cooling was filtered. The filtrate was distilled at atmospheric pressure. The first fraction (2.3 g.) was obtained near the boiling point of toluene. The boiling temperature then rose rapidly to 178°, and 15.3 g. was obtained from that temperature to 183°. The residue was distilled at 24 mm. pressure, and came over as a solid (22 g.) around 210°.

The solid that had been filtered from the reaction product still contained *p*-bromotoluene. It was washed with ether, and the ether washings distilled at 2 mm. pressure, after the removal of the ether, to obtain the bromotoluene. The first fraction was redistilled at atmospheric pressure, 6.6 g. being obtained at 176–185°. The second fraction, 25.5 g. of a solid, came over at 160–190°.

Each portion of each product was identified. The *p*-bromotoluene was oxidized to

[11] Marvel, Gauerke and Hill, THIS JOURNAL, **47**, 3009 (1925).

[12] Slotta and Jacobi, *J. prakt. Chem.*, **120**, 249 (1929).

p-bromobenzoic acid, and the acid identified by the mixed melting point method. The mixed melting point method was also used to identify the solid product, 3,5-dibromoisobutyrylmesitylene. The total yield of *p*-bromotoluene was 21.9 g., or 68.4% of the theoretical. After a few recrystallizations from methanol, there remained 46.5 g. of the dibromo ketone melting at 69.5–71°, a yield of 71.5%.

Summary

The halogenation of hindered ketones by treatment with solutions of alkali hypohalites has been extended to include methyl, ethyl and isopropyl ketones as well as one 1,3-diketone.

The resulting α-halogen ketones have been described and certain reactions characteristic of the type have been studied.

Cleavage with alkali has been shown to be very difficult to effect. Only in the case of α,α,α-tribromoacetylmesitylene was the cleavage successfully carried out. In some cases the alkali acts as a dehalogenating agent.

It has been shown that these compounds are dehalogenated by treatment with phenol, *p*-halophenols being formed.

Dehalogenation has been effected also by treatment with the Grignard reagent. This reaction involves an interchange of radicals.

URBANA, ILLINOIS

[FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND COMPANY, PAPER NO. 463]

ALKYLATED DIKETOPYRAZOLIDINES AND TETRAKETOPYRAZOPYRAZOLES FROM ALKYLMALONIC ESTERS AND HYDRAZINE

BY ARTHUR W. DOX

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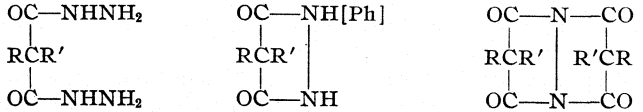
Condensations of alkylmalonic acid derivatives with hydrazines have thus far yielded three types of products.



Type I is the simple dihydrazide resulting from direct condensation between an alkylmalonic ester and hydrazine hydrate. A series of such dihydrazides has recently been prepared by de Graaf.[1]

Type II is represented by the "diethylmalonylhydrazine" which Einhorn and Feibelmann[2] obtained in the condensation of diethylmalonyl chloride with hydrazine; by the diethyl- and dipropyl-1-phenyl-3,5-"pyrazololidone" obtained by Conrad and Zart[3] from the dialkylmalonic esters and

[1] De Graaf, Dissertation, Leiden, 1930.

[2] Einhorn and Feibelmann, *Ann.*, **359**, 186 (1908).

[3] Conrad and Zart, *Ber.*, **39**, 2282 (1906).

phenylhydrazine in the presence of sodium ethoxide; and by the corresponding dimethyl derivative prepared by Michaelis and Schenk[4] from dimethylmalonic acid, *sym.*-acetylphenylhydrazine and phosphorus trichloride. More recently Kaufmann[5] obtained similar derivatives with substituents on both nitrogens by condensing diethylmalonyl chloride with symmetrically disubstituted hydrazines.

Type III represents a condensation between hydrazine and two alkylmalonyl groupings. Obviously only unsubstituted hydrazines, or hydrazines with easily detachable substituents could react in this manner. Two examples of type III have been described, namely, the tetraethyl and tetrapropyl derivatives prepared by Freund and Fleischer[6] by a reaction between the dialkylmalonyl chlorides and benzalsemicarbazone.

It is of interest to note that the two examples of type III contain dialkyl- rather than monoalkyl-malonyl groupings. In type II the dialkylmalonyl derivatives predominate. The only examples of type II with one substitution in the malonyl but none in the hydrazine grouping appear to be the benzyl and *m*-methylbenzyl derivatives described by Curtius.[7]

Experimental

The simplest procedure for effecting the ring condensation is that of Conrad and Zart,[3] which uses the ester of the malonic acid, and sodium ethoxide as the condensing agent. It is obviously an adaptation of the Fischer and Dilthey[8] barbituric acid synthesis. Its chief advantage lies in its use of esters which are much more readily available than acid chlorides. Conrad and Zart did not, however, apply the reaction to esters of monoalkylmalonic acids or to unsubstituted hydrazine.

The writer's interest in this reaction began with an attempt to determine the selectivity between the pyrazolidone and the barbituric acid condensations. Semicarbazide, for example, contains both hydrazine and urea groupings, and when condensed with a malonic ester might yield either a pyrazolidone-N-carboxamide or an isomeric N-aminobarbituric acid. Neither of these substances, however, was obtained. It appears that the semicarbazide first breaks down into biurea and hydrazine, the latter then condensing with the malonic ester.

From ethyl diethylmalonate and semicarbazide hydrochloride with sodium ethoxide in absolute alcohol two products were obtained and easily separated, one soluble and the other insoluble in sodium hydroxide. The first melted at 267° and the second at 263° with evolution of gas. The

[4] Michaelis and Schenk, *Ber.*, **40**, 3568 (1907).
[5] Kaufmann, *Z. angew. Chem.*, **40**, 69 (1927).
[6] Freund and Fleischer, *Ann.*, **379**, 27 (1910).
[7] Curtius, *J. prakt. Chem.*, **94**, 273 (1916).
[8] Fischer and Dilthey, *Ann.*, **333**, 334 (1904).

analyses agreed with values calculated for 4,4-diethyl-3,5-diketopyrazolidine and biurea, respectively.

	C	H	N
Alkali-sol. product: found	53.41	7.70	18.04
$C_7H_{12}O_2N_2$: calcd.	53.85	7.69	17.94
Alkali-insol. product: found	20.05	4.96	47.13
$C_2H_6O_2N_4$ (biurea): calcd.	20.34	5.08	47.46

Since biurea contains two urea groupings which failed to condense with the malonic ester it is apparent that unsubstituted hydrazine is more reactive.

In extending the hydrazine condensation to homologous alkylmalonic esters the interesting observation was made that disubstituted esters invariably yielded pyrazolones of type II, whereas monosubstituted esters invariably gave the double condensation represented by type III. In neither case could the types be interchanged by varying the proportions of the reacting substances. With a stable substituent on the hydrazine, as in phenylhydrazine, a double condensation is obviously precluded.

The following derivatives were prepared from the appropriate malonic esters and hydrazine monohydrochloride, or phenylhydrazine, by heating the mixture with alcoholic sodium ethoxide for five to seven hours in an

TYPE II

3,5-Diketopyrazolidines[9]	M. p., °C.	Formula	Found, % C	H	N	Calculated, % C	H	N
4,4-Diethyl	267	$C_7H_{12}O_2N_2$	54.10	7.89	18.01	53.85	7.69	17.94
4,4-Dipropyl	254	$C_9H_{16}O_2N_2$	58.54	8.75	15.26	58.69	8.70	15.22
4,4-Dibutyl	220	$C_{11}H_{20}O_2N_2$	62.36	9.56	13.40	62.26	9.43	13.21
4,4-Diisoamyl	289–290	$C_{13}H_{24}O_2N_2$	65.17	10.18	11.93	65.00	10.00	11.67
4-Ethyl-4-isoamyl	228	$C_{10}H_{18}O_2N_2$	60.01	9.14	14.32	60.61	9.09	14.14
4-Ethyl-4-hexyl	182	$C_{11}H_{20}O_2N_2$	61.49	9.38	13.05	62.26	9.43	13.21
4-*Sec.*-butyl-4-allyl	186–187	$C_{10}H_{16}O_2N_2$	60.84	7.90	14.31	61.22	8.16	14.29
4-Ethyl-4-phenyl	196–197	$C_{11}H_{12}O_2N_2$	64.66	5.98	13.61	64.70	5.88	13.73
4-Ethyl-1-phenyl	108	$C_{11}H_{12}O_2N_2$	64.02	6.13	13.36	64.70	5.88	13.73
4-*Sec.*-butyl-1-phenyl	94	$C_{13}H_{16}O_2N_2$	66.94	6.97	11.84	67.24	6.90	12.07
4,4-Diethyl-1-phenyl	114	$C_{13}H_{16}O_2N_2$	67.87	6.99	12.23	67.24	6.90	12.07

TYPE III

1,3,5,7-Tetraketopyrazo-[1,2-α] pyrazoles[10]								
2,6-Diethyl	246–247	$C_{10}H_{12}O_4N_2$	52.75	5.46	12.15	53.57	5.36	12.50
2,6-Dipropyl	278	$C_{12}H_{16}O_4N_2$	56.93	6.48	11.11	57.14	6.35	11.11
2,6-Di-*sec.*-butyl	207	$C_{14}H_{20}O_4N_2$	59.33	7.03	10.23	60.00	7.14	10.00

[9] Three of the above Type II pyrazolones have been previously described. Einhorn and Feibelmann[2] prepared the 4,4-diethyl derivative by a different method and report a melting point of 256°. Three different preparations of our product all melted at 267–268° corr. Conrad and Zart[3] prepared the 4,4-diethyl-1-phenyl derivative, m. p. 114–115°, and Michaelis and Schenk [*Ber.*, **41**, 3871 (1908)] the 4-ethyl-1-phenyl derivative, m. p. 105°, by a different method.

[10] The nomenclature of the Type III derivatives was kindly supplied by Dr. Austin M. Patterson.

oil-bath at 100–110°. The condensation product then present as the sodium salt was dissolved in water and precipitated by addition of hydrochloric acid, after shaking the alkaline solution with ether to remove any unreacted ester.

A tentative explanation of the difference in behavior between the monoalkyl- and dialkyl malonic esters is a possible enolization of the intermediate monoalkyldiketopyrazolidine which renders it capable of further reaction to form the pyrazopyrazole. This enolization would consist in a shifting of the 4-hydrogen to an adjacent carbonyl. The dialkyl derivatives, on the other hand, with no labile hydrogen in this position, could enolize only by a lactim–lactam tautomerism by which one of the nitrogens becomes tertiary and incapable of further reaction. The dialkyldiketopyrazolidine should therefore fail to condense with the ester of either a mono- or a dialkylmalonic acid. This was found to be the case.

Diethyldiketopyrazolidine and ethyl ethylmalonate were heated for seven hours at 100–105° with two equivalents of sodium dissolved in absolute alcohol. The clear homogeneous solution was then evaporated and the residue dissolved in water, shaken twice with ether to remove unreacted ester, and acidified. The crystalline product which separated melted at 267–268° and contained 18.03% N; calculated for $C_7H_{12}O_2N_2$, 17.94%; for $C_{12}H_{16}O_4N_2$, 11.11%. It consisted therefore of the original pyrazole and not the pyrazopyrazole derivative. The recovery was 77.4%.

The three pyrazopyrazole derivatives described above contain methylene hydrogens which are readily replaced by bromine. The reaction was performed by dissolving the substance in glacial acetic acid, adding a glacial acetic acid solution of bromine until a permanent yellow color was obtained, and then precipitating the product by addition of **water.**

2,6-Dibromo-1,3,5,7-tetraketo-pyrazo [1,2-α-] pyrazole	M. p., °C.	Formula	Br, % Found	Br, % Calcd.
2,6-Diethyl	171–173	$C_{10}H_{10}O_4N_2Br_2$	41.49	41.88
2,6-Dipropyl	138	$C_{12}H_{14}O_4N_2Br_2$	39.03	39.02
2,6-Di-*sec.*-butyl	111	$C_{14}H_{18}O_4N_2Br_2$	36.38	36.52

The alkyldiketopyrazolidines (Type II) are isomeric with the hydantoins, representing merely a transposition of one CONH grouping. They represent also the corresponding barbituric acids after removal of the urea carbonyl. Of special interest is the ethylphenyl derivative, which is Luminal without the urea carbonyl, and Nirvanol[11] transposed. Both of these drugs are potent hypnotics. Moreover, the pyrazoline structure suggests the possibility of antipyretic properties. Tests made by Dr. O. M. Gruhzit of this Laboratory showed some antipyretic properties, but the entire absence of hypnotic action. The pharmacological data will be published elsewhere.

[11] German Patent 309,508 (1918); Wernicke, *Deut. med. Wochschr.*, **42**, 1193 (1916).

Incidentally, the ethyl ethylphenylmalonate used in this preparation was obtained from a commercial source and contained some ethyl ethylphenylacetate. This accounts for a by-product obtained in the hydrazine condensation and readily separated by its insolubility in alkali. It melted at 218–219°.

Anal. Calcd. for $C_{20}H_{24}O_2N_2$: C, 74.07; H, 7.41; N, 8.64. Found [di-(ethylphenylacetyl) hydrazine]: C, 74.24; H, 7.36; N, 8.97.

Summary

A series of 4,4-dialkyl-3,5-diketopyrazolidines and of 2,6-dialkyl-1,3,5-7-tetraketopyrazo-[1,2-α]-pyrazoles has been prepared by condensing esters of alkylmalonic acids with hydrazine in the presence of sodium ethoxide.

The esters of dialkylmalonic acids yield the monocyclic pyrazolones, whereas those of monoalkylmalonic acids yield the dicyclic pyrazo-[1,2-α]-pyrazole derivatives.

DETROIT, MICHIGAN

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE CLEAVAGE OF ALPHA-DIACYL AND OF ALPHA-MONOACYL BETA-KETO DERIVATIVES OF DIETHYL SUCCINATE, GLUTARATE AND ADIPATE

BY ROBERT NEVILL ISBELL, BRUNO WOJCIK AND HOMER ADKINS

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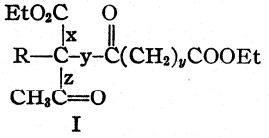
It has been noted[1] in the hydrolysis of 1,3-diketones and β-keto esters of the types shown in formulas I and II, that cleavage and decarboxylation occurred in such a way as to produce more of the ketone RCH_2COCH_3 than of the keto acid $RCH_2CO(CH_2)_yCOOH$, from compounds of type I, and more of the keto acid $CH_3COCH_2(CH_2)_yCOOH$ than of $RCOCH_2(CH_2)_yCOOH$ from compounds of type II. That is to say, the removal of the acetyl group occurred to a less extent from compounds of type I, and to a greater extent from compounds of type II, than is desirable from the standpoint of the synthesis from acetoacetic ester of high molecular weight keto acids.



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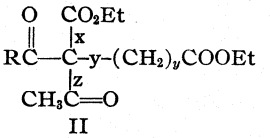


II

It may clarify the ensuing discussion if it is pointed out that compounds of these two types may upon hydrolysis cleave at three points

[1] G. M. Robinson and R. Robinson, *J. Chem. Soc.*, 175 (1925); G. M. Robinson, *ibid.*, 745 (1930).

in the molecule as indicated by "x," "y" and "z." The "x" linkages are stable toward ethanol so that alcoholysis occurs at only "y" or "z." The "x" linkage is labile toward hydrolysis and is cleaved along with either "y" or "z." Thus there may be produced either by alcoholysis or hydrolysis two sets of products depending upon whether "y" or "z" is the more reactive linkage.

It has been observed in this Laboratory[2] that the ratio of the two possible sets of products obtained in the cleavage of unsymmetrical 1,3-diketones is dependent upon the environment during cleavage as well as upon the structure of the diketones. It therefore seemed desirable to apply to the compounds of types I and II the following methods of cleavage: (1) alcoholysis at 60° and under one atmosphere pressure using hydrogen chloride as a catalyst; (2) alcoholysis at 150–250°, under 100 atmospheres, using traces of water or aluminum ethoxide as catalysts; (3) hydrolysis at 150–250° under 100 atmospheres.

For this purpose two compounds of type I, *i. e.*, diethyl α-*n*-butyl-α-acetyl-β-keto-adipate (R=C_4H_9, *y*=2) and diethyl α-*n*-lauryl-α-acetyl-β-keto-adipate (R=$C_{12}H_{25}$, *y*=2) and five compounds of type II, *i. e.*, diethyl α-benzoyl-α-acetyl-succinate (R=C_6H_5, *y*=1), diethyl α-benzoyl-α-acetylglutarate (R=C_6H_5, *y*=2), diethyl α-*n*-butyryl-α-acetylsuccinate (R=C_3H_7, *y*=1), diethyl α-*n*-butyryl-α-acetylglutarate (R=C_3H_7, *y*=2) and diethyl α-trimethylacetyl-α-acetylglutarate (R=*tert.*-C_4H_7, *y*=2) have been subjected to various conditions inducing cleavage. In addition the alcoholysis of diethyl α-acetylsuccinate and glutarate was studied in order to ascertain the behavior on cleavage of these monoacyl esters which might be intermediate products of the diacylsuccinic and glutaric esters of type II.

Alcoholysis of Keto Esters in Presence of Hydrogen Chloride.—There are recorded in Table I representative data obtained in subjecting α-acetylsuccinic and glutaric, α-acetyl-α-butyrylsuccinic and glutaric and α-acetyltrimethylacetylglutaric esters to alcoholysis at 60° in the presence of hydrogen chloride. The procedures were essentially the same as those previously described.[3] In brief the data show that the acetylglutaric and especially the succinic esters are rather inactive toward ethanol at 60° even in the presence of a high concentration of hydrogen chloride. (It may be recalled that acetoacetic ester itself is not cleaved at all under these conditions.) The diacylsuccinic and glutaric esters undergo more than 80% alcoholysis under these same conditions, the ratio of cleavage being such that in the case of the succinate the ratio of acetyl to butyryl cleavage is approximately 1 to 2 while with the glutarate it is about 1 to 4. The acetyltrimethylacetylglutaric ester is much more resistant to alcoholysis

[2] Connor and Adkins, THIS JOURNAL, **54**, 3420 (1932).

[3] Kutz and Adkins, *ibid.*, **52**, 4036 (1930).

TABLE I

ALCOHOLYSIS OF KETO ESTERS IN PRESENCE OF HYDROGEN CHLORIDE[a]

Diethyl ester of	Millimoles Ester	Millimoles HCl	Cleavage Acetyl	Cleavage % total
α-Acetylsuccinate	10	25	..	11
α-Acetylsuccinate	10	50	..	9
α-Acetylglutarate	6.5	25	..	19
α-Acetylglutarate	6.5	50	..	20
α-Acetyl-α-butyrylsuccinate	10	12	35	83
α-Acetyl-α-butyrylsuccinate	10	25	35	85
α-Acetyl-α-butyrylglutarate	5	50	16	83
α-Acetyl-α-butyrylglutarate	5	12	21	83
α-Acetyl-α-trimethylacetylglutarate	5	25	31	46

[a] Temperature 60°, time 96–120 hours, 435 millimoles of ethanol. An extensive study had shown that if the ratio of hydrogen chloride to ester was lower than indicated in the table, alcoholysis was slow and incomplete. Higher ratios of catalyst did not facilitate the reaction. If the temperature was as high as 68°, ethyl chloride was formed and no advantages were secured.

than the diacyl ester having only normal chains while the ratio of cleavage products is correspondingly more favorable to acetyl cleavage. That is to say, the amount of acetyl cleavage in a given length of time is approximately the same (14 to 17%) for acetyltrimethylacetylglutaric as it is or acetylbutyrylglutaric ester while the non-acetyl cleavage is much less for the trimethylacetyl (35%) than for the butyryl (66%).

Alcoholysis at 150–200°.—There is recorded in Table II a summary of the data obtained in subjecting four acyl substituted succinic and glutaric esters to the action of ethanol at 150–250° under a pressure of approximately 100 atmospheres. The procedure was essentially the same as that described.[2]

The data show that diethyl α-acetylsuccinic ester is quite stable at 150° in the presence of ethanol dried over aluminum ethoxide, and that it is cleaved to the extent of only 11% with ethanol dried over lime only. Aluminum ethoxide is a catalyst for the alcoholysis of this β-keto ester as has been previously observed for the simple 1,3-diketones. Diethyl α-acetyl-α-*n*-butyrylglutarate was considerably more resistant to alcoholysis than was the corresponding succinate as shown by the fact that under similar conditions the former was cleaved to the extent of only 11% while the latter showed 56% alcoholysis, the extent of cleavage being measured by the amount of ethyl acetate (determined as acetic acid) produced by alcoholysis.

The diacylsuccinic and glutaric esters, since they are 1,3-diketones as well as β-keto esters, are cleaved more rapidly and at a lower temperature than are the monoacyl esters. This is indicated by the fact that alcohol dried with aluminum ethoxide brought about 91% alcoholysis of acetylbutyrylsuccinic ester within ten hours, while under the same conditions

the monoacetylsuccinic ester was cleaved to the extent of only 4%. The ratio of cleavage of acetyl to butyryl cleavage was approximately 2 to 3. The diacylsuccinate is more rapidly cleaved than is the glutarate. The proportion of acetyl cleavage for the glutarate is lower, being approximately 1 to 4.

TABLE II

ALCOHOLYSIS AND HYDROLYSIS OF KETO ESTERS AT 100 ATMOSPHERES PRESSURE

Diethyl ester of	Millimoles Ester	Millimoles Reagent	Reagent	Temp., °C.	Cleavage Acetyl m.moles	Cleavage %	Cleavage Total
α-Acetylsuccinate	40	200	EtOH[a]	200	..	..	56[d]
α-Acetylsuccinate	40	200	EtOH[a]	150	..	..	11[d]
α-Acetylsuccinate	40	200	EtOH[b]	150	..	..	74[d]
α-Acetylsuccinate	40	200	EtOH[c]	150	..	..	4[d]
α-Acetylglutarate	40	200	EtOH[a]	200	..	..	11[d]
α-Acetyl-α-butyrylsuccinate	40	200	EtOH[c]	150	..	56	58[d]
α-Acetyl-α-butyrylsuccinate	100	1400	EtOH[c]	150	..	41	91[d]
α-Acetyl-α-butyrylsuccinate	100	1000	H_2O	150	25.0[f]	..	[e]
α-Acetyl-α-butyrylsuccinate	200	3447	H_2O	150	50.0[f]	..	[e]
α-Acetyl-α-butyrylglutarate	100	500	EtOH[a]	150	..	20	41[d]
α-Acetyl-α-butyrylglutarate	100	1000	H_2O	200	0	..	[e]
α-Acetyl-α-butyrylglutarate	100	1217	H_2O	200	1	..	[e]
α-Acetyl-α-trimethylacetylglutarate	94	940	H_2O	200	1	..	[e]

[a] Ethanol dried over lime. [b] Ethanol contained 4.3 millimoles of $Al(OC_2H_5)_3$ per 100 millimoles of ethanol. [c] Ethanol dried over aluminum ethoxide. [d] Ten hours. [e] 26 to 39 hours. [f] The ratio of acetyl to butyryl cleavage on the basis of the ratio of acetic to butyric acid obtained indicated that the acetyl cleavage was 39–40% of the total.

Hydrolysis of Esters at 150–200°.—There is also recorded in Table II a summary of the data obtained as the result of subjecting α-acetyl-α-butyrylsuccinic, α-acetyl-α-butyrylglutaric and α-acetyl-α-trimethylacetylglutaric esters to hydrolysis at 150–200°. The hydrolysis of diacylsuccinic and glutaric esters differs in two respects from their alcoholysis. Decarboxylation as well as hydrolysis occurs and there is produced a mixture of four acids and their esters.

Decarboxylation is complete after eight or ten hours and probably within a very much shorter time. This is shown by the fact that at the end of the first period of hydrolysis (eight to ten hours) the pressure was approximately fifteen atmospheres higher than before the hydrolysis, while in subsequent periods there was no such increase in pressure. Furthermore, there is a weight loss observed after the first period of hydrolysis which corresponds to the loss of one molecule of carbon dioxide by one molecule of the diacyl ester. For example, the weight loss in runs which did not involve decarboxylation were of the order of 0.9 g., while the losses in three runs in which decarboxylation did occur were 4.94, 4.69, 5.60, respectively. The difference between the average of these values and the normal weight

loss is close to the weight of carbon dioxide (4.4 g.) which should have been produced.

The greater number and higher boiling points of some of the components of the hydrolysis mixture (as compared with the mixture from alcoholysis) made it impossible to obtain as accurate an evaluation of the ratio of volatile acids produced as has been hitherto possible. It is, of course,

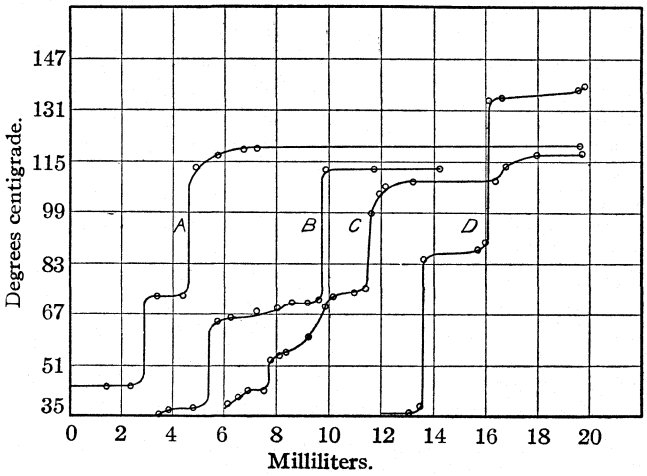


Fig. 1.—Distillation curves of products of hydrolysis (A, B and C at 3–4 mm., D at 14–15 mm.). A. Diethyl α-acetyl-α-butyrylglutarate: butyric acid, 41°, neut. equiv. 89, calcd. 88; ethyl Δ-ketohexanoate 73°, sapon. equiv. 149, calcd. 158; Δ-ketohexanoic acid, 120°, neut. equiv. 133, calcd. 130. B. Diethyl α-acetyl-α-trimethylacetylglutarate: trimethylacetic acid, 38°, (solid) neut. equiv. 105, calcd. 102; ethyl Δ-ketohexanoate, 72°, sapon. equiv. 156; Δ-ketohexanoic acid, 113°, neut. equiv. 134. C. Diethyl α-acetyl-α-butyrylsuccinate: butyric, γ-ketovaleric, γ-ketoheptanoic and the esters of the two latter were present but no clear cut separations were obtained. D. Diethyl α-acetyl-α-butyrylsuccinate (hydrolysis product saponified and dry acids obtained before fractionation): acetic, 36°, butyric, 87°, γ-ketovaleric, 136°, neut. equiv. 119, calcd. 116; γ-ketoheptanoic 150°, m. p. 43–45° (m. p. 46–47°) Bouveault and Bongert, *Bull. soc. chim.*, [3] **27**, 1088 (1902).

feasible to distil out the acetic acid and ethyl acetate produced, but it was not found possible to distil all the butyric acid out of the hydrolysis mixture, after it had been made up to standard volume with ethanol in the standard procedure. However, the analytical results obtained show very clearly the differences in the behavior of the three diacyl esters under consideration.

Diethyl α-acetyl-α-butyrylsuccinate cleaved so that the amount of

the acetyl cleavage was between 25 and 40% of the total cleavage. The two diacylglutarates gave little, if any, acetyl cleavage and in the case of acetyl-*n*-butyryl ester there was *no trace* of acetic acid formed.

The conclusions based on distillation and partition of the acids are amply supported by the results obtained through the distillation of the residual higher boiling portion of the hydrolysis product. The distillation curves of these products are given in Fig. 1. For example, from acetylbutyrylglutaric ester there were obtained about 3 g. of butyric acid, about 2 g. of Δ-keto-hexanoic acid and about 14 g. of its ethyl ester. Similarly the distillation of the hydrolysis product from α-acetyl-α-trimethylacetylglutaric ester gave a small amount of trimethylacetic acid and the remainder was Δ-keto-hexanoic acid and its ethyl ester. (The greater portion of the butyric and trimethylacetic acids had been previously distilled out of the hydrolysis product in subjecting it to the standard procedure for the determination of the amount and ratio of volatile acids.)

The distillation of the higher boiling products from the hydrolysis of acetylbutyrylsuccinic ester did not give as clear cut results as has been noted above for the glutaric esters. This is true because both γ-ketovaleric (levulinic) acid and ester and γ-keto-heptanoic acid and ester were produced. However, the largest fraction was that containing γ-ketovaleric acid and its ester as would be expected upon the basis of the fact that the butyryl predominated over the acetyl cleavage. The relative ratio of these two cleavages is further evidenced by the distillation curve for the acids obtained after saponification of the mixture of esters. There were obtained 3.4 g. of γ-ketovaleric and 2.4 g. of γ-keto-heptanoic. The ratio of acetic and butyric acids obtained is not significant since the loss of the more water-soluble acids is greater.

TABLE III

HYDROLYSIS OF CERTAIN KETO ESTERS (25 HRS., 100 ATM., AT 200°)

Name of ester	Ester, g.	Water, g.	Yield of products
Diethyl α-acetyl-α-benzoylsuccinate	13	7.3	β-Benzoylpropionic acid 69%; acetic acid 64%; benzoic acid 31%
Diethyl α-acetyl-α-benzoylglutarate	16.7	7.2	β-Benzoylbutyric acid 79%; acetic acid 80%; benzoic acid 21%
Diethyl α-acetyl-α-*n*-butyl-β-keto-adipate	28.2	18.0	γ-Keto-nonanoic acid 18%; acetic acid 45%; heptanone-2 59%
Diethyl α-acetyl-α-*n*-lauryl-β-keto-adipate	10.6	4.6	γ-Keto-margaric acid 33%; acetic acid 30%; tridecanone-2 66%

There is given in Table III a summary of the yields of products obtained from the hydrolysis of a diacylsuccinate and glutarate, and from two acyl alkyl keto adipates. These data show that the acetyl cleavage greatly predominated over the benzoyl cleavage for the succinate and the

glutarate. In the case of the substituted adipates the formation of succinic acid predominated over that of acetic acid. For the butyl derivative the cleavage at the "z" linkage of formula 1 was in the ratio of 3 to 4 at the "y" linkage, while for the lauryl derivative the cleavage at "z" was less than 1 as compared to 2 at the "y" linkage. The figures just given for the butyl derivative would lead one to expect somewhat greater yields of the keto nonanoic acid than was obtained. However, the yield of keto-margaric acid was in good agreement with the cleavage of the "y" linkage as measured by the yield of tridecanone-1.

Experimental Part

The procedure followed in working up the products of the hydrolyses referred to in Table III was as follows. The reaction product from the succinate was refluxed for one hour with 100 ml. of a 1.37 *N* solution of sodium hydroxide. The mixture was cooled and acidified with 92 ml. of a 1.52 *N* sulfuric acid solution. The resulting crystals of benzoic and β-benzoylpropionic acid were filtered off after the mixture had been cooled in an ice–salt mixture. The crystals were washed with ice cold water, and after drying weighed 6.5 g. A titration in alcohol of a sample of this mixture of solid acids gave a value of 160.5 for the average molecular weight. This corresponds to a mixture of 31.3% benzoic and 68.7% β-benzoylpropionic acid. The mixture of acetic and levulinic acids which remained in solution when the solid acids were precipitated was fractionated from a modified Claisen flask until 175 ml. of distillate was obtained. Seventy-five ml. of water was then added to the residue and distilled out. The combined distillates were then made up to 250 ml. and an aliquot titrated. The amount of acetic acid found was 0.026 mole, which corresponds to a yield of 64%.

The hydrolysis product from the glutarate was treated in the same manner as that from the succinate. There was obtained 8.9 g. of solid acids, neutral equivalent 177, which corresponds with 21.4% benzoic acid and 78.6% β-benzoylbutyric acid. The yield of acetic acid (0.04 mole) was 80% of the theoretical amount. The hydrolysis product from diethyl α-acetyl-α-*n*-butyl-β-keto-adipate was saponified as in the case of the succinate and glutarate. The ketone was extracted with ether, the solution dried over sodium sulfate. Fractionation of the material gave 6.4 g. of heptanone-2, b. p. 143–146 (740 mm.). The aqueous solution of the salts of the acids was then concentrated to one-half its volume and acidified, and, after cooling, the 8.2 g. of solid acids was filtered off. The mixture of succinic and γ-keto-nonanoic acids was then shaken in 25 ml. of ether. The succinic acid is insoluble in ether and 5.2 g. was obtained. γ-Ketononanoic acid (2.8 g.), m. p. 69–69.5°, was obtained from the ether solution. The neutral equivalent was found to be 172.5; the calculated is 172.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.79; H, 9.30. Found: C, 62.88; H, 9.21.

The amount of acetic acid found by distillation was 44.7% of the theoretical.

The hydrolysis products from diethyl α-acetyl-α-lauryl-β-keto-adipate were worked up in a similar fashion. Tridecanone-2 (3.7 g.), m. p. 39–40°, γ-keto-margaric acid (2.3 g.), m. p. 97–98° and 0.4 g. of acetic acid were obtained. The neutral equivalent of the γ-keto-margaric acid was found to be 288, calcd. 284.

Anal. Calcd. for $C_{17}H_{32}O_3$; C, 71.83; H, 11.26. Found: C, 72.02; H, 11.18.

Certain data and information in regard to the preparation of the reagents used in the experiments on alcoholysis and hydrolysis are given in Table IV and in the footnotes to Table IV.

TABLE IV

PREPARATIONS OF REAGENTS

Products and methods	Yield g.	Yield %	Reactants	g.		g.	d_{25}^{25}	n_D^{25}	Boiling range °C.	Mm.	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found	
Diethyl α-acetylsuccinate[a]	173	62	Acetoacetic ester	130	Ethyl chloroacetate[i]	122			121–123	4–5						
Diethyl α-acetylglutarate[a]	120	52	Acetoacetic ester	130	Ethyl β-bromopropionate[f]	181			132–134	3–4						
Ethyl α-benzoyl-α-acetylacetate[b]	118	67	Acetoacetic ester	100	Benzoyl chloride	109			165–167	10						
Diethyl α-acetyl-α-butyrylsuccinate[c]	30	53	Diethyl α-acetylsuccinate	43.2	*n*-Butyryl chloride	21.3	1.0793	1.4460	184–150	4	58.77	58.22	58.07	7.75	7.69	7.70
Diethyl α-acetyl-α-benzoylsuccinate[d]	89	55	Diethyl α-acetylsuccinate	108	Benzoyl chloride	70	1.145	1.5021	178–182	1	63.73	63.69	63.41	6.27	6.35	6.30
Diethyl α-acetyl-α-benzoylsuccinate[d]	44	54	Ethyl α-acetyl-α-benzoylacetate	58	Ethyl chloroacetate	31			180–184	1–2						
Diethyl α-acetyl-α-benzoylglutarate[d]	95	57	Diethyl α-acetylglutarate	115	Benzoyl chloride	70	1.1426	1.4990	184–187	1	64.69	64.75	64.85	6.59	6.73	6.76
Diethyl α-acetyl-α-*n*-butyrylglutarate[e]	31	52	Diethyl α-acetylglutarate	46	*n*-Butyryl chloride	22	1.0621	1.4420	156–159	3	59.96	59.76	59.67	8.05	8.11	8.10
Diethyl α-acetyl-α-trimethylacetylsuccinate[c]	20	30	Diethyl α-acetylsuccinate		Trimethylacetyl chloride		1.0533	1.4478	143–146	4–5	59.96	59.64		8.05	7.99	7.97
Diethyl α-acetyl-α-trimethylacetylglutarate[e]	21	33	Diethyl α-acetylglutarate		Trimethylacetyl chloride		1.0502	1.4506	148–153	4–5	61.11	60.70	60.81	8.34	8.26	8.31
Diethyl α-acetyl-α-*n*-butyl-β-keto-adipate[d]	68	48	Ethyl *n*-butylacetoacetate[h]	94	β-Carbethoxypropionyl chloride[g]	77	1.0539	1.4501	147–150	1	61.14	60.93		8.25	8.29	
Diethyl α-acetyl-α-*n*-lauryl-β-keto-adipate[d]	28	39	Ethyl *n*-laurylacetoacetate[h]	46	β-Carbethoxypropionyl chloride	20	0.9810	1.4515	234–239	1	67.60	67.83	67.62	9.86	9.88	9.89

[a] Sodium (23 g.) was slowly added to 400 ml. of anhydrous alcohol, contained in a 3-necked, 3-liter flask fitted with a dropping funnel, a reflux condenser and a stirrer. The reaction mixture was heated on a steam-bath to complete the reaction. One hundred and thirty grams of acetoacetic ester was then slowly added followed by 122.5 g. of ethyl chloroacetate (or the equivalent amount of ethyl β-bromopropionate). The reaction mixture was then refluxed for four hours after the addition of the ester, the mixture cooled, centrifuged, the salt layer washed with alcohol and again centrifuged. The alcohol was removed by fractionation from a modified Claisen flask, and the esters carefully fractionated at 4–5 mm. through a Widmer column having a glass spiral 20 mm. in length.

[b] Claisen's[4] procedure apparently gave a better product than did that of Shriner and Schmidt,[5] when the temperature of the reaction mixture was kept below 10° as recommended by Claisen.

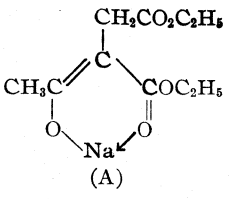
[4] Claisen, *Ann.*, **291**, 67 (1896).

[5] Shriner and Schmidt, THIS JOURNAL, **51**, 3637 (1929).

[c] Sodium (4.6 g.) was powdered under xylene, thoroughly washed with ether, suspended in 240 ml. of ether, and 43.2 g. of ethyl α-acetylsuccinate (or an equivalent amount of the acylglutarate or alkyl acetoacetic ester) slowly added from a dropping funnel while the reaction mixture refluxed. *n*-Butyryl chloride (21.3 g.) (or an equivalent amount of another acid chloride) was slowly added to the rapidly stirred and gently refluxing mixture. The reaction mixture was then allowed to cool to room temperature and to stand with stirring for ten hours. It was then heated on a steam-bath, stirred and refluxed overnight. The salt was removed by centrifuging, the ether by distillation, and the esters were fractionated through a Widmer column.

[d] This ester was made by essentially the same procedure as has been described in (*c*) except that the distillation of the product was made at 1 mm. from a Wood's metal bath kept at 205–220°. Bumping was prevented by the use of capillary tubes sealed off at the upper end, since it is very important that no air be allowed to enter the distillation flask.

[e] This ester was prepared by the same procedure as described in (*c*) and (*d*) except that it was necessary (due to the insolubility in ether of the sodium derivative) to stir the α-acylglutarate for ten hours with sodium in order to complete the reaction. The sodium derivative of diethyl α-acetylsuccinate is soluble in ether while that of the corresponding glutarate is insoluble in ether. This means, according to Sidgwick's views on the sodium derivative of 1,3-diketones, that the sodium derivative of the succinate is in ether, a covalent chelate compound of formula (A), while the glutarate is a simple salt.[6]



(A)

[f] "Organic Syntheses," John Wiley and Sons, New York, 1923, Vol. III, p. 51.

[g] Blaise, *Bull. soc. chim.*, [3] **21**, 641 (1899).

[h] "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 36.

[i] Conrad, *Ann.*, **188**, 217 (1877), 556 g. of ester was obtained from 600 g. of acid.

Summary

This study of the ratio of cleavage products in the alcoholysis and hydrolysis of five α,α-diacylsuccinic and glutaric esters, and of two α-acetyl-α-alkyl-β-keto-adipic esters has brought to light a number of facts with regard to the relative stability and mode of cleavage of these compounds. However, the number of compounds studied is too few to more than indicate the complexity of the factors which determine the ratio of cleavage products. It is clear, however, that the ratio of products from these compounds is not determined by the relative acidity of the acids produced by cleavage. This is shown by the fact that the ratio of acetic to benzoic acid was 2 to 1 for the hydrolysis of acetylbenzoylsuccinic ester and 4 to 1 for the corresponding glutaric ester. Similarly, the ratio of acetic acid to butyric acid was approximately 2 to 5 for acetylbutyrylsuccinic ester while from acetylbutyrylglutaric ester no acetic acid was produced. The effect of the size of the alkyl group is also pronounced as is evidenced by the fact that the acetyl cleavage was only two-thirds as much in α-lauryl-α-acetyl-β-keto-adipic ester as it was in the corresponding

[6] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929, p. 145–151; Sidgwick and Brewer, *J. Chem. Soc.*, **127**, 2379 (1925).

butyl compound. A number of conclusions previously arrived at with regard to the cleavage of simple 1,3-diketones have been found also to hold for these more complex 1,3-diketones which are also β-keto esters.

MADISON, WISCONSIN

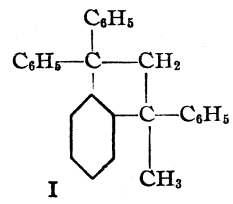
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ABSORPTION SPECTRUM OF METHYLDIPHENYLCHLOROMETHANE PLUS STANNIC CHLORIDE. THE PREPARATION OF 9,10-DIPHENYLPHENANTHRENE FROM TETRAPHENYLETHYLENE DICHLORIDE[1]

BY C. S. SCHOEPFLE AND J. D. RYAN

RECEIVED MAY 12, 1932 PUBLISHED SEPTEMBER 5, 1932

In an earlier communication[2] it was shown that 1,1,3-triphenyl-3-methylhydrindene (I) is obtained in practically quantitative yield by adding anhydrous stannic chloride to a benzene solution of methyldiphenylchloromethane at room temperature. It was also shown that the reaction is a general one and can be used with other alkylarylmethyl halides and that other reagents such as antimony pentachloride, aluminum chloride, etc., can replace the stannic chloride. The reaction mechanism which was suggested postulated the formation of a quinonoid salt as an intermediate step, and in support of this assumption it was noted that the reaction is always accompanied by a transitory color and that the reagents used are those which are known to produce quinoidation of the triarylmethyl halides.



I

Preliminary absorption spectra measurements in the visible region failed to establish the identity of the intermediate colored compound or compounds since the point of maximum absorption was found to lie beyond the range of the visual apparatus. Spectrographic measurements of the absorption in the ultraviolet region have now been made which confirm the existence of a quinonoid modification of methyldiphenylchloromethane in the reaction mixture.

The quantitative absorption curves for methyldiphenylcarbinol, methyldiphenylchloromethane and asymmetrical diphenylethylene are shown in Fig. 1. (The curve for diphenylethylene was determined inasmuch as this compound is readily formed by loss of hydrogen chloride from methyldiphenylchloromethane.) The curves for the carbinol and the chloride

[1] This paper represents the second part of a dissertation submitted to the Graduate School by Mr. Ryan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Schoepfle and Ryan, THIS JOURNAL, **52**, 4021 (1930).

show a marked similarity to those of triphenylcarbinol and triphenylchloromethane.[3]

An absolute quantitative curve could not be obtained in the case of the methyldiphenylchloromethane–stannic chloride mixture, due to the fact that the concentration of the chloride drops and other compounds are formed as the reaction proceeds. However, the absorption of the solution in ethylene chloride was measured directly after adding the stannic chloride and the resulting curve is shown in Fig. 2 (Curve 1). This curve is entirely different from that of the chloride in the absence of stannic chloride, but is very similar in some respects to the quantitative absorption curves for the triphenylchloromethane–stannic chloride addition compound (Curve 2) and for triphenylmethyl acid sulfate (Curve 3). (The absorption curve of the latter compound has been determined by Anderson[4] and is inserted here to facilitate comparison.) Since the quinonoid character of triphenylmethyl acid sulfate has been established,[4,5] it follows from a comparison of the three curves that the band in Curve 1 with maximum frequency 2300 mm.$^{-1}$ is due to a quinonoid addition compound of methyldiphenylchloromethane.

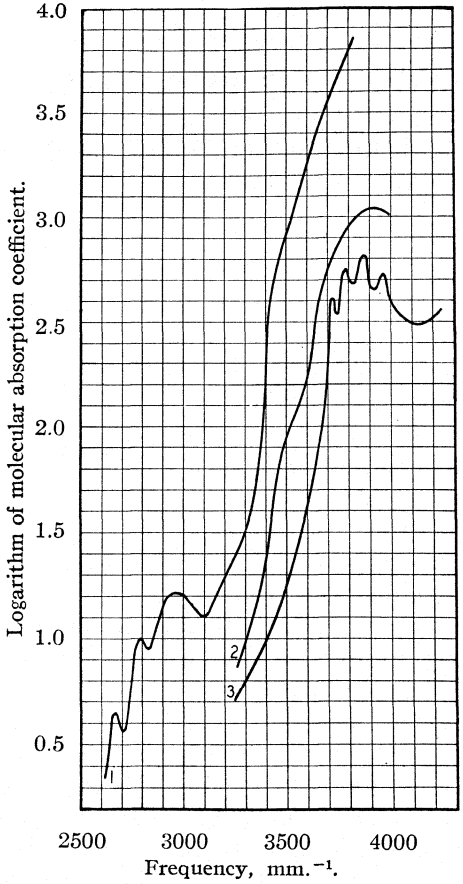


Fig. 1.—Curve 1, asymmetrical diphenylethylene in ether; Curve 2, methyldiphenylchloromethane in petroleum ether; Curve 3, methyldiphenylcarbinol in ether.

The solution of methyldiphenylchloromethane and stannic chloride is at first red in color but after standing a short time the color changes to a greenish-red due to an increase

[3] Anderson, THIS JOURNAL, **50**, 208 (1928).

[4] Anderson, *ibid.*, **52**, 4567 (1930).

[5] (a) Gomberg, *Ber.*, **40**, 1853 (1907); (b) Gomberg and Blicke, THIS JOURNAL, **45**, 1770 (1923).

in intensity of the absorption band with maximum frequency 1660 mm.$^{-1}$. A benzene solution of asymmetrical diphenylethylene and stannic chloride develops a pure green color and shows an absorption band at approximately this same frequency. It is possible that this band is due to the presence of a quinonoid form of 1,1,3,3-tetraphenyl-1-chlorobutane which may result from the addition of hydrogen chloride to 1,1,3,3-tetraphenyl-1-butene, inasmuch as diphenylethylene is known to polymerize in the presence of stannic chloride to give the latter compound. Attempts to prepare 1,1,3,3-tetraphenyl-1-chlorobutane from the corresponding butanol were unsuccessful, the butene being obtained instead.

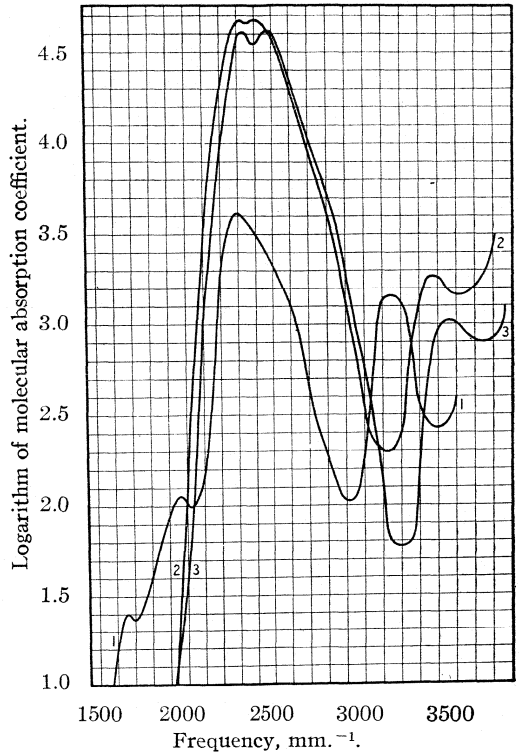


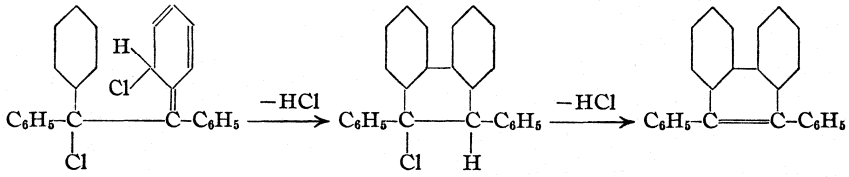
Fig. 2.—Curve 1, methyldiphenylchloromethane plus stannic chloride in ethylene chloride; Curve 2, triphenylchloromethane plus stannic chloride in ethylene chloride; Curve 3, triphenylmethyl acid sulfate in sulfuric acid (95%).

Bergmann and co-workers[6] have shown that compounds similar to 1,1,3,3-tetraphenyl-1-chlorobutane in the presence of stannic chloride split off a molecule of acid with ring closure to give hydrindene derivatives. Since the absorption measurements of the methyldiphenylchloromethane–stannic chloride mixture indicate the possibility that a quinonoid form of 1,1,3,3-tetraphenyl-1-chlorobutane may be present in addition to the quinonoid form of methyldiphenylchloromethane, no definite conclusion can be drawn from these measurements as to which of the two chlorides is the intermediate product in the formation of triphenylmethylhydrindene.

Attention was called in the previous paper[2] to the striking resemblances to be found in comparing the preparation of hydrindene derivatives from alkylarylchloromethanes and the preparation of fluorene derivatives from triarylchloromethanes. Another reaction analogous to these is the prepa-

[6] Bergmann, Taubadel and Weiss, *Ber.*, **64**, 1493 (1931).

ration of 9,10-diphenylphenanthrene (IV) from tetraphenylethylene dichloride. This reaction as carried out by Schmidlin and Von Escher[7] consists in treating tetraphenylethylene dichloride with aluminum chloride in benzene or carbon disulfide solution, and according to Prins[8] is an example of an intramolecular Friedel–Crafts reaction. It has now been found that in solvents favoring quinoidation the aluminum chloride may be replaced with advantage by stannic chloride, so that in this respect the reaction differs from the usual Friedel–Crafts reaction. A possible explanation of the reaction mechanism is that the ortho quinonoid modification of tetraphenylethylene dichloride (II) loses a molecule of hydrochloric acid to give a radical which rearranges to 9,10-diphenyl-9-chloro-(9,10-dihydrophenanthrene) (III), which compound then loses another molecule of hydrochloric acid to give 9,10-diphenylphenanthrene (IV). Or perhaps two rings become quinonoid and both molecules of hydrochloric acid are split off simul-



II III IV

taneously. In general, a para quinonoid form reacts in preference to the corresponding ortho form but this need not hold for reactions in which a stable product can result from the ortho but not from the para modification.

Tetraphenylethylene dichloride dissolved in chloroform and treated with stannic chloride was found to give an intensely colored purple solution which gradually becomes colorless after a few hours, a 95% yield of 9,10-diphenylphenanthrene being obtained. The purple color is undoubtedly due to the formation of the quinonoid modification of tetraphenylethylene dichloride. This conclusion is supported by the fact that tetrakis-(dimethylaminophenyl)-ethylene adds chlorine directly to give a violet colored chloride[9] to which Kehrmann[10] and Recsei[11] assign a quinonoid configuration.

A study of the reaction of tetraphenylethylene dichloride and stannic chloride in various solvents showed that the character of the solvent has a marked effect on the formation of diphenylphenanthrene. In ethylene chloride, chloroform, nitrobenzene and benzonitrile, a quinonoid salt is produced, as manifested by the development of an intense purple color, and excellent yields of diphenylphenanthrene are obtained. On the other

[7] Schmidlin and von Escher, *Ber.*, **43**, 1153 (1910).

[8] Prins, *J. prakt. Chem.*, [2] **89**, 438 (1914).

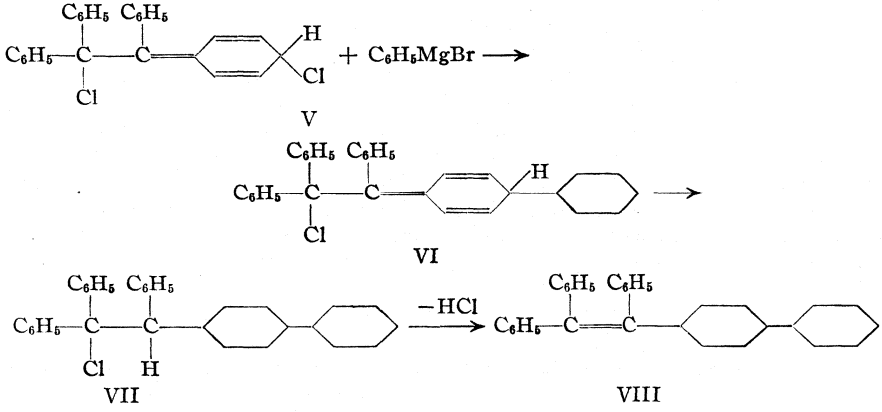
[9] Wizinger, *Ber.*, **60**, 1383 (1927).

[10] Kehrmann, *ibid.*, **60**, 1913 (1927).

[11] Recsei, *ibid.*, **60**, 2383 (1927); see also Madelung and Oberwegner, *ibid.*, **60**, 2469 (1927).

hand, under the same conditions no color is developed in benzene, carbon tetrachloride or carbon disulfide and little or no diphenylphenanthrene is obtained, most of the tetraphenylethylene dichloride being recovered unchanged. Since color develops in polar solvents and not in non-polar solvents, it is evident that the former favor quinoidation.[12] And while the fact that the reaction proceeds only in solvents which favor quinoidation does not necessarily indicate that a quinonoid salt must be an intermediate step in the preparation of diphenylphenanthrene, it does nevertheless lend plausibility to such an hypothesis.

Further support for the suggested mechanism is found in the reaction of tetraphenylethylene dichloride and phenylmagnesium bromide. Norris[13] carried out this reaction in the hope of preparing hexaphenylethane, but instead obtained tetraphenylethylene and 4-phenyltetraphenylethylene. No attempt was made to interpret the mechanism of formation of the latter compound, and yet it can be logically explained by the assumption that the para quinonoid modification of tetraphenylethylene dichloride (V) reacts with phenylmagnesium bromide. The resulting product (VI) rearranges to 1,1,2-triphenyl-2-biphenyl-1-chloroethane (VII), which then yields 4-phenyltetraphenylethylene (VIII) by loss of a molecule of hydrochloric acid.



Other Grignard reactions which substantiate this hypothesis will be discussed in a separate communication.

9,10-Diphenylphenanthrene may also be prepared in 25% yield by treating tetraphenylethylene in chloroform solution with bromine at −40° in the presence of stannic chloride. The reaction is of interest since the addition of bromine to the double bond must be postulated as an intermediate step, and tetraphenylethylene has repeatedly been cited as a classi-

[12] See also Dilthey, *J. prakt. Chem.*, [2] **109**, 273 (1925).

[13] Norris, Thomas and Brown, *Ber.*, **43**, 2955 (1910).

cal example of a compound which would not add bromine although it does add chlorine, and also sodium.

The measurements of the absorption spectra were made with the assistance of Dr. L. C. Anderson of this Laboratory to whom we wish to express our appreciation.

Experimental

Absorption Spectra Data.—For the measurement of quantitative absorption spectra in the ultraviolet region, a Judd-Lewis sectorphotometer and a Hilger quartz spectrograph, size C, were employed. Absorption spectra in the visible region were determined by the use of a Nutting photometer and a Hilger constant wave length spectrometer. The procedure was that described by Anderson and Gomberg.[14]

Asymmetrical diphenylethylene was prepared by the action of 30% sulfuric acid on methyldiphenylcarbinol[15] and was fractionated several times under reduced pressure; b. p. 148° at 17 mm.; f. p. 8°.

Methyldiphenylcarbinol was prepared by the action of phenylmagnesium bromide upon ethyl acetate and was purified by recrystallization from ether plus petroleum ether, m. p. 81°.

Methyldiphenylchloromethane could not be isolated in crystalline form. It was prepared by saturating a petroleum ether solution of the corresponding carbinol with dry hydrogen chloride at 0° in the presence of anhydrous calcium chloride. The calcium chloride was filtered off and a stream of dry air passed through the solution under reduced pressure at 0° to remove the solvent and excess hydrogen chloride. An analysis of the residual oil gave 98% of the theoretical amount of chlorine, indicating that no appreciable decomposition had taken place. Preliminary measurements showed that hydrogen chloride had no effect on the absorption of methyldiphenylchloromethane when dissolved in petroleum ether; therefore the solutions used for obtaining the absorption (Fig. 1, Curve 2) were made in the following manner. A weighed amount of the carbinol was dissolved in about 5 cc. of pure petroleum ether and the solution cooled and diluted to 25 cc. with cold petroleum ether saturated with hydrogen chloride, after which anhydrous calcium chloride was added and the mixture allowed to stand overnight at 0°. Five cc. of the solution was then pipetted off, diluted with petroleum ether to the proper concentration and the absorption measured. A sample which had been kept for three days at 0° gave results identical with those obtained with a sample which had been allowed to stand for eighteen hours.

The solution used for obtaining the absorption of methyldiphenylchloromethane plus stannic chloride (Fig. 2, Curve 1) was prepared in a similar manner using ethylene chloride as the solvent, except that the final dilution was made with ethylene chloride which was saturated with hydrogen chloride and contained 1% by volume of anhydrous stannic chloride. The entire curve was obtained with a 0.0025 molar solution since the absorption differs somewhat with different concentrations.

9,10-Diphenylphenanthrene.—Tetraphenylethylene dichloride was prepared by passing dry chlorine through a carbon tetrachloride solution of tetraphenylethylene at 0°[16] and recrystallizing the product thus obtained from a mixture of carbon disulfide and ethyl acetate.[17] One gram of the dichloride was dissolved in 40 cc. of pure chloroform and cooled in a freezing mixture to a temperature of −5 to −10°. Two cc. of

[14] Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928).

[15] Lebedev, Andreevskii and Matiushkina, *Ber.*, **56**, 2349 (1923).

[16] Finkelstein, *Ber.*, **43**, 1534 (1910).

[17] Norris, THIS JOURNAL, **38**, 707 (1916).

anhydrous stannic chloride was added, whereupon the solution assumed a deep purple color which gradually faded. After a few hours, the solution became colorless and was then washed thoroughly with water, dried and concentrated. Crystallization of the solid residue from absolute alcohol gave 9,10-diphenylphenanthrene in 90–95% yield, m. p. 235°. When mixed with an authentic specimen, no lowering in melting point was observed. Schmidlin and von Escher,[7] who carried out this reaction using aluminum chloride, obtained a 60% yield. At higher temperatures the reaction proceeds more rapidly but chlorinated products are formed which decrease the yield of diphenylphenanthrene.

Repetition of the experiment described above using ethylene chloride, nitrobenzene or benzonitrile as the solvent instead of chloroform gave a similar result. When benzene, carbon disulfide or carbon tetrachloride was used, however, no color was observed and only a trace of diphenylphenanthrene was obtained. About 60–70% of the tetraphenylethylene dichloride was recovered unchanged, along with an appreciable amount of chlorinated products.

Diphenylphenanthrene was also prepared from tetraphenylethylene and bromine. Five grams of tetraphenylethylene was dissolved in 100 cc. of chloroform and treated with 7 cc. of anhydrous stannic chloride. The green solution thus obtained was cooled to −40° and 2.4 g. (1 mole) of bromine was added. A deep purple color developed which had not disappeared after two hours, whereupon the solution was treated with a calcium chloride freezing mixture. Addition of the aqueous solution resulted in the disappearance of the purple color but considerable bromine was still present which was removed by washing with bisulfite solution. When the chloroform layer was dried and concentrated, a crystalline product was obtained which after repeated crystallization gave a 25% yield of pure 9,10-diphenylphenanthrene melting at 235°. The remainder of the material consisted of unchanged tetraphenylethylene and a small amount of brominated products. At room temperature a mixture of tetraphenylethylene and various bromination products of tetraphenylethylene and diphenylphenanthrene was obtained.

When the reaction was carried out in ethylene dichloride, the results were similar to those obtained in chloroform, but in carbon disulfide or carbon tetrachloride the purple color was not developed and little or no diphenylphenanthrene was obtained.

1,1,3,3-Tetraphenyl-1-butanol.—Five grams of finely ground β,β-diphenylbutyrophenone prepared by the method of Kohler[18] was added to an ether solution of phenylmagnesium bromide made from 3 g. of magnesium. The mixture was refluxed for one hour, then decomposed with ice and acid, and the ethereal layer washed, dried and concentrated. The solid residue crystallized from alcohol in plate-like prisms melting at 124–125°; yield, 75%. The carbinol is readily soluble in the common organic solvents except petroleum ether.

Attempts to prepare the corresponding chloride, 1,1,3,3-tetraphenyl-1-chlorobutane, by saturating a benzene solution of the carbinol with dry hydrogen chloride at −5° in the presence of anhydrous calcium chloride gave instead a quantitative yield of 1,1,3,3-tetraphenyl-1-butene.

The butene is also obtained if the butanol is dissolved in glacial acetic acid at room temperature and a few drops of concentrated sulfuric acid added. However, if 1 g. of the powdered butanol is treated with 25 cc. of concentrated sulfuric acid, 1,1,3-triphenyl-3-methylhydrindene is formed in approximately 25% yield, the remaining product consisting principally of asymmetrical diphenylethylene with a small amount of tetraphenylbutene. The triphenylmethylhydrindene appears to be formed from the carbinol and not by rearrangement of the butene, for when 3 g. of the butene was treated

[18] Kohler, *Am. Chem. J.*, **31**, 657 (1904); *ibid.*, **38**, 558 (1907).

with 15 cc. of concentrated sulfuric acid and the mixture allowed to stand for forty-eight hours at room temperature, the product obtained proved to be unchanged butene, a small amount of diphenylethylene, and water-soluble sulfonated products. No triphenylmethylhydrindene could be isolated. When a similar mixture was allowed to stand for six weeks, only about 0.1 g. of the hydrindene was obtained, although Bergmann and Weiss[19] state that the hydrindene can be readily prepared from the butene by means of sulfuric acid.

Summary

1. The quantitative absorption spectra of the following compounds have been obtained: asymmetrical diphenylethylene, methyldiphenylcarbinol, methyldiphenylchloromethane, methyldiphenylchloromethane plus stannic chloride, and triphenylchloromethane plus stannic chloride.

2. The preparation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and stannic chloride has been investigated and the effect of polar and non-polar solvents noted.

3. A reaction mechanism involving quinoidation has been postulated to explain the formation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and also the formation of 4-phenyltetraphenylethylene from tetraphenylethylene dichloride and phenylmagnesium bromide.

[19] Bergmann and Weiss, *Ann.*, **480**, 49 (1930).

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

ORGANIC REACTIONS WITH BORON FLUORIDE. III. THE CONDENSATION OF PROPYLENE WITH PHENOL

BY F. J. SOWA, H. D. HINTON AND J. A. NIEUWLAND

RECEIVED MAY 16, 1932 PUBLISHED SEPTEMBER 5, 1932

The condensation of unsaturated hydrocarbons with phenols in the presence of condensing agents has been studied by various investigators. Amylene, di-isobutylene,[1] cyclohexane,[2] styrene,[3] isoprene,[4] acetylene,[5] and propylene[6,7] have been condensed with phenol or phenolic type compounds to yield substituted phenols, phenyl ethers or substituted phenyl ethers.

In an earlier publication a study was made of the rearrangement of isopropyl phenyl and cresyl ethers[8] in an attempt to determine the position occupied by the isopropyl group after the rearrangement. The results

[1] Niederl and Natelson, THIS JOURNAL, **53**, 272 (1931).

[2] Liebermann and Hartmann, *Ber.*, **25**, 957 (1892).

[3] König, *ibid.*, **24**, 3889 (1891).

[4] Claisen, German Patent 374,142, 1923.

[5] Wenzke and Nieuwland, THIS JOURNAL, **46**, 177 (1924).

[6] Howard and Blagden, British Patent 214,866, 1923.

[7] Sowa, Sc. M. Dissertation, University of Notre Dame, 1930.

[8] Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 2019 (1932).

obtained by using boron fluoride were shown to be similar to those previously reported.[9]

Gasselin[10] studied the action of boron fluoride on phenol and found that one mole of boron fluoride was absorbed by two moles of phenol. The boron fluoride was evolved quantitatively on heating, and the phenol remained unchanged.

Butlerow and Goriainow[11,12] stated that boron fluoride polymerized propylene to products more complex than a trimer even at ordinary temperatures. No such action was noted throughout the present work. However, the experimental conditions are entirely different in each case.

Theoretical Part

The action of propylene on phenol in the presence of boron fluoride may be represented by the following equations as taking place through a series of condensations and subsequent rearrangements.

$$C_6H_5OH + CH_3CH{=}CH_2 \xrightarrow{\text{Condensation}} C_6H_5OC_3H_7 \text{ (isopropyl phenyl ether)} \quad (I)$$

$$C_6H_5OC_3H_7 \xrightarrow{\text{Rearrangement}} C_6H_4(C_3H_7)OH \text{ (}o\text{-isopropylphenol)} \quad (II)$$

$$C_6H_4(C_3H_7)OH + C_3H_6 \longrightarrow C_6H_4(C_3H_7)OC_3H_7$$
(o-isopropylphenyl isopropyl ether) (III)

$$C_6H_4(C_3H_7)OC_3H_7 \longrightarrow C_6H_3(C_3H_7)_2OH \text{ (2,4-diisopropylphenol)} \quad (IV)$$

$$C_6H_3(C_3H_7)_2OH + C_3H_6 \longrightarrow C_6H_3(C_3H_7)_2OC_3H_7$$
(2,4-diisopropylphenyl isopropyl ether) (V)

$$C_6H_3(C_3H_7)_2OC_3H_7 \longrightarrow C_6H_2(C_3H_7)_3OH \text{ (2,4,6-triisopropylphenol)} \quad (VI)$$

$$C_6H_2(C_3H_7)_3OH + C_3H_6 \longrightarrow C_6H_2(C_3H_7)_3OC_3H_7$$
(2,4,6-triisopropylphenyl isopropyl ether) (VII)

By progressive reactions of this type, substituted phenols and phenyl ethers of increasing molecular weight are gradually built up. These reactions may be controlled to a certain extent by varying the temperature, per cent. of boron fluoride, time of contact of ethers with the boron fluoride and quantity of propylene added. Temperature control is very important. For example, at 0°, reaction (I) predominates, and reaction (II) takes place to some extent. At 20°, the product of (I) is present only in a negligible quantity. The products of reactions (II) and (V) predominate at this temperature, while the products of (III), (IV), (VI) and (VII) are present in much smaller quantities. However, when the reaction took place at 40° the only products isolated were the substituted phenol and phenyl ether in reaction (VII). The latter was obtained in good yield while the former was present in only a small amount. Attempts to carry the condensation of propylene with phenol further have failed.

[9] Niederl and Natelson, THIS JOURNAL, **53**, 1928 (1931).

[10] Gasselin, *Ann. chim. phys.*, [7] **3**, 67 (1894).

[11] Butlerow, *Ann.*, **189**, 44 (1877).

[12] Goriainow and Butlerow, *ibid.*, **169**, 147 (1873).

Since 2-isopropylphenyl isopropyl ether, 2,4-diisopropylphenyl isopropyl ether and 2,4,6-triisopropylphenyl isopropyl ether have not been reported it was necessary to undertake the proof of their respective structures. The corresponding substituted phenols will be discussed in a later paper on rearrangements. The product in condensation (I) was shown to be identical with isopropyl phenyl ether by the synthesis of the latter according to the method of Williamson.[13] It has been reported[8] that isopropyl phenyl ether rearranges to *o*-isopropylphenol in the presence of boron fluoride. In the same report it was shown that isopropyl *o*-cresyl and isopropyl *p*-cresyl ethers rearrange to 2-methyl-4-isopropylphenol and 4-methyl-2-isopropylphenol, respectively. By synthesizing 2-isopropylphenyl isopropyl ether from *o*-isopropylphenol, it was shown to be identical with the product of reaction (III). The same procedure was carried out to prove the products in reactions (V) and (VII). It should be noted in reaction (VI) that the only active position to which the isopropyl group can rearrange is the 6-position, thereby forming the symmetrical tri-isopropylphenol. (The Zeisel reaction was used with each ether to show the nature of the alkyl group attached to the oxygen.)

Experimental Part

Isopropyl Phenyl Ether.[14]—One mole of phenol was weighed in a three-necked round-bottomed flask; 5 g. of boron fluoride (prepared as previously described[15]), and 100 g. of benzene were added to the phenol. The flask was fitted with a mechanical stirrer and immersed in an ice brine bath, so as to keep the temperature between −2° and 2°. Propylene was passed in at the rate of 10 g. per hour of propylene. The absorption was carried out under a pressure of 7.6–10.2 cm. of mercury. When 21 g. (0.5 mole) of propylene had been added the flow of the gas was stopped. The mixture was transferred to a separatory funnel and 100 cc. of cold 10% potassium hydroxide solution was added. Two layers separated. The upper layer was washed with 20-cc. portions of the 10% potassium hydroxide solution until a portion of the alkali extract, upon acidifying with hydrochloric acid, gave no evidence of phenol separating. The benzene extract of the upper layer was dried over calcium chloride or anhydrous potassium carbonate. The benzene was removed by distillation. The second fraction was shown to be isopropyl phenyl ether; 37 g. of the product was isolated. This corresponds to a 54% yield based on the propylene used; b. p. 178°; sp. gr. 0.975 (20°); n_D^{20} 1.4992.

***o*-Isopropylphenol.**[16]—The alkali extracts obtained from the above mixture, under isopropyl phenyl ether, were combined and acidified either by passing a stream of carbon dioxide into it until no more phenol separated or by the addition of hydrochloric acid. Two layers appeared. The phenol layer was separated and the aqueous portion extracted once with ether. The latter was added to the phenol layer and washed with 100 cc. of cold water. After separating and drying the ether layer over anhydrous potassium carbonate it was fractionated; 28 g. of *o*-isopropylphenol was obtained, a

[13] Williamson, *J. Chem. Soc.*, **4**, 106 (1851).

[14] Perkin, *ibid.*, **69**, 1187, 1250 (1896).

[15] Bowlus and Nieuwland, THIS JOURNAL, **53**, 3835 (1931).

[16] Spica, *Gazz. chim. ital.*, **9**, 442 (1879).

yield of 41% based on the propylene used; 66 g. of phenol was recovered, b. p. 212–214°; sp. gr. 1.0140 (20°); n_D^{20} 1.5310.

o-Isopropylphenyl Isopropyl Ether.—The method used in the preparation of this compound was the same as in the preparation of isopropyl phenyl ether with two exceptions. The temperature was maintained between 13 and 17° and two moles of propylene was added for one mole of phenol used.

Fraction	I	II	III
B. p., °C.	177–180	222–230	238–250
Grams	6	74	20

Fraction (I) was identified as isopropyl phenyl ether. It was shown in an earlier paper[17] that isopropyl phenyl ether is rearranged to *o*-isopropylphenol by means of boron fluoride. *o*-Isopropylphenol was treated with potassium hydroxide, then with isopropyl bromide. The compound thereby obtained appears to be identical with fraction (II). Fraction (III) appears to be 2,4-di-isopropylphenyl isopropyl ether and will be discussed under the preparation of that compound. The 74 g. of fraction (II) corresponds to a 41% yield based on the propylene used; b. p. 225–227°; sp. gr. 0.9192 (25°); n_D^{25} 1.4948; calcd. mol. wt. 178.1; found, 176.0.

2,4-Di-isopropylphenyl Isopropyl Ether.—Since the product of the reaction served as an excellent solvent and at the reaction temperature the phenol–boron fluoride mixture was liquefied at the start of the absorption, no solvent was added; 3.5 g. of boron fluoride was passed into each mole of phenol. The temperature of the mixture did not rise above 22° at any time during the reaction. The absorption of propylene took place under a pressure of 20 cm. of mercury. After one mole of propylene had been added the mixture was treated as described under isopropyl phenyl ether. The fractions isolated were

	Alkali Soluble			Alkali Insoluble	
Fraction	B. p., °C.	G.	Fraction	B. p., °C.	G.
I	213–220	44	I	220–230	5
II	230–240	12	II	240–250	41
III	240-256	10	III	258–265	18

Fraction (I) under alkali soluble was identified as *o*-isopropylphenol. Further work is being done on Fractions (II) and (III). Fraction (I) under alkali insoluble is *o*-isopropylphenyl isopropyl ether. Fraction (II) was proved by synthesis to be 2,4-di-isopropylphenyl isopropyl ether (see theoretical part). Fraction (III) appears to be 2,4,6-tri-isopropylphenyl isopropyl ether and will be discussed under the preparation of that compound. A yield of 30% of 2,4-di-isopropylphenyl isopropyl ether was obtained; b. p. 248° (uncorr.); sp. gr. 0.9432 (25°); n_D^{25} 1.5087; calcd. mol. wt. 220.1; found, 217.5.

2,4,6-Tri-isopropylphenyl Isopropyl Ether.—The method used in the preparation of this compound was the same as the procedure in the preparation of 2,4-di-isopropylphenyl isopropyl ether except that the temperature of the reaction was maintained between 30 and 40° and propylene was passed into the mixture until practically no more absorption took place. A product weighing 241 g., insoluble in alkali and boiling between 258 and 265° was isolated. The structure of this compound was discussed in the theoretical part of this paper. A 92% yield based on the phenol used was obtained; b. p. 263° (uncorr.); sp. gr. 0.9132 (25°); n_D^{25} 1.4982; calcd. mol. wt. 262.2; found, 258.8.

[17] Sowa, Hinton and Nieuwland, THIS JOURNAL, **54**, 2019 (1932).

Further work is being carried out in this Laboratory in an effort to study the condensation of a number of different unsaturated compounds with phenols in the presence of boron fluoride.

The authors wish to express their appreciation to the E. I. du Pont de Nemours Company for supplying the propylene used in this investigation.

Summary

A procedure has been outlined by which propylene may be condensed with phenol using boron fluoride as a catalyst.

The catalyst used serves two purposes, namely, as condensing agent and rearranging agent. This affords a method for the formation of a series of condensations and subsequent rearrangements to form phenyl ethers, substituted phenols and substituted phenyl ethers in one operation.

The synthesis of isopropyl phenyl ether and its homologs has been described.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

REDUCTION STUDIES OF SCHIFF BASES. II. THE POLYMERIC STATES AND THE STRUCTURES OF METHYLENE-ANILINE AND METHYLENE-PARA-TOLUIDINE. THE CONDENSATION OF ANILINE AND ACETALDEHYDE[1]

BY JOHN G. MILLER AND E. C. WAGNER

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N-Methylene-aniline and N-methylene-*p*-toluidine are Schiff bases which have been obtained only in polymerized forms.[2] Published evidence as to their polymeric states is in part conflicting,[2d,3] and that as to their structures is scanty and unconvincing.[2a,b,3,4]

Methylene-aniline has long been recognized as trimeric. Methylene-*p*-toluidine, stated by Bischoff[2d] to be trimeric, was later reported by Ingold and Piggott[3] to be dimeric at ordinary temperature, a finding shown below to be incorrect. Though the degree of polymerization is affected by conditions such as temperature and presence of the bases in hot solvents, the

[1] From the thesis presented by John G. Miller in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Pennsylvania, June, 1932.

[2] (a) Wellington and Tollens, *Ber.*, **18**, 3298 (1885); (b) Miller and Plöchl, *ibid.*, **25**, 2020 (1892); (c) Pulvermacher, *ibid.*, **25**, 2762 (1892); (d) Bischoff, *ibid.*, **31**, 3248 (1898).

[3] Ingold and Piggott, *J. Chem. Soc.*, **123**, 2745 (1923).

[4] (a) Pratesi, *Gazz. chim. ital.*, **14**, 351 (1884); (b) Tröger, *J. prakt. Chem.*, [2] **35**, 225 (1887); (c) Grünhagen, *Ann.*, **256**, 285 (1890); (d) Eibner, *ibid.*, **302**, 349 (1898); (e) Löb, *Z. Elektrochem.*, **4**, 428 (1898); (f) Goecke, *ibid.*, 9, 470 (1903).

polymers referred to here, when perfectly pure, are relatively stable under ordinary conditions, and have the characteristics of definite compounds.

Ring structures were assigned to polymerized methylene-aniline and methylene-*p*-toluidine by Bischoff, on the basis of analytic and molecular weight values.[2d,5] Löb,[4e] by electro-reduction of *p*-nitrotoluene in acid solution containing formaldehyde, obtained dimethyl-*p*-toluidine, whose formation was interpreted as evidence for the ring structure of the presumably intermediate methylene-*p*-toluidine, some of which appeared as a product.

Ingold and associates,[6] as a result of experiments on the thermal "division" of certain coupled azomethines, stated them to be compounds containing the 1,3-dimethinediazidine ring, and Ingold and Piggott[3] concluded that methylene-*p*-toluidine is a stable example of this type, *i. e.*, a cyclic dimer. The validity of these conclusions hinges upon the molecular weight of methylene-*p*-toluidine, for which a single value 254 was reported, that calculated for the dimer being 238. In the present study, however, the molecular weight of methylene-*p*-toluidine was found, by cryoscopic determinations in four solvents, to be 353, that calculated for the trimer being 357. Ingold and Piggott's representation of methylene-*p*-toluidine as N,N′-bis-(*p*-tolyl)-1,3-dimethinediazidine is therefore inadmissible. The successful extension, to methylene-aniline and methylene-*p*-toluidine, of the method of structure proof used by Wagner[7] in the case of methylene-*p*-aminophenol is described below.

The Polymeric States of Methylene-aniline and Methylene-*p*-toluidine.—Pure methylene-aniline (m. p. 141.2° corr.) was shown, by cryoscopic determinations in benzene, nitrobenzene, ethylene bromide and 1,4-dioxane (temperatures 5 to 12°), to be definitely trimeric, the results of fourteen concordant values averaging 320; the calculated value for the trimer is 315. In boiling benzene the result was likewise 320, but in molten camphor the value obtained was 255, indicating partial depolymerization at 176°.

The amorphous "higher polymeride" of methylene-aniline (decomp. above 210°), stated by Bischoff to be approximately tetrameric in boiling benzene, was found to have in molten camphor the molecular weight 254, identical with that of initially trimeric methylene-aniline under the same conditions; the agreement suggests that this value may represent the average polymeric state at 176°.

Pure methylene-*p*-toluidine (m. p. 127.9° corr.) was found, as already noted, to be definitely trimeric when examined cryoscopically in benzene,

[5] Synthetic evidence of ring structure was obtained by Grünhagen[4c] and by Eibner (Ref. 4d, p. 355), but the indications were actually somewhat misleading.

[6] Ingold and Piggott, *J. Chem. Soc.*, **121**, 2381, 2793 (1922); Ingold, *ibid.*, **125**, 87 (1924); **127**, 1141 (1926); Ingold and Shoppee, *ibid.*, 1199 (1929).

[7] Wagner, THIS JOURNAL, **54**, 660 (1932).

nitrobenzene, ethylene bromide and 1,4-dioxane, sixteen results averaging 353. In boiling benzene the value was 338 (trimeric), but in molten camphor it was 213, *i. e.*, about 11% below the molecular weight of the dimer. Ingold and Piggott reported this compound to be monomeric at 250° (Victor Meyer method).

The amorphous "higher polymeride" of methylene-*p*-toluidine (m. p. 225–227°), reported by Bischoff to be approximately tetrameric in boiling benzene, was found to have at 176° (in molten camphor) the molecular weight 249, or 5% above that of the dimer.

The slight solubilities of the two higher polymers in cold benzene, etc., prevented determination of their molecular weights at lower temperatures. Collected results of the molecular weight determinations of methylene-aniline and methylene-*p*-toluidine are given in Table I.

The Reduction of Methylene-aniline and of Methylene-*p*-toluidine.—The trimeric bases, and also their higher polymerides, were reduced by zinc dust and concentrated hydrochloric acid at 5–10°, this temperature being presumably favorable to the stability of the several polymers. The maximum extent of hydrolysis under the same conditions was independently determined by recovery of the aniline or *p*-toluidine produced.

Reduction of trimeric methylene-aniline and of its amorphous higher polymeride yielded aniline (in excess of that attributable to hydrolysis), methylaniline and dimethylaniline. In the procedure developed for the separation and estimation of these products,[8] dimethylaniline was precipitated as the hydroferrocyanide,[9] aniline as the zincichloride,[10] and finally methylaniline as the benzenesulfonyl derivative. The usefulness of this separation was established by both qualitative and quantitative tests using mixtures of known composition.

Reduction of trimeric methylene-*p*-toluidine and of its amorphous higher polymeride was almost quantitative, and yielded *p*-toluidine (in excess of that attributable to hydrolysis), methyl-*p*-toluidine, and dimethyl-*p*-toluidine. The primary and secondary bases were separated and estimated as their benzenesulfonyl derivatives by the Hinsberg–Kessler procedure,[11] and dimethyl-*p*-toluidine as its nearly insoluble

[8] The Hinsberg–Kessler method was found to be unsatisfactory due to interaction of the reagent with dimethylaniline to form a blue dye [Hassencamp, *Ber.*, **12**, 1275 (1879); Michler and Meyer, *ibid.*, **12**, 1791 (1879); Wahl, *Rev. gen. mat. color.*, **32**, 176 (1928); *Chem. Abstracts*, **23**, 1896 (1929)].

[9] Fischer, *Ann.*, **190**, 184 (1878); Eisenberg, *ibid.*, **205**, 265 (1880); Beckmann and Correns, *Ber.*, **55**, 854 (1922).

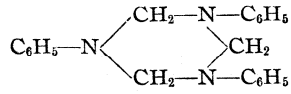
[10] Lachowicz and Bandrowski, *Monatsh.*, **9**, 510 (1888); Frankland, Challenger and Nicholls, *J. Chem. Soc.*, **115**, 198 (1919).

[11] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. II, 1916, p. 24.

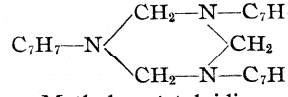
picrate. Tests of this method of separation showed its accuracy to approach the quantitative.

Results of reduction and hydrolysis experiments conducted semi-quantitatively are given in Table II.

The Structures of Methylene-aniline and Methylene-*p*-toluidine.—The formation of primary, secondary and tertiary amines, all as major reduction products of methylene-aniline and methylene-*p*-toluidine (both the trimeric and the higher forms), constitutes evidence as to structure. The appearance of the dimethylated bases is perhaps of most significance, as it indicates the original molecule to contain nitrogen attached to two methylene groups. As, furthermore, crystalline methylene-aniline and methylene-*p*-toluidine are shown conclusively to be trimeric within the range 5 to 80°, there is thus available the first definite evidence that these compounds have cyclic structures



Methylene-aniline,
M. p. 141.2° corr.



Methylene-*p*-toluidine,
M. p. 127.9° corr.

Equally definite conclusions cannot be reached for the amorphous higher polymers, due to ignorance of their molecular weights at lower temperatures. The evidence of reduction admits the possibility of rings, ring-aggregates or (if the molecular weights are large) of indeterminate chain structures of the Staudinger[12] type

$$\ldots.CH_2NCH_2NCH_2NCH_2N\ldots.$$
$$\quad\quad Ar \quad Ar \quad Ar \quad Ar$$

The Condensation of Aniline and Acetaldehyde.—Condensations of aniline with lower normal aliphatic aldehydes other than formaldehyde[13] were shown by Miller and Plöchl and their students[2b] to yield in each case as one product an oil stated to be the simple azomethine $C_6H_5N{=}CHR$, which changed into a dimeric molecule represented, *e. g.*, $C_6H_5NHCH(CH_3)CH_2CH{=}NC_6H_5$, due to an aldol-like condensation.[14] The "polymerization" of the azomethines $C_6H_5N{=}CHR$ was thus indicated to be entirely different from that of the azomethines $ArN{=}CH_2$ from formaldehyde. In the present study the reaction of acetaldehyde with aniline was examined to determine whether the monomeric azomethine could be isolated, and whether it might not polymerize after the manner of methylene-aniline and methylene-*p*-toluidine.

[12] Staudinger, *Ber.*, **59**, 3019 (1926).

[13] For the behavior of isobutyraldehyde and isovaleraldehyde see Friedjung and Mossler, *Monatsh.*, **22**, 460 (1901); Eibner and Purucker, *Ber.*, **33**, 3658 (1900).

[14] Eibner, *Ber.*, **27**, 1281 (1894); **29**, 2977 (1896); *Ann.*, **318**, 58 (1901); **328**, 121 (1903). Eibner obtained the above compound by condensation of aldol and aniline. See also Strain, THIS JOURNAL, **54**, 1221 (1932).

Condensations of aniline and impure acetaldehyde, especially if effected without continued cooling, yielded oily and colored products such as those mentioned. When both reactants were pure, and were condensed with chilling, the product was a white crystalline solid found to be ethylidene-dianiline $(C_6H_5NH)_2CHCH_3$, previously prepared by Eibner.[15] Efforts to force azomethine formation by use of acetaldehyde in excess were unsuccessful, the product being in every case the di-imine. This tendency of straight-chain aliphatic aldehydes to yield di-imines had been observed by Eibner.[16] Ethylidene-dianiline appeared to be stable only in the cold; on standing at room temperature it liquefied and became colored, presumably with gradual conversion to the "dimer."

Acetaldehyde and aniline therefore appear to yield no isolable azomethine, either as the monomer or a true polymer. The "dimers" of Miller and Plöchl are probably products formed by secondary changes.

Experimental

Chemicals.—The formaldehyde was Baker's "C. P." grade (35%). The acetaldehyde (Coleman and Bell "C. P.") was distilled through a column, only the portion boiling constant at 20.8° being taken. The other chemicals were the best Eastman Kodak Company grades, purified as follows. Aniline was redistilled from zinc dust under reduced pressure. Methylaniline and dimethylaniline were redistilled under reduced pressure. Methyl-*p*-toluidine and dimethyl-*p*-toluidine were fractionally distilled. Ethylaniline was freed from traces of diethylaniline by hydrolysis of the recrystallized acetyl compound of m. p. 54°, and the recovered base dried and distilled. Benzenesulfonyl chloride was distilled *in vacuo*. The molecular weight solvents benzene, nitrobenzene, ethylene bromide and 1,4-dioxane were purified by partial freezings of the redistilled compounds, and camphor by sublimation.

Preparation and Purification of the Schiff Bases Studied

Methylene-aniline (Trimeric).—A mixture of aniline with ten parts of water was chilled, and a slight excess of formalin added with stirring. The precipitated product was filtered off the next day, and dried *in vacuo*. To purify, it was extracted rapidly with about five parts of boiling alcohol, the extract filtered quickly, and the filtrate chilled at once with stirring, some water being added gradually to hasten the separation and decrease the conversion of the trimer to the higher polymer. The product melted at 140° with slight opacity (trace of higher polymer), and was considered satisfactory for the reduction experiments. For molecular weight determinations it was recrystallized from hot 95% alcohol, or better from 60–80° ligroin, working rapidly, and filtering off the crystals which separated immediately upon chilling. Recrystallization from benzene was found unsatisfactory due to invariable formation of the higher polymer.

Pure methylene-aniline was obtained as thin transparent prisms, showing oblique extinction, and melting sharply to a clear liquid at 139.5° (141.2° corr.). It distilled apparently without change *in vacuo* (60–64° at 29 mm.).

Amorphous methylene-aniline (the higher polymer) was accumulated in small portions as a by-product of recrystallizations of the trimer, and was freed from trimer by extraction with benzene. It was also made from crude methylene-aniline by re-

[15] Eibner, *Ber.*, **30**, 1444 (1897).

[16] Eibner, *Ann.*, **302**, 349 (1898); **316**, 89 (1901); **328**, 121 (1903).

peatedly boiling it with benzene and then extracting with hot ligroin. It was obtained as a white powder, without crystalline structure or optical activity. It decomposed above 210° without melting, and was almost insoluble in hot benzene, ligroin, alcohol, etc.

Methylene-*p*-toluidine (Trimeric).—A solution of *p*-toluidine in six parts of 95% alcohol was chilled, vigorously stirred, and an excess (two equivalents) of formalin added all at one time. After thirty minutes the mass of crystals was filtered off, washed with cold alcohol, and dried *in vacuo;* the yield was 90%. To purify, it was extracted rapidly with hot ligroin (60–80°) and the extract filtered quickly; the higher polymer remained on the filter. The filtrate was cooled rapidly, but only to room temperature, so as to retain any di-imine in solution. The crystals were washed with cold ligroin.

Pure trimeric methylene-*p*-toluidine was obtained as silky needles, showing oblique extinction, and melting sharply to a clear liquid at 127° (127.9° corr.); it was distillable *in vacuo*.

Amorphous methylene-*p*-toluidine (the higher polymer) was obtained in small portions as a by-product as mentioned above. It was prepared in 59% yield by condensing *p*-toluidine and excess formaldehyde in alcohol, and then warming the well-stirred mixture to 50–60° in the water-bath. The insoluble product was extracted three times with boiling ligroin to remove any trimer. The higher polymer was a white amorphous powder, without optical activity, and practically insoluble in the solvents used. It melted at 225–227° with decomposition.

Ethylidene-dianiline.—An ice-chilled solution of pure acetaldehyde in 60 parts of water was treated with one equivalent of aniline. After some minutes the liquid was decanted from the white granular precipitate, which was washed with ice water five times by decantation. The product, collected in an ice-jacketed filter and dried *in vacuo* in an ice-chilled "pistol" in presence of "desicchlora," melted at 49°; this and the results of reduction (see later) identified it as ethylidene-dianiline. The same product resulted when an excess of aldehyde (up to two equivalents) was used. As mentioned above, this compound became oily and colored on standing at room temperature; similar colored oils were obtained by cold condensation of ordinary (not purified) aniline and acetaldehyde.

Molecular Weight Determinations.—The two Beckmann thermometers used were certified by the Bureau of Standards. For molecular weights by the Rast method there was used an untested "turpentine thermometer" graduated from 145 to 200° in 0.2°. Ebullioscopic measurements were made using the Cottrell apparatus. To determine the concentration of the solute an aliquot was removed and the solvent evaporated; the bases thus recovered were found to have undergone partial conversion to the higher polymers. Results of molecular weight determinations are collected in Table I.

Reduction and Hydrolysis Experiments

The general reduction procedure was as follows. An intimate mixture of the Schiff base with about twice its weight of zinc dust was added in small portions to 15 parts of concentrated hydrochloric acid initially at 0° and chilled thereafter in an ice-bath. Reduction proceeded smoothly, without frothing, and yielded finally a clear solution. The liquid was made alkaline and steam distilled. The distillate was extracted with ether, the extract dried with sodium sulfate, filtered into a tared beaker, the ether evaporated, and the residue of mixed bases weighed and then treated to separate the individual components, as outlined in the following examples. In the semi-quantitative experiments the precipitates were collected in glass filter crucibles, suitably washed and dried, and weighed.

Methylene-aniline.—The mixed bases were dissolved in the least amount of 6 *N* hydrochloric acid and treated in the cold with strong potassium ferrocyanide solution. The precipitated dimethylaniline-hydroferrocyanide was washed with cold water

TABLE I

MOLECULAR WEIGHT DETERMINATIONS FOR METHYLENE-ANILINE AND METHYLENE-*p*-TOLUIDINE

Methylene-aniline m. p. 141.2°	Methylene-*p*-toluidine m. p. 127.9°	Methylene-aniline m. p. 141.2°	Methylene-*p*-toluidine m. p. 127.9°
Benzene (cryoscopic)		1,4-Dioxane (cryoscopic)	
318	352	312	385
334	349	307	338
	356	319	348
	355	315	370
	350	Benzene (ebullioscopic)	
Nitrobenzene (cryoscopic)		322	302
312	328	300	385
303	337	308	328
317	326	350	
309		Camphor (cryoscopic)	
Ethylene bromide (cryoscopic)		264	209
318	375	245	217
325	363	Higher polymer m. p. above 210°	Higher polymer m. p. 225–227°
338	375	261	249
333	371	246	249

and alcohol, and dried at 80°. The base was identified by conversion to *p*-nitrosodimethylaniline, m. p. 85°. The filtrate was made alkaline, extracted with ether, the ether evaporated and the chilled residue treated with excess of strong zinc chloride solution (containing only enough hydrochloric acid to keep it clear). The aniline zinc chloride was washed with ligroin and dried at 80°. A little more aniline was recovered later, as noted below. The filtrate was made alkaline, extracted with ether, the ether evaporated and the residual oil dissolved in dilute hydrochloric acid. The solution was made strongly alkaline and was shaken with an excess of benzenesulfonyl chloride. The precipitated benzenesulfonyl derivative of methylaniline (blue-tinted due to a trace of dimethylaniline) was filtered off, washed, and dried *in vacuo*. After crystallization from alcohol it melted at 76–77° uncorr. The alkaline filtrate on acidification yielded a further small quantity of aniline as the benzenesulfonyl derivative (m. p. 110–111° uncorr.).

Methylene-*p*-toluidine.—The mixed bases obtained by reduction were shaken in the cold with aqueous sodium hydroxide and benzenesulfonyl chloride, the mixture was finally acidified, and the benzenesulfonyl derivatives extracted in ether. The aqueous liquid was made alkaline and extracted with ether. The solvent was evaporated, the residual oil dissolved in dilute acetic acid, and dimethyl-*p*-toluidine precipitated and weighed as the picrate, which, after recrystallization from alcohol, melted at 129° uncorr. The ether solution of the mixed benzenesulfonyl derivatives was shaken with dilute sodium hydroxide. The aqueous layer was acidified, chilled, and the precipitated benzenesulfonyl derivative of *p*-toluidine filtered off, washed and dried at 80°; it melted at 120°. The ether layer was evaporated, and the residue refluxed with sodium alcoholate. The liquid was diluted with water, the alcohol evaporated, and the N-(methyl-*p*-tolyl)-benzenesulfonamide filtered off; it melted at 65° uncorr. The filtrate on acidification yielded a little more N-(*p*-tolyl)-benzenesulfonamide.

The *extent of hydrolysis* of methylene-aniline and methylene-*p*-toluidine by acid

was tested by the procedure used for reduction, with omission of the zinc. The steam-volatile oils were found to consist of aniline and *p*-toluidine, respectively (no secondary or tertiary bases), which were determined as in the reduction experiments. That the hydrolysis occurred during the contact with acid and not during the steam distillation in presence of alkali was shown by experiments made to test the latter possibility, no steam-volatile products being obtained.

Results of reduction and hydrolysis experiments appear in Table II.

TABLE II

REDUCTION AND HYDROLYSIS OF METHYLENE-ANILINE AND METHYLENE-*p*-TOLUIDINE[a]

	Methylene-aniline				Methylene-*p*-toluidine			
Experiment	Taken g.	Aniline %	Methyl-aniline %	Di-methyl-aniline %	Taken g.	Toluidine %	Methyl-toluidine %	Di-methyl-toluidine %
Test of sepn. of 1, 2 and 3° amines	[b]	96.7	66.6	85.1	[c]	98.4	102.7	95.9
Hydr. of trimer by concd. HCl at 5–10°	5.0	3.9	Nil	Nil	4.5	19.2	Nil	Nil
Cold redn. of trimer (5–10°)	5.0	19.2	18.6	8.5	4.5	36.3	39.5	21.0
Hot redn. of trimer (70°)	5.0	21.1	1.8	0.4	...	..	...	..
Hydr. of amorphous higher polymer (5–10°)	4.0	3.7	..	..	2.4	30.8	...	..
Redn. of amorphous higher polymer (5–10°)	4.0	25.2	17.0	14.0	2.4	40.3	29.6	24.3

[a] Results for primary, secondary and tertiary amines obtained in reduction and hydrolysis experiments are corrected for the determined errors in the methods of separation. [b] Mixture contained 0.615 g. of aniline, 0.997 g. of methylaniline and 1.012 g. of dimethylaniline. [c] Mixture contained 0.987 g. of *p*-toluidine, 0.525 g. of methyl-*p*-toluidine and 0.564 g. of dimethyl-*p*-toluidine.

Ethylidene-dianiline was reduced by adding it in small portions to chilled concentrated hydrochloric acid, followed at once by zinc dust. The mixture of bases obtained by steam distillation was shaken in the cold with aqueous alkali and *p*-toluenesulfonyl chloride. The mixture was acidified, and the toluenesulfonyl derivatives extracted in ether. The aqueous liquid after suitable treatment was tested with picric acid; no diethylaniline was present. The ether solution of the mixed *p*-toluenesulfonyl derivatives was treated by the procedure outlined above for the benzenesulfonyl derivatives of *p*-toluidine and methyl-*p*-toluidine. After crystallization from alcohol the derivative of aniline melted at 102° (103.2° corr.) and that of ethylaniline at 87° (88° corr.).

The method used for the separation just outlined was tested semi-quantitatively with a mixture of 1.044 g. of aniline, 0.572 g. of ethylaniline, and 1.002 g. of diethylaniline. The recoveries were, respectively, 92.3, 84.4 and 104.1%.

Summary

1. Crystalline methylene-aniline and methylene-*p*-toluidine, prepared in very pure condition, were shown to be definitely trimeric at lower temperatures (5 to 80°), the average molecular weights decreasing at higher temperature (176°).

2. The method for the determination of the structures of polymerized Schiff bases by strong reduction, first used in the case of methylene-*p*-aminophenol, was successfully extended to trimeric methylene-aniline and methylene-*p*-toluidine, whose cleavage into primary, secondary and tertiary bases indicated their cyclic structures.

3. Amorphous methylene-aniline and methylene-*p*-toluidine (the higher polymers) were examined similarly and with similar results, but their structures cannot yet be fixed because of lack of knowledge of their molecular magnitudes at lower temperatures.

4. Examination of the apparently aberrant condensation of aniline and acetaldehyde (representing the straight-chain aliphatic aldehydes) showed the products hitherto obtained to be due to secondary reactions, the primary product being the di-imine. There seems to be no satisfactory evidence for the intermediate formation of the monomeric azomethine.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE ISOMERS IN "DIISOBUTYLENE." II[1]

BY C. O. TONGBERG AND J. D. PICKENS WITH M. R. FENSKE AND FRANK C. WHITMORE

RECEIVED MAY 17, 1932 PUBLISHED SEPTEMBER 5, 1932

The separation of the isomers in diisobutylene has been completed by means of two highly efficient packed columns constructed for the study of the composition of Pennsylvania petroleum.[2]

The diisobutylene used was prepared from tertiary butyl alcohol which had been recrystallized until its freezing point was above 23° (m. p. of pure tertiary butyl alcohol 25.5°). The diisobutylene was freed from all but traces of isobutylene and triisobutylene and higher polymers by a preliminary distillation.

The properties of the isomers are as follows

	B. p. (Cottrell), °C. 737 mm.	760 mm.[3]	d_4^{20}	n_D^{20}	F. p., °C.
2,4,4-Trimethylpentene-1	100.1	101.2	0.7151	1.4082	− 93.6 ± 0.1
2,4,4-Trimethylpentene-2	103.4	104.5	0.7211[4]	1.4158	−106.5 ± 0.1[5]

The high purity of the two isomers is indicated by their cooling curves.

[1] Presented by C. O. Tongberg in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College. See Whitmore and Wrenn, THIS JOURNAL, **53**, 3136 (1931).

[2] For a detailed description of these columns, their operation and this separation, see Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[3] The experimentally determined relation $\Delta p/\Delta$ b. p. = 21.8 mm./1°C. was used in making the correction.

[4] The value given in the first paper is in error.

[5] An isomorphic form was sometimes obtained with m. p. −108.3 ±0.1°.

Experimental

Purification of Tertiary Butyl Alcohol.—The best grade of the commercial alcohol from the Hydrocarbon Products Company of New York showed freezing points from 15 to 20°. The chief impurity was water. This alcohol was chilled until approximately two-thirds had crystallized. The crystals were separated by suction on large Büchner funnels. They were then melted and frozen again. This process was continued until the freezing point of the melted crystals was above 23°. The mother liquors were used directly with concentrated hydrochloric acid to make tertiary butyl chloride for other researches.

Preparation of Diisobutylene.—Slight modifications of the earlier procedures were used.[1] A cooled mixture of 2500 cc. of c. p. sulfuric acid and 2500 cc. of water was used with 3500 cc. of purified tertiary butyl alcohol. The time of heating on the steam-bath was shortened to three hours. Longer heating only increased the amount of higher isomers. The hydrocarbon layer was then carefully separated and refluxed with a few grams of metallic sodium. Less than 1 g. of sodium reacted with 5 liters of the crude hydrocarbon. Suction was then applied to remove considerable quantities of dissolved isobutylene. Finally one-tenth of the hydrocarbon was distilled under diminished pressure. Then the remainder was distilled through a short column until the b. p. reached 105° (737 mm.). The yield of "diisobutylene" was about the same as under the older procedure but the labor and time involved were much less. The total amount of diisobutylene prepared in this way, from *tert.*-butyl alcohol melting above 23°, was 50 liters.

Fractionation of the Diisobutylene.—The details of the fractionations through the 27-ft. and the 52-ft. columns are given elsewhere.[6] Boiling points of the fractions were taken in a Cottrell apparatus. In the case of the earlier fractions, dissolved isobutylene vitiated the boiling points.[6] More consistent results were obtained by taking the "50 per cent. boiling point" by allowing half of each sample to boil out of the Cottrell apparatus and then reading the b. p. The boiling points were taken at pressures of 728–737 mm. and were corrected to the latter pressure. The following is a summary of the distillation of 4.5 liters of diisobutylene (n_D^{20} 1.4102) through the 52 ft. column.

Fractions	B. p. (737 mm.) (Cottrell) Initial	50 Per cent.	n_D^{20}	Cc.
1–2	88.7°		1.3990–1.4063	90
3–5	95.9	100.1	1.4067–1.4076	107
6–10	99.0	100.1	1.4079–1.4081	215
11–15	99.6	100.1	1.4081	222
16–20	100.0	100.1	1.4082	223
21–65	100.1	100.1	1.4082	2303
66–75	100.1–102.9		1.4083 to 1.4147	393

[6] Fenske and co-workers, *Ind. Eng. Chem.*, **24**, 408 (1932).

Fractions	B. p. (737 mm.) (Cottrell) Initial	50 Per cent.	n_D^{20}	Cc.
76–83	103.1–103.15		1.4150 to 1.4156	312
84–89	103.3		1.4158	264
Residue			1.4225	175
Hold-up in column				50
Loss				146

A charge of 45.5 liters of diisobutylene (n_D^{20} 1.4102) was distilled through the 27-ft. column with a take-off rate of 250–750 cc. per hour. The results obtained were essentially like those with the 52-foot column. The distillation gave 156 fractions of 250 cc. each. Fractions 6 to 97 with a volume of 23 liters boiled at 100.1 to 100.15° at 737 mm. and had n_D^{20} 1.4081–1.4083. Fractions 147 to 156 with a volume of 2360 cc. boiled at 103.25 to 103.4° at 737 mm. and had n_D^{20} 1.4158. The residue of 1900 cc. had n_D^{20} 1.4290 (value for triisobutylene is 1.4315). The hold-up and loss amounted to 1250 cc. The temperature of the still walls as taken by a thermocouple varied from 107 to 212° during the distillation.

Refractionation of the Intermediate Fractions.—A charge of 4.5 liters from fractions 122–140 from the 27-ft. column with b. p. (737 mm.) 100.7 to 103.0° and n_D^{20} 1.4098 to 1.4150 was distilled through the 52-foot column. The refractive index of the mixture was 1.4123, corresponding to a 1:1 mixture of the isomers. The take-off was at the rate of 40-50 cc. per hour. Forty-eight *fractions* were taken. Fractions 1 to 15 with a volume of 1400 cc. boiled at 99.7 to 100.1° at 737 mm. and had refractive indices of 1.4080 to 1.4083. Fractions 30 to 42, volume 765 cc., had b. p. (737 mm.) 102.9 to 103.1° and n_D^{20} 1.4143 to 1.4154; fractions 43 to 48, volume 558 cc., b. p. (737 mm.) 103.3 to 103.4° and indices 1.4157 to 1.4158.

Refractionation of the Higher Isomer.—A charge of 3.7 liters from fractions 141 to 156 of the distillation in the 27-ft. column, with b. p. 103.0 to 103.5° and indices 1.4150 to 1.4158 was distilled through the 52-ft. column. The start of the distillation was made with a reflux ratio of 45:1. This was decreased when the index of refraction of the distillate rose to 1.4158. The following is a summary of this distillation, which established the identity and properties of the more difficultly obtainable isomer in diisobutylene.

Fractions	B. p., (737 mm.) (Cottrell), °C.	n_D^{20}	Cc.
1–5		1.4142–1.4145	263
6–10		1.4146–1.4150	270
11–15	102.9 to 103.1	1.4150–1.4152	295
16–27	103.15[7]	1.4152–1.4155	647
28–35	103.2–103.4	1.4157–1.4158	570
36–53	103.4	1.4158	1600
Residue		1.4180	650

[7] The distillation curve consistently showed a flat portion at this temperature. The nature of this material has not been determined. Its cooling curve shows it to differ decidedly from the pure 2,4,4-trimethylpentene-2. See Fig. 1, G.

Freezing Point Data.—A chromel–copel thermocouple was used to read the temperatures. A sample of about 20 cc. was placed in a glass-jacketed test-tube, which was put in a large Dewar flask containing liquid

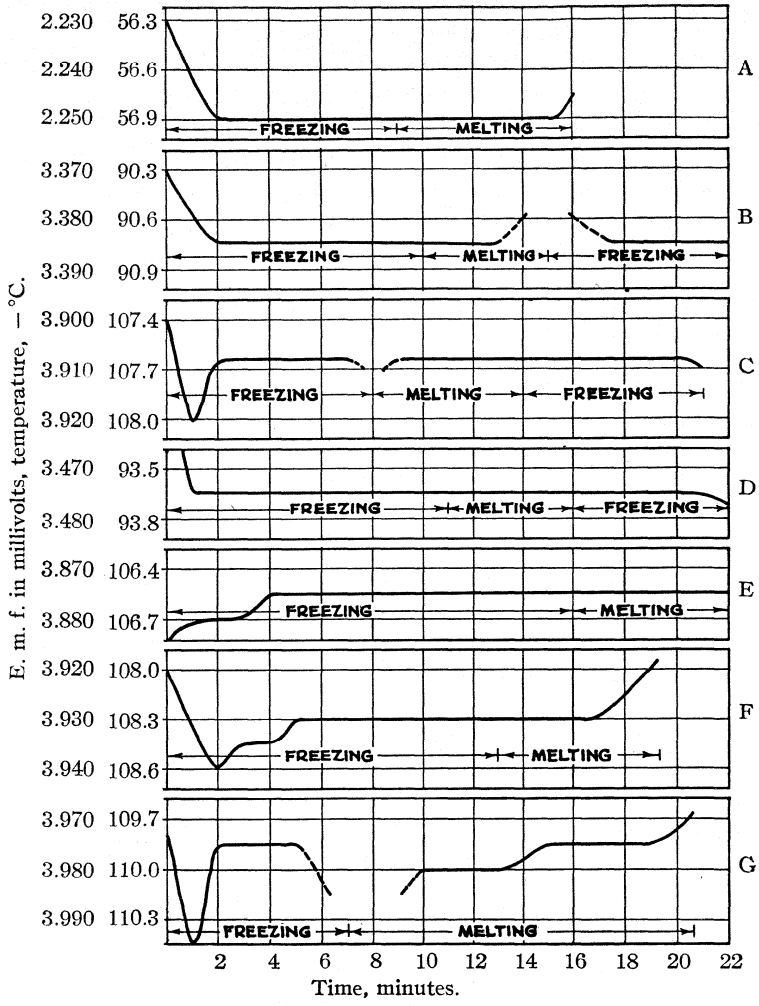


Fig. 1.—Freezing and melting curves.

	Substance	B. p. (760 mm.), °C.	n_D^{20}	F. p., m. p., °C.
A	*n*-Octane	125.4	1.3970	– 56.9
B	*n*-Heptane	98.4	1.3878	– 90.7
C	2,4,4-Trimethylpentane	99.3	1.3912	–107.7
D	2,4,4-Trimethylpentene-1	101.2	1.4082	– 93.6
E	2,4,4-Trimethylpentene-2	104.5	1.4158	–106.5
F	Isomorphic form of E	104.5	1.4158	–108.3
G	"Low fraction" of E	104.2	1.4150	–109.8 to –110.0

air. The sample was stirred very vigorously and the e. m. f. taken every twenty seconds with a Leeds and Northrup No. 8662 Portable, Double Range, Precision Potentiometer. The sample was cooled slowly until it was practically impossible to move the stirrer, then the glass-jacketed test-tube was transferred to an empty Dewar flask and the sample allowed to melt slowly. In this way freezing and melting curves were obtained, Fig. 1.

With the exception of 2,4,4-trimethylpentene-2, the substances did not supercool more than 0.3°, if at all. 2,4,4-Trimethylpentene-2, however, sometimes supercooled as much as 10°, despite the most vigorous stirring used. Ordinarily this isomer had a freezing point of 106.55°, but sometimes a value of 108.3° was obtained. Both were definite fixed points.

The thermocouple was calibrated at the following points

	E. m. f., millivolts	°C.
Mercury	1.568	− 38.9
n-Octane	2.250	− 56.9
Carbon dioxide snow	3.000	− 78.9
n-Heptane	3.385	− 90.7
2,4,4-Trimethylpentane, "iso-octane"	3.908	−107.7

Summary

1. The separation of diisobutylene into 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 has been accomplished by single distillations through the highly effective columns constructed for the separation of Pennsylvania petroleum into its constituents.

2. The purity of the isomers has been established by accurate determinations of their cooling curves.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE ISOMERS IN "DIISOBUTYLENE." III.[1] DETERMINATION OF THEIR STRUCTURE[2]

BY FRANK C. WHITMORE AND JAMES M. CHURCH

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Butlerow, the discoverer of diisobutylene, recognized it as a mixture of two isomeric octylenes, 2,4,4-trimethylpentene-1 (I) and 2,4,4-trimethylpentene-2 (II).[3] The oxidation products upon which this conclusion was based included acetone, acetic acid, formic acid, trimethylacetic acid, tertiary-butylacetic acid and methyl neopentyl ketone. Recently the

[1] See preceding article.

[2] Presented by James M. Church in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[3] Butlerow, *Ann.*, **189**, 46–83 (1877); *J. Russ. Phys.-Chem. Soc.*, **14**, 201 (1882); Wagner, *Ber.*, **21**, 1230 (1888); Prileshajew, *J. Russ. Phys.-Chem. Soc.*, **39**, 769 (1907).

presence of the two isomers has been established definitely by ozonolysis experiments.[4] These indicated (I) and (II) to be present in a ratio of approximately 4:1. The separation of the isomers in this Laboratory showed the lower-boiling isomer to be present in four times the amount of the higher-boiling product. This, taken in conjunction with the work of McCubbin and Adkins, indicated that the lower boiling isomer was (I). This would also agree with the generalizations of Boord and his co-workers[5] on the influence of the position of the double bond on the boiling points of isomeric olefins. Since some of the work on rearrangements in this Laboratory[6] necessitated a definite knowledge of the structure of the higher-boiling diisobutylene, the pure isomers were ozonized. The result was a complete confirmation of the conclusions drawn from the results of McCubbin and Adkins and from the separation of the isomers in this Laboratory.

The lower boiling isomer (b. p. 101.2° (760 mm.)) gave formaldehyde, methyl neopentyl ketone and a trace of tertiary-butylacetic acid but no acetone. It was thus proved to be 2,4,4-trimethylpentene-1.

The higher boiling isomer (b. p. 104.5° (760 mm.)) gave acetone, trimethylacetaldehyde and trimethylacetic acid but no formaldehyde. It was thus 2,4,4-trimethylpentene-2.

The absence of acetone and of formaldehyde in the ozonization of the samples of the lower and the higher boiling isomers, respectively, indicated the completeness of the separation of the two isomers by the special columns used.[7]

Since the literature contains almost no detailed directions for the ozonolysis of relatively simple olefins and no quantitative data on such processes, the present experiments are given in full detail.

Experimental

1. General Method of Ozonization and Hydrolysis of Ozonides.—An ozonizer similar to that of L. I. Smith[8] was used. Two sets of three Berthelot Pyrex ozonizer tubes were connected in parallel. The inner portion of each tube was filled with dilute copper sulfate solution. Into this dipped the inner electrodes each consisting of two heavy copper wires twisted together. The outer electrodes were two large strips of copper in the water-bath containing the ozonizer tubes. The current was supplied by a 10,000 volt "Neon sign" transformer. Oxygen from a cylinder was bubbled through concd. sulfuric acid, over activated alumina, and through a spray and dust tower full of glass wool. A flowmeter was used. When the rate was 15 liters per hour the exit gas from three tubes of the ozonizer contained 6 to 8% ozone. All connections were made by means of mercury-sealed cup joints. The olefins were dissolved in a low-boiling saturated hydrocarbon (b. p. 0–35°) supplied by the Viking Corporation of Charleston,

[4] McCubbin and Adkins, THIS JOURNAL, **52**, 2547 (1930).

[5] C. E. Boord, "Some Generalizations on the Physical Properties of Olefins," Buffalo Meeting, American Chemical Society, Sept. 2, 1931.

[6] See the following article.

[7] Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[8] Smith, THIS JOURNAL, **47**, 1844 (1925).

West Virginia. The solution was contained in a special tall 500-cc. ozonizing bottle with a sealed-in bubble tube. The exit tube was supplied with a rubber tube leading to a hood. As soon as ozone ceased to be absorbed by the olefin, the excess caused the rubber tube to crack off. This indication was as sensitive as the usual starch–potassium iodide test. The ozonizations were conducted at −10°.

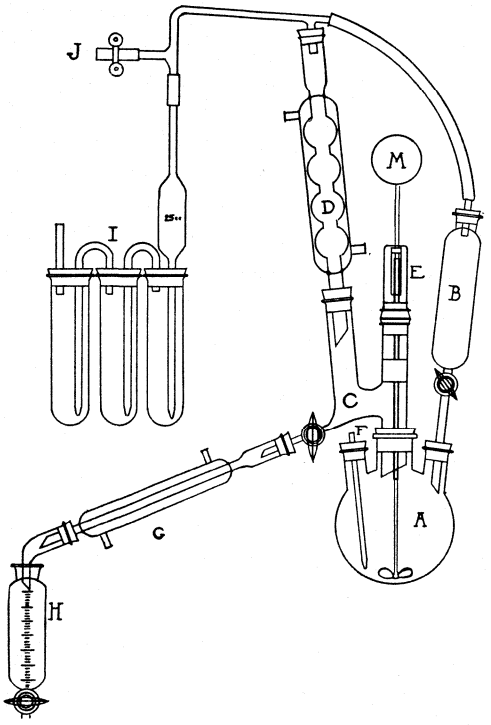

Fig. 1.—A, a 1000-cc. three-necked flask containing water, zinc and catalysts; B, dropping funnel containing liquid ozonide; C, special distilling adapter; D, reflux condenser held at desired temperature; E, mercury seal stirrer; F, entrance for nitrogen gas; G, water-cooled condenser; H, graduated receiver; I, absorption apparatus for volatile materials; J, emergency valve; M, motor.

The solvent was removed from the ozonide solution under reduced pressure at 35°. The clear, slightly yellow or colorless liquid ozonide was weighed. In a few isolated cases the ozonides decomposed violently. Consequently the containers were always kept in wire gauze holders. The hydrolysis of the ozonides was done in a special apparatus developed with P. A. Krueger of this Laboratory (Fig. 1). The liquid ozonide was added from a dropping funnel to a stirred boiling mixture of 300–500 cc. of water and an amount of zinc dust equivalent to the ozonide together with traces of hydroquinone and silver nitrate. A stream of nitrogen was used to carry the volatile products to a suitable condensing and scrubbing system. The aqueous layer of the distillate was added to the main flask and distilled through the system again until no more oily products formed. The final aqueous distillate was saved for testing for water-soluble products.

Separation, Identification and Estimation of the Ozonolysis Products.—The aqueous distillate was tested for formaldehyde, formic acid and acetone by standard methods.

The oily layer was fractionally distilled through a 70 × 1 cm. glass, indented, adiabatic (electrically heated and insulated with two glass jackets), total condensation, variable take-off column.[9]

Ozonolysis of the Lower-boiling Diisobutylene.—This is typical of many experiments with this substance. One-half mole (56 g.) of a sample of b. p. 100.1° (737 mm.), n_D^{20} 1.4082 and d_4^{20} 0.715 was dissolved in 300 cc. of the low-boiling hydrocarbon and ozonized at −10°; time, sixteen hours. Removal of the solvent at 35° gave 75.5 g. of a slightly greenish yellow liquid ozonide with a little solid product; yield, 94.5%. The ozonide was decomposed as outlined above. The process was very violent. The distillate contained 57 cc. of oil and 200 cc. of a water layer. The nitrogen gas was washed at 0° with 50 cc. of ether which was then used to extract the aqueous layer after the de-

[9] See THIS JOURNAL, p. 3451.

termination of formaldehyde in it. The total crude products obtained amounted to a yield of 93% based on the ozonide. Qualitative tests for formaldehyde with fuchsin reagent, Tollens' reagent and 1% aqueous resorcinol were obtained. Iodimetric titration showed 13.4 g. of formaldehyde or a yield of 94.6%. Three distillations of the oily product through the 70 × 1 cm. column gave the following fractions at 738 mm.

Fraction	B. p., °C.	Wt., g.	n_D^{20}
A 1	36–120	2.7	1.3994
2	120–123	2.9	1.4018
3	123–124.5	36.8	1.4030
4	124.5–180	3.6	1.4067
5	180–190	1.2	1.4116
6	Residue	3.7	1.4355

Fraction A 3 gave a semicarbazone which after two crystallizations from petroleum ether (b. p. 70–90°) melted at 176° (corr.), corresponding to the m. p. of the semicarbazone of methyl neopentyl ketone as obtained by McCubbin and Adkins.[4] Fraction A 5 gave an acid amide which was difficultly purified by crystallization from ethyl acetate and petroleum ether to give m. p. 130–131°. This was not lowered by mixing with the known amide of tertiary-butylacetic acid, m. p. 132°.

The low-boiling diisobutylene thus gave yields of formaldehyde and methyl neopentyl ketone of 94.6 and 67.8%, respectively, as well as a small amount of tertiary-butylacetic acid, thus proving it to be 2,4,4-trimethylpentene-1. The iodimetric titration of the aqueous solution gave no iodoform, proving the absence of acetone and consequently the absence of the high-boiling isomer in the material ozonized.

Ozonolysis of the Higher-boiling Diisobutylene.—A typical run was as follows. One-half mole (56 g.) of a sample of b. p. 103.4° (737 mm.), n_D^{20} 1.4158 and d_4^{20} 0.721 was ozonized as above. Considerable amounts of white solid separated in the apparatus, clogging the delivery tube at times. The crude ozonide weighed 69 g., a yield of 86.2%. It was a colorless oil containing a small amount of a white solid. This solid exploded when heated on a spatula. The ozonide was decomposed in the usual way. The reaction was even more violent than with the isomeric ozonide. The addition to the boiling decomposition mixture required three hours. The products were 37 cc. of oil and 150 cc. of aqueous distillate. The mixture in the decomposition flask was a thick grayish-white mass. Treatment with 100 cc. of 25% sulfuric acid and distillation gave an additional 14 cc. of oil. The total weight of oil was 41 g. This, with 13.9 g. of acetone found in the water layer, represented a yield of 88.8% based on the ozonide.

The aqueous layer gave no test for formaldehyde. The dibenzal derivative of acetone was obtained, m. p. 110°. Iodimetric titration showed the presence of 13.9 g. of acetone in the aqueous layer. Iodoform was formed.

The oily layer was separated by six distillations through the 70 × 1 cm. column. The final fractions obtained at 733 mm. were:

Fraction	B. p., °C.	Wt., g.	n_D^{20}
B 1	53–58	6.3	1.3652
2	58–72	1.4	1.3741
3	72–77	4.9	1.3808
4	77–121	2.5	1.3945
5	121–124	1.5	1.4028
6	124–158	3.8	1.4073
7	158–162	8.6	1.4107
8	Residue	2.4	1.4409

Fraction B 1 gave dibenzalacetone, m. p. 110°. The m. p. of a mixture with the known substance was 109°. Fraction B 3 gave the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, m. p. 210°, mixed m. p. 210°. Fraction B 7 gave the amide of trimethylacetic acid, m. p. 153°, mixed m. p. 151°. Most of this acid product was obtained from the acidification of the decomposition mixture. No semicarbazone could be obtained from Fraction B 5.

The high-boiling diisobutylene thus gave yields of acetone, trimethylacetaldehyde and trimethylacetic acid of 81.3, 13.2 and 21.5%, respectively, thus proving it to be 2,4,4-trimethylpentene-2. The absence of formaldehyde and methyl neopentyl ketone among the ozonolysis products showed the completeness of the separation from the low-boiling isomer.

Summary

1. The low-boiling and high-boiling isomers of diisobutylene have been proved to be 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2, respectively.

2. The completeness of the separation of these isomers is confirmed by the fact that neither gives ozonolysis products which would be expected from the other.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE DEHYDRATION OF SECONDARY CARBINOLS CONTAINING A NEOPENTYL SYSTEM. I. ISOPROPYL-*TERT.*-BUTYLCARBINOL. PRELIMINARY PAPER[1]

BY FRANK C. WHITMORE AND A. L. HOUK

RECEIVED MAY 17, 1932 PUBLISHED SEPTEMBER 5, 1932

The dehydration of this carbinol was studied because it presents three possibilities.[2] (1) Normal dehydration by the removal of the secondary hydroxyl and the tertiary hydrogen, similar to the dehydration of methylisopropylcarbinol to give trimethylethylene, would produce the higher boiling di-isobutylene, 2,4,4-trimethylpentene-2, which has been thoroughly characterized in this Laboratory.[3] (2) A shift of the tertiary hydrogen would given an organic "ion"[4] related to the two di-isobutylenes. This would be expected to lose a proton to give these two substances in the ratio of 4:1, the lower boiling isomer, 2,4,4-trimethylpentene-1, predominat-

[1] Presented by A. L. Houk in partial fulfilment of the requirements for the degree of Ph.D. at the Pennsylvania State College.

[2] This carbinol was prepared and dehydrated at Northwestern University in 1928 by H. C. Benedict, Jr. No definite knowledge of the resulting olefins was then obtained because of the inadequacy of the distillation equipment available; *cf.* Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[3] See preceding article.

[4] See *ibid.*, p. 3274.

ing.[5] (3) The shift of a methyl group from the neopentyl system would give an "ion" related to the 2,3,4-trimethylpentenes. Thus at least five different octylenes could be formed from the carbinol by known reactions.

At the time the present study of this carbinol was undertaken (1930), the current conception of alcohol rearrangements in this Laboratory followed the ideas of Meerwein[6] in regarding a true ionization of an acid derivative as the first step in such processes. It was argued, therefore, that a "dehydration" of the carbinol in the absence of acid and ionizing conditions might prevent rearrangement. The method used was to heat the Grignard complex (alcoholate) obtained from *tert.*-butylmagnesium chloride and isobutyraldehyde. Preliminary experiments showed that olefins could be thus formed by the elimination of XMgOH from similar Grignard products. It was expected, then, that the product would be the higher boiling diisobutylene, 2,4,4-trimethylpentene-2. Such was not the case. Decomposition of the Grignard complex of isopropyl-*tert.*-butylcarbinol by heat gave essentially the same complex mixture of olefins that was obtained from the carbinol by ordinary dehydration with sulfuric acid. None of the normal dehydration product was obtained in either case. It was thus concluded that the organic "ion" first formed was the same in both cases and did not depend on any ordinary process of ionization but was the result of the breaking of the $:\ddot{\underset{\cdot\cdot}{C}}:\ddot{\underset{\cdot\cdot}{O}}:$ linkage with the complete octet going with the oxygen atom, thus leaving the carbon with only six electrons.[7]

Isopropyl-*tert.*-butylcarbinol has been prepared by Faworsky[8] and by Conant and Blatt[9] from *tert.*-butylmagnesium chloride and isobutyraldehyde and by Haller and Bauer[10] by the reduction of pentamethylacetone with sodium and alcohol.

About two liters of the olefin mixture obtained from the Grignard complex was twice distilled through a 52-ft. adiabatic column using a reflux ratio of about 50:1.[11] Most of the material boiled above 105° and consequently could contain none of the di-isobutylenes. Moreover, the refractive indices of the fractions did not correspond to these substances. About 400 cc. distilled below 105° and had n_D^{20} 1.4070 to 1.4118. Repeated distillations through the 90 × 1.2 cm. adiabatic, partial condensation column[12] failed to give any fraction having the properties of 2,4,4-trimethylpentene-2 (b. p. 103.4° (737 mm.), n_D^{20} 1.4158). The only indication of a

[5] Unpublished results of S. N. Wrenn in this Laboratory.

[6] See THIS JOURNAL, p. 3277.

[7] See *ibid.*, p. 3278.

[8] Faworsky, *J. prakt. Chem.*, [2] **88,** 651 (1913).

[9] Blatt, THIS JOURNAL, **51,** 1227 (1929).

[10] Haller and Bauer, *Ann. chim. phys.*, [8] **29,** 317 (1913).

[11] For description of the column and its operation, see Fenske and co-workers, *Ind. Eng. Chem.*, **24,** 408 (1932).

[12] See THIS JOURNAL, p. 3453.

homogeneous fraction was obtained with b. p. 92–93° (730 mm.) and n_D^{20} 1.4060. Since these properties corresponded to no probable product it was assumed to be an azeotropic mixture. It was mixed with pure tertiary butyl alcohol and fractionated. The main fractions were washed with water to remove the alcohol, dried and distilled. The product had a b. p. of 101.5° (738 mm.) and n_D^{20} 1.4084 corresponding to the properties of the lower di-isobutylene, 2,4,4-trimethylpentene-1 (b. p. 100.1° (737 mm.), n_D^{20} 1.4082). The original two liters of olefin mixture contained less than 150 cc. of this azeotropic mixture which in turn contained less than 100 cc. of the 2,4,4-trimethylpentene-1. The other olefins have not been identified. No trace of the normal dehydration product has been obtained.

Experimental

Preparation of the Grignard Complex, $(CH_3)_3CCH(OMgCl)CH(CH_3)_2$.—This was done in 6–8 mole runs. A typical 6-mole run was as follows. To 144 g. of freshly turned magnesium in a 3-liter flask equipped with a stirrer, a reflux condenser and a dropping funnel, were added a crystal of iodine and then 20–25 cc. of a solution of 555 g. of *tert.*-butyl chloride in 750 cc. of dry ether. As soon as the reaction began, 300 cc. of dry ether was added, the stirrer was started and 750 cc. of the halide solution was added at such a rate as to maintain gentle refluxing. The remainder of the halide solution was diluted with 450 cc. of dry ether and added similarly. The solution was then heated for one hour on a steam-bath. Titration of a sample showed a yield of 85% of Grignard reagent.[13] The solution was cooled to 15° and a solution of 327 g. of isobutyraldehyde in an equal volume of dry ether was added at such a rate as to cause gentle refluxing. The mixture was warmed with stirring on a water-bath for three hours.

Decomposition of the Grignard Complex by Heat.—The material from one run was placed in two 1-liter distilling flasks provided with thermometers and heated in baths of copper shot. After gradual heating to remove the ether, the baths were heated slowly to the full heat of a large Méker burner. The baths were then at 350–400°. The highest boiling point registered by the distilling products was 140°. The fraction collected contained much ether. It was highly unsaturated.

Fractionation of the Olefin Mixture.—The combined products from runs starting with a total of 48 moles of *tert.*-butyl chloride were fractionated through the 52 ft. column.[11]

After the ether had been removed, the following fractions were obtained.

Fraction	Pressure	B. p., °C.	Amt., cc.	n_D^{20}
A 1, 1a, 1b	724	49–94	500	1.3880–1.4077
2–12	728	94–105.4	370	1.4081–1.4118
13–40	735	105.4–129.4	600	1.4120–1.4259
41, 44	740	129.4–135	100	1.4259–1.4140

No cuts were obtained having the boiling point and refractive index for any known octylene. Fractions A 2–4 were distilled through the 90 × 1.2 cm., *partial condensation* column[14] at 730 mm.

[13] This method of making the *tert.*-butyl Grignard reagent is due to A. R. Lux of this Laboratory. It gives somewhat better yields than the ordinary method.

[14] See THIS JOURNAL, p. 3453.

Fraction	B. p., °C.	Amt., cc.	n_D^{20}
B 1–3	81–91	16	1.4020–1.4061
4–8	91–93	40	1.4052–1.4054
9–16	93–103.2	40	1.4076–1.4112

Fractions B 6–7 were mixed with 20 cc. of *tert.*-butyl alcohol (m. p. 23°) and distilled through a 70 × 1.2 cm. indented, adiabatic, total condensation column[15] at 738 mm.

Fraction	B. p., °C.	Amt., cc.	After washing with water and drying Amt., cc.	B. p. (Cottrell), cc.	n_D^{20}
C 1	72–76	1.5	0		
2–6	78–82	26	11	101.5 (738 mm.)	1.4084
7	82–87	2	1.3		1.4095
8	Residue	6	2		1.4032

Fractions C 2–6 thus had the correct boiling point and refractive index for 2,4,4-trimethylpentene-1,[16] a rearranged product.

Fractions A 8–10 were distilled through the 90 × 1.2 cm. partial condensation column at 727 mm.

Fraction	B. p., °C.	Amt., cc.	n_D^{20}
D 1–4	85–96	21	1.4012–1.4052
5–19	101–104.4	91	1.4080–1.4120

No fraction having the properties of a diisobutylene was obtained.

Dehydration of Isopropyl-*tert.*-butylcarbinol by Sulfuric Acid.—Two runs of the Grignard product from a total of 12.2 moles of isobutyraldehyde were decomposed with ammonium chloride solution in the usual way. The product consisted of a 35% yield of the carbinol, b. p. 148–150° (740 mm.), n_D^{20} 1.4288, a similar yield of isobutyl alcohol and a 7.5% yield of a solid material which melted at 51–52° after crystallization from petroleum ether. A 1.5% yield of hexamethylethane was also isolated.

A mixture of 117 g. of the carbinol and 5.5 cc. of concd. sulfuric acid was heated under a 40 × 1.8 cm. column until olefin began to distil. The pressure was then reduced slightly and the olefin and water were distilled as fast as formed. When half the calculated amount of water had distilled, the process was stopped, the residue was washed with potassium carbonate solution and added to the distillate. After drying, the product was distilled through the 70 × 1.2 cm. column. The boiling points of 15 fractions ranged from 100 to 148° and the refractive indices from 1.4076 to 1.4288. Two similar dehydrations and distillations were carried out. The average distribution of the products in the three runs was as follows.

Per cent.	B. p., °C.	n_D^{20}
4.5	100–105	1.4076–1.4153
45	105–114	1.4146–1.4254
50	114–148	1.4222–1.4288

As with the product from thermal decomposition of the Grignard complex, no fraction was obtained having the boiling point and refractive index of the normal dehydration product.

Finally, all the remaining fractions boiling up to 120° from the first distillation through the 52 ft. column were combined and distilled once more through that column at 724 mm.

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[15] See THIS JOURNAL, p. 3451.

[16] See preceding article.

Fraction	B. p., °C.	Amt., cc.	n_D^{20}
E 1–10	64–90	470	1.3990–1.4066
11–13	94–104.4	185	1.4096–1.4112
14–22	104.4–112.9	335	1.4122–1.4210

Again, no fraction was obtained having the properties of 2,4,4-trimethylpentene-2. This study is being continued.

Summary

1. Isopropyl-*tert.*-butylcarbinol presents a variety of possible dehydrations.

2. None of the normal dehydration product has been obtained either by dehydration of the carbinol or by thermal decomposition of the Grignard complex from which it is prepared.

3. About 5% of 2,4,4-trimethylpentene-1 has been isolated from the complex olefin mixture.

4. The study of the other dehydration products of the carbinol is being continued.

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[CONTRIBUTION FROM THE MAYO FOUNDATION, ROCHESTER, MINNESOTA]

SOME DERIVATIVES OF DIIODOTYROSINE AND THYROXINE. THE ACTION OF ACETIC ANHYDRIDE ON DIIODOTYROSINE[1]

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The methyl ethers of diiodotyrosine and thyroxine were prepared for a study of their physiologic activity. In general, the procedure used by Karrer[3] for the preparation of O-methyl-*l*-tyrosine was followed. The color reaction with nitrous acid, described by Kendall,[4] which depends on the presence of two iodine atoms ortho to a free hydroxyl group, was conveniently used to determine the completion of the methylation. The spontaneous decomposition of acetylthyroxine, observed by Kendall,[4] which occurs when an aqueous solution of the sodium salt is neutralized, presented some difficulty. This was overcome by performing this step in the procedure in 80% alcohol.

In connection with the synthesis of the methyl ether of diiodotyrosine, it was necessary to establish the identity of N-acetyldiiodotyrosine. The levo form of this derivative was obtained by treating the sodium salt of di-

[1] Abridgment of thesis submitted to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry, 1932.

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[3] Karrer, *Helv. Chim. Acta*, 5, 469 (1922).

[4] Kendall, "Thyroxine," Chemical Catalog Co., New York, 1929.

iodo-*l*-tyrosine with acetic anhydride. In a second preparation, the methyl ester of diiodotyrosine was treated with acetic anhydride and, also, with acetyl chloride. Characterization of the products obtained in each case leaves no doubt that the compound described by Wheeler and Jamieson[5] is not the simple acetyl of diiodotyrosine. The racemic form of the monoacetyl was obtained by racemization of the levo derivative, according to the procedure of Bergmann and Zervas,[6] and was characterized by several of its derivatives.

Wheeler and Jamieson obtained the compound, described by them as the monoacetyl of diiodotyrosine, by boiling diiodotyrosine with a large excess of acetic anhydride. Although this treatment usually produces the azlactone of the amino acid used, instead of the simple acetyl, the insolubility of their product in alcohol and its high decomposition point (225°) are not characteristic of azlactones. The preparation of the azlactones of monoacetyl- and diacetyldiiodotyrosine, described here, showed that their product is not a simple azlactone.

As shown by Bergmann and co-workers[6,7,8] and by Nicolet,[9] amino acids, containing an especially active group other than the amino and carboxyl groups, do not form the corresponding azlactones when treated with excess acetic anhydride. Because of its highly acidic hydroxyl group, the reaction of diiodotyrosine with excess acetic anhydride might, therefore, be expected to be abnormal.

Further investigation of the product obtained by Wheeler and Jamieson showed it to be insoluble in all the usual organic solvents, in dilute and concentrated acids (except concentrated sulfuric acid), readily soluble in aniline, phenol and pyridine, rapidly decomposing in the latter. The compound is optically inactive, and is readily hydrolyzed by dilute sodium hydroxide to N-acetyldiiodo-*d,l*-tyrosine. The iodine content of numerous preparations varied from 53.27 to 54.61%. After further purification, by precipitating the product from phenol with alcohol, the analyses were in good agreement: C, 28.58; H, 2.12; I, 54.59. The decomposition point and other properties remained unchanged after this purification treatment.

From the molecular weight determination and elementary analysis, the empirical formula for the compound is approximately $C_{24}H_{18}O_6N_2I_4$. From the evidence at hand the substance is an anhydride of N-acetyldiiodotyrosine with the hydroxyl groups only partially acetylated. The characteristic yellow color of the nitrous acid color reaction, which turns to pink on making alkaline with ammonium hydroxide, may be noted on the particles

[5] Wheeler and Jamieson, *Am. Chem. J.*, **33**, 365 (1905).
[6] Bergmann and Zervas, *Biochem. Z.*, **203**, 280 (1928).
[7] Bergmann, Stern and Witte, *Ann. Chem.*, **449**, 277 (1926).
[8] Bergmann and Köster, *Z. physiol. Chem.*, **159**, 179 (1926).
[9] Nicolet, THIS JOURNAL, **52**, 1192 (1930).

of the compound suspended in water. N-Acetyldiiodotyrosine forms the anhydride at a more rapid rate than does diiodotyrosine.

Of the several structures possible for an anhydride consisting of two molecules of an amino acid, the diketopiperazine structure was most seriously considered. Accordingly, the acetylated levo diketopiperazine of diiodotyrosine was prepared, but was not found to resemble the anhydride under investigation in any way. However, the racemic diketopiperazine, which proved to be identical with the anhydride reported by West,[10] was more promising inasmuch as its physical properties, particularly a high decomposition point and insolubility in acetic anhydride, alcohol and all other ordinary organic solvents, agree well with those of the compound described by Wheeler and Jamieson. Attempts to acetylate this diketopiperazine failed, however, owing to its complete insolubility in acetic anhydride, and suitable solvents. It was not acetylated when heated to 150° in a sealed tube, with excess acetic anhydride.

Further, the anhydride reacts with concentrated ammonium hydroxide, phenol, and sodium ethylate to form the amide, phenyl ester, and ethyl esters, respectively, of diiodotyrosine, which were recovered in yields of 70 to 80%. From these reactions structures II and III, suggested by Levene and Steiger[11] for their double azlactone of acetyl-α-aminoisobutyric acid, might be considered as possibilities for the structure of the diiodotyrosine complex providing both molecules involved in these configurations would react in the same way with the reagents mentioned above.

That the presence of the highly acidic hydroxyl group of diiodotyrosine determines the formation of the anhydride is evidenced by the fact that diacetyldiiodotyrosine follows the normal course of reaction to yield the corresponding azlactone. If the reaction of diiodotyrosine with excess acetic anhydride is carried out in the presence of anhydrous sodium acetate, the hydroxyl groups are completely acetylated and the azlactone formed instead of the condensation product.

It seems probable that the anhydride is formed through the azlactone of acetyldiiodotyrosine, for the azlactone was isolated from the amorphous product obtained when the reaction was stopped just as the condensation product began to separate from the acetic anhydride. When this amorphous soluble substance was dried and further treated with acetic anhydride, the condensation product was formed.

Preliminary experiments have shown that substitution of the hydroxyl group diminishes the effect of diiodotyrosine and thyroxine on amphibian metamorphosis, whereas O-methylthyroxine produces no effect when administered intravenously or subcutaneously to a normal individual, in amounts comparable with the physiologic dose of thyroxine.

[10] West, *Proc. Soc. Exptl. Biol. Med.*, **23**, 629 (1926).

[11] Levene and Steiger, *J. Biol. Chem.*, **93**, 581 (1931).

Experimental

O-Acetyl-N-acetyldiiodo-*l*-tyrosine.—Ten grams of pure diiodo-*l*-tyrosine was dissolved in 100 cc. of 2 *N* sodium hydroxide. To this solution, while shaking and externally cooling, 11.0 cc. of acetic anhydride was added slowly. After standing at room temperature for two hours, the solution no longer gave a color reaction with nitrous acid. On acidifying the solution with 35 cc. of 6 *N* hydrochloric acid, the diacetyl was precipitated in an amorphous form. This was filtered out and dissolved in about 100 cc. of hot alcohol. If this solution showed any color, it was treated with a small amount of charcoal and filtered. Hot water, containing a few cubic centimeters of hydrochloric acid, was added until the solution became turbid. On cooling in the refrigerator, the product separated in long colorless blade-like crystals. After drying these in a vacuum over concentrated sulfuric acid, and then in a high vacuum heated to 110°, they melted at 186 to 187° (uncorr.), and gave no color reaction with nitrous acid; yield, 9.3 g.

Anal. Calcd. for $C_{13}H_{12}O_5NI_2$: C, 30.17; H, 2.51; I, 49.12; neut. equiv. (150 mg. in alcohol) 2.9 cc. of 0.1 *N* NaOH (phenolphthalein). Found: C, 30.15; H, 2.55; I, 49.02; neut. equiv., 2.84 cc. of 0.1 *N* NaOH. *Rotation.* $[\alpha]^{30°}_{546}$ +21.52; (1.44% in absolute alcohol).

O-Acetyl-N-acetyldiiodo-*d,l*-tyrosine.—Three grams of O-acetyl-N-acetyldiiodo-*l*-tyrosine was dissolved in 30 cc. of glacial acetic acid containing 0.6 g. (mol. equiv.) of acetic anhydride. After refluxing the solution for one hour, the greater part of the acetic acid was removed under diminished pressure and the residue taken up with water. The undissolved material was filtered out, and recrystallized from hot 25% alcohol. The optically inactive diacetyl was thus obtained in long colorless blade-like crystals which melted at 186°.

Anal. Found: C, 30.19; H, 2.60; I, 48.99; neut. equiv., 150 mg. required 2.84 cc. of 0.1 *N* NaOH.

N-Acetyldiiodo-*l*-tyrosine.—Two grams of the diacetyldiiodo-*l*-tyrosine was dissolved in 150 cc. of alcohol containing 20 cc. of 5 *N* sodium hydroxide. The alcohol was replaced on the steam-bath with water, maintaining a volume of about 100 cc. After standing at room temperature for several hours, the solution was slowly poured into 200 cc. of hot water containing 10 cc. of 20% hydrochloric acid. On cooling, the slightly yellow product separated. This was filtered out, its alcoholic solution treated with a small amount of charcoal and filtered. On adding hot water to the filtrate to the point of turbidity, and then cooling in the refrigerator, the product separated in crystalline form as irregular or hexagonal plates. These were readily soluble in alcohol, ethyl acetate and acetone, but insoluble in ether and cold water. After drying in a high vacuum, heated to about 80°, the compound turned yellow at 185° and decomposed, with frothing, at 198 to 200°; yield, 1.6 g. Both monoacetyl and diacetyldiiodo-*l*-tyrosine hold tenaciously to one-half molecule of water as determined by iodine analyses before and after heating in a high vacuum.

Anal. Calcd. for $C_{11}H_{10}O_4NI_2$: C, 27.78; H, 2.32; I, 53.45; neut. equiv. (220.8 mg. in alcohol), 9.28 cc. of 0.1 *N* NaOH (phenolphthalein). Found: C, 27.70; H, 2.34; I, 53.42; neut. equiv., 9.3 cc. of 0.1 *N* NaOH. *Rotation.* $[\alpha]^{30°}_{546}$ +34.54° (1.44% in absolute alcohol).

This derivative was also prepared by treating the methyl ester of diiodo-*l*-tyrosine with both acetyl chloride and acetic anhydride. The products thus obtained were identical with that described above.

The methyl ester of N-acetyldiiodo-*l*-tyrosine was prepared by treating the solution of the above product in absolute methyl alcohol with dry hydrochloric acid. The solution was neutralized and poured into water to precipitate the product. On recrystalliza-

tion from hot dilute alcohol, the methyl ester was obtained in long, colorless, needle-like crystals which melted at 152 to 153.5°, and proved to be identical with the products obtained from the reaction of the methyl ester of diiodo-*l*-tyrosine with acetyl chloride or acetic anhydride.

Anal. Calcd. for $C_{12}H_{13}O_4NI_2$: C, 29.44; H, 2.65; I, 51.94; neut. equiv. (150 mg. in alcohol), 3.07 cc. of 0.1 *N* NaOH (phenolphthalein). Found: C, 29.40; H, 2.62; I, 51.82; neut. equiv., 3.03 cc. of 0.1 *N* NaOH.

N-Acetyldiiodo-*d,l*-tyrosine.—This compound was obtained by hydrolysis of the racemic diacetyl of diiodotyrosine under the same conditions as was the levo isomer obtained from the optically active diacetyl. The compound crystallized from hot dilute alcohol in microscopic hexagonal plates which turned brown at about 185°, and decomposed, with frothing, at 205 to 206°, when heated at the same rate as was the levo isomer. It is less soluble in alcohol and ethyl acetate than is the levo form. The methyl ester of the inactive acetyl was obtained as long meshed, needle-like crystals which melted at 136 to 137°.

Anal. Found: C, 29.43; H, 2.63; I, 51.75; neut. equiv. (150 mg. in alcohol), 3.08 cc. of 0.1 *N* NaOH (phenolphthalein).

The ethyl ester crystallized from hot dilute alcohol in clusters or rosets of short needle-like crystals which melted at 140 to 141°.

Anal. Calcd. for $C_{13}H_{15}O_4NI_2$: C, 31.01; H, 2.98; I, 50.49; neut. equiv. (150 mg. in alcohol), 2.97 cc. of 0.1 *N* NaOH (phenolphthalein). Found: C, 30.89; H, 3.00; I, 50.38; neut. equiv., 2.93 cc. of 0.1 *N* NaOH.

O-Methyl-N-acetyldiiodo-*l*-tyrosine.—To a solution of 3.0 g. of N-acetyldiiodo-*l*-tyrosine in 15 cc. of alcohol containing 1.0 cc. of 5 *N* sodium hydroxide were added 0.5-cc. portions of dimethyl sulfate, alternately, with 1.0-cc. portions of 5 *N* sodium hydroxide, while shaking vigorously and allowing the heat of reaction to subside between each addition of the reagents. A total of 5 cc. of alkali and 2.5 cc. of dimethyl sulfate was added before the reaction solution gave a negative nitrous acid color reaction. About 15 cc. of alcohol was then added and the solution acidified with 20% hydrochloric acid. On pouring this solution into 100 cc. of hot water containing 2 cc. of hydrochloric acid, and cooling, the product separated in crystalline form. It was redissolved in alcohol, and treated with charcoal. The filtrate from the charcoal was poured slowly into about 300 cc. of hot water containing 1 cc. of concentrated hydrochloric acid. The methyl ether separated as colorless, microscopic leaves, which, after drying in a desiccator over concentrated sulfuric acid, melted at 207 to 208°, without decomposition. The product gave no color reaction with nitrous acid and was readily soluble in methyl alcohol, ethyl alcohol, ethyl acetate and acetone, sparingly soluble in cold water and insoluble in ether. The yield was 2.54 g.

Anal. Found for $C_{12}H_{13}O_4NI_2$: C, 29.40; H, 2.72; I, 51.83; neut. equiv. (150 mg. in alcohol), 3.03 cc. of 0.1 *N* NaOH (phenolphthalein). *Rotation.* $[\alpha]_{546}^{28.5}$ +14.5° (1.44% in absolute alcohol).

O-Methyldiiodo-*l*-tyrosine.—Three grams of O-methyl-N-acetyldiiodo-*l*-tyrosine was dissolved in 40 cc. of alcohol containing 30 cc. of 10% sulfuric acid. The alcohol was evaporated on the steam-bath and the aqueous solution heated at 90 to 100° for sixteen hours. On removing the alcohol, much of the material separated from solution but gradually redissolved after several hours of heating. The acid solution was evaporated to dryness under diminished pressure, and the residue dissolved in the smallest possible amount of alcohol. About 100 cc. of water was added and the methyl ether precipitated by making the solution neutral to litmus with sodium bicarbonate. The product was filtered out, dissolved in hot water with the aid of a few drops of acetic acid,

and this solution was treated with charcoal. On filtering and cooling, the methyl ether was obtained as colorless, meshed, needle-like crystals which gave a negative nitrous acid color reaction, decomposed at 204 to 206° and were insoluble in water, sparingly soluble in ethyl alcohol.

Anal. Calcd. for $C_{10}H_{11}O_3NI_2$: C, 26.85; H, 2.48; I, 56.82; neut. equiv. (150 mg. in alcohol), 3.35 cc. of 0.1 *N* NaOH (phenolphthalein). Found: C, 26.78; H, 2.49; I, 56.58. *Rotation.* $[\alpha]_{546}^{23.5}$ −3.2 (2.5% in 5% NaOH).

The sodium salt of O-methyldiiodo-*l*-tyrosine was obtained from 15% sodium hydroxide in the form of large rectangular plates.

Reaction of the Condensation Product of Acetyldiiodotyrosine: with Sodium Hydroxide.—One gram of the anhydride was allowed to stand at room temperature with 25 cc. of 0.5 *N* sodium hydroxide. The suspension was occasionally shaken and kept in the dark. The material was completely dissolved at the end of twenty hours and was precipitated by acidifying the solution with dilute hydrochloric acid. The precipitate, dissolved in alcohol, was treated with charcoal. The alcoholic solution was then poured into 100 cc. of hot acidulated water. On cooling, the product crystallized out in irregular or hexagonal plates which turned brown at 185° and decomposed with frothing at 206°; yield, 0.85 g. From the elementary analysis, neutral equivalent, "mixed" melting point, preparation of its methyl ester, and its general physical properties, this compound proved to be N-acetyldiiodo-*d,l*-tyrosine, described above. On heating with a large excess of acetic anhydride, the condensation product was again obtained.

With Sodium Ethylate.—To 10 cc. of absolute ethyl alcohol, to which had been added 75 mg. of metallic sodium, 1.5 g. of the anhydride was added. After shaking for fifteen minutes, the substance was completely dissolved to form a clear, yellow solution. This was acidified with a few drops of concentrated hydrochloric acid and then poured into several volumes of hot water. On cooling, 1.2 g. of the ethyl ester of acetyldiiodo-*d,l*-tyrosine separated in sheaves and rosets of short needles.

With Concentrated Ammonium Hydroxide.—A suspension of 2.0 g. of the anhydride in 30 cc. of concentrated ammonium hydroxide was allowed to stand at room temperature for seventy-two hours with occasional shaking. The resulting solution was filtered, aerated and then acidified with dilute hydrochloric acid. The precipitate obtained crystallized from alcohol in microscopic plates which darkened at 195° and decomposed at 204 to 206°; yield, 1.45 g. The substance gave a positive color reaction with nitrous acid, and readily yielded ammonia when gently warmed with dilute sodium hydroxide. From the latter reaction and the following analyses, this was identified as the amide of N-acetyldiiodo-*d,l*-tyrosine. It is only moderately soluble in cold alcohol, readily soluble in hot alcohol and insoluble in ether, chloroform, benzene and water.

Anal. Calcd. for $C_{11}H_{12}O_3N_2I_2$: C, 27.84; H, 2.74; N, 5.90; I, 53.58; neut. equiv. (150 mg. in alcohol), 3.15 cc. of 0.1 *N* NaOH (phenolphthalein). Found: C, 27.79; H, 2.70; N, 5.82; I, 53.48; neut. equiv., 3.15 cc. of 0.1 *N* NaOH.

With Phenol.—A solution of 3.0 g. of the acetyl anhydride in 15 g. of phenol was heated at the boiling point of the solvent for five minutes. The excess phenol was removed by distillation in a vacuum. The residual oil was washed with a small amount of cold ether and dissolved in alcohol. The alcoholic solution was treated with charcoal. After filtering out the charcoal, the product was precipitated from the alcohol with water, and was thus obtained as a white, non-crystalline powder which would not crystallize from dilute alcohol nor on spontaneous evaporation of its alcoholic solution. It melted indefinitely between 95 and 115°, and gave a positive nitrous acid color reaction. On allowing a solution of this substance in normal sodium hydroxide to stand at room temperature for a short time, N-acetyldiiodo-*d,l*-tyrosine and phenol were recovered.

The substance was undoubtedly a mixture of the phenyl esters of monoacetyl and diacetyldiiodotyrosine, containing approximately 65% of the latter, as calculated from the following analyses.

Anal. Calcd. for $C_{17}H_{15}O_4NI_2$: C, 38.44; H, 2.72; I, 46.18; neut. equiv. (200 mg. in alcohol), 3.37 cc. of 0.1 *N* NaOH (phenolphthalein). Calcd. for $C_{19}H_{17}O_5NI_2$: C, 37.09; H, 2.86; I, 42.76. Found: C, 37.95; H, 2.77; I, 43.82; neut. equiv., 1.20 cc. of 0.1 *N* NaOH.

Azlactone of N-Acetyldiiodo-*d,l*-tyrosine.—Three grams of diiodotyrosine was gently heated with 15 cc. of acetic anhydride. As soon as the resulting solution showed any turbidity due to the separation of the acetyl anhydride of diiodotyrosine, the solution was quickly cooled in an ice-bath, and then filtered free of the small amount of the double anhydride already formed. On adding several volumes of cold water to the filtrate, a yellow amorphous mass separated immediately. This was soluble in alcohol and ethyl acetate, and, after drying, yielded the acetyl anhydride when treated again with excess acetic anhydride.

The amorphous substance was dissolved in as small an amount of hot chloroform as possible, and petroleum ether added carefully, to precipitate the yellow material. On filtering out the latter, and adding more petroleum ether, a white, flocculent precipitate was obtained. This was dissolved in chloroform. On allowing the solvent to evaporate spontaneously, the product crystallized out in short rods which sintered at 75° and melted at 135 to 138°. The compound gave a strongly positive color reaction with nitrous acid, and on titrating it in alcohol with sodium hydroxide, using phenolphthalein as the indicator, the alkali was neutralized rapidly, at first, to give a temporary end-point, and then more slowly until a permanent end-point was reached after several hours when two equivalents of sodium hydroxide had been added. Thus, the compound titrated typically like an azlactone. It reacted with ammonia to form the amide of N-acetyldiiodo-*d,l*-tyrosine and was slowly hydrolyzed to the monoacetyl.

Anal. Calcd. for $C_{11}H_9O_3NI_2$: C, 28.66; H, 1.97; I, 55.58; neut. equiv. (150 mg. in alcohol), 6.3 cc. of 0.1 *N* NaOH (phenolphthalein). Found: C, 28.58; H, 1.93; I, 55.43; neut. equiv., 6.23 cc. of 0.1 *N* NaOH.

Azlactone of O-Acetyl-N-acetyldiiodo-*d,l*-tyrosine.—This was obtained by heating diacetyldiiodo-*l*-tyrosine for one hour at 100° with 15 cc. of acetic anhydride. The excess acetic anhydride was removed by evaporation under diminished pressure, the last part being removed by repeated evaporation in a vacuum with xylene. The residual sirup was dissolved in a small amount of chloroform, and the yellow impurities precipitated by careful addition of petroleum ether. Further addition of petroleum ether precipitated the azlactone, which was finally obtained by allowing its chloroform solution to evaporate spontaneously, as stout prisms which sintered at 60°, melted at 87 to 89° and gave no color reaction with nitrous acid. The product titrated with alkali like a typical azlactone, formed the amide of acetyldiiodotyrosine when treated with concentrated ammonium hydroxide at room temperature, and was slowly hydrolyzed, on standing with water for two or three days, to diacetyldiiodotyrosine. Like the azlactone of acetylphenylalanine,[7] it is comparatively stable to alcohol.

Anal. Calcd. for $C_{13}H_{11}O_4NI_2$: C, 31.20; H, 2.20; I, 50.90. Found: C, 31.31; H, 2.22; I, 50.79.

O-Methyl-N-acetyl-*d,l*-thyroxine.—To a solution of 400 mg. of acetyl-*d,l*-thyroxine in 25 cc. of alcohol containing 1.0 cc. of 5 *N* sodium hydroxide, were added 0.5-cc. portions of dimethyl sulfate, alternately, with 1.0-cc. portions of 5 *N* sodium hydroxide while shaking. The solution no longer gave a color reaction with nitrous acid, after 5 cc. of 5 *N* sodium hydroxide and 2.5 cc. of dimethyl sulfate had been used. The alcoholic

solution was acidified with 3 cc. of 20% hydrochloric acid. If this neutralization is carried out in aqueous solution or in the absence of sufficient alcohol, a decomposition of the methylated product occurs with the liberation of iodine. The acidified solution was slowly poured into 175 cc. of water at 90°. After standing in the refrigerator for several hours, the separated product was redissolved in 40 cc. of alcohol and treated with charcoal. The filtrate from the charcoal was poured into 200 to 250 cc. of hot water containing 2 cc. of concentrated hydrochloric acid, and the alcohol removed on the steam-bath. On cooling, the acetyl of the methyl ether of thyroxine separated in tufts of short needles which softened at 205° and melted, without decomposition, at 214 to 217°. The nitrous acid color reaction was negative; yield, 355 mg.

Anal. Calcd. for $C_{18}H_{15}O_5NI_4$: C, 25.93; H, 1.80; I, 60.98. Found: C, 25.82; H, 1.82; I, 60.32.

O-Methyl-*d,l*-thyroxine.—In a large Pyrex tube, 200 mg. of O-methyl-N-acetyl-*d,l*-thyroxine was dissolved in 15 cc. of alcohol containing 0.5 cc. of 5 *N* sodium hydroxide. The alcohol was replaced with water on the steam-bath and the total volume made up to 20 cc. with water containing 3.5 cc. of 5 *N* sodium hydroxide to make a solution of 4% sodium hydroxide. The solution was heated at 100° for twenty-four hours, the test-tube being fitted with a one-holed rubber stopper carrying a large pipet to act as a reflux condenser. After cooling, 3 cc. of concentrated sodium hydroxide was added, and the solution allowed to stand in the refrigerator for several hours. The sodium salt, which separated, was centrifuged out, dissolved in 15 to 20 cc. of alcohol, the solution acidified with 20% hydrochloric acid, and then poured into 200 cc. of hot water to precipitate the product. For purification, the methyl ether was dissolved in hot alcohol, treated with a small amount of charcoal, and obtained in the form of long, meshed needles after the addition of several volumes of hot water to the alcoholic filtrate. These showed no color reaction with nitrous acid and decomposed with frothing at 210 to 213°. The methyl ether is insoluble in water, ether and chloroform, but moderately soluble in alcohol when freshly precipitated from solution and still moist.

Anal. Calcd. for $C_{16}H_{13}O_4NI_4$: C, 24.27; H, 1.64; I, 64.22. Found: C, 24.20; H, 1.69; I, 64.09.

Summary

The syntheses of the following are described: O-methyl-, O-methyl-N-acetyl, N-acetyl- and its methyl ester and O-acetyl-N-acetyl-, diiodo-*l*-tyrosine; N-acetyldiiodo-*d,l*-tyrosine and its amide, azlactone and methyl, ethyl and phenyl esters; O-acetyl-N-acetyl-diiodo-*d,l*-tyrosine and its azlactone; O-methyl- and O-methyl-N-acetyl-, *d,l*-thyroxine.

The compound described in the literature as acetyldiiodotyrosine is shown to be a condensation product resulting from the action of excess acetic anhydride on diiodotyrosine and involving two molecules of acetyldiiodotyrosine. Some chemical and physical properties of this product are described, and its structure is considered.

ROCHESTER, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STUDIES OF ORGANIC LEAD COMPOUNDS. IV. THE USE OF LITHIUM DERIVATIVES IN THE SYNTHESIS OF LEAD ARYLS. THE PREPARATION OF AMINO COMPOUNDS

BY PAUL R. AUSTIN[1]

RECEIVED MAY 19, 1932 PUBLISHED SEPTEMBER 5, 1932

The synthesis of new types of organic lead compounds has seemed of importance due to the prevalent interest in their therapeutic value. No derivatives containing acid or basic groups have been known up to the present time and this paper describes the preparation of a series of compounds containing a tertiary amino group.

The similarity in the reactions of the Grignard reagent and lithium aryls suggested that the latter might be useful in the synthesis of other organometallic compounds, especially since lithium derivatives of unusual types may be prepared. It has been shown[2] that mercuric chloride reacts readily with benzyllithium to form dibenzylmercury and in preliminary studies it was found that di-*p*-tolylmercury and tetra-*p*-tolyltin could be easily prepared from *p*-tolyllithium and the corresponding metallic halides.

$$2RLi + HgCl_2 \longrightarrow R_2Hg + 2LiCl \quad (I)$$

$$4RLi + SnCl_4 \longrightarrow R_4Sn + 4LiCl \quad (II)$$

With lead chloride the lithium aryls apparently react in a manner analogous to the Grignard reagent.

$$PbCl_2 + 2RLi \longrightarrow R_2Pb + 2LiCl \quad (III)$$

$$3R_2Pb \xrightarrow{(heat)} 2R_3Pb + Pb$$

$$4R_3Pb \xrightarrow{(heat)} 3R_4Pb + Pb$$

Lead chloride and phenyllithium gave a mixture of tetraphenyllead and triphenyllead when the reaction mixture was not heated long enough to complete the conversion of triphenyllead to the tetravalent compound.

The action of lithium aryls on organic lead salts was next investigated and under suitable conditions replacement of the halogen atom was effected.

$$R_3PbCl + R'Li \longrightarrow R_3R'Pb + LiCl \quad (IV)$$

$$R_2PbCl_2 + 2R'Li \longrightarrow R_2PbR'_2 + 2LiCl \quad (V)$$

It was necessary to use equimolecular proportions of the two reactants, since an excess of lithium aryl replaced the aryl groups already attached to lead. Triphenyllead chloride or diphenyllead dichloride treated with the calculated amount of *p*-tolyllithium gave triphenyl-*p*-tolyllead and diphenyldi-*p*-tolyllead. When triphenyllead chloride was heated with an excess of *p*-tolyllithium a small amount of the expected triphenyl-*p*-tolyllead was formed and, in addition, some tetra-*p*-tolyllead was isolated from

[1] National Research Fellow in Chemistry.

[2] Ziegler, *Ber.*, **64**, 445 (1931).

the mixture of reaction products. This must have come from the replacement of phenyl groups by tolyl. An attempt to use this reaction to prepare tetra-*p*-tolyllead from tetraethyllead and *p*-tolyllithium gave only di-*p*-tolyl; no tolyllead derivative could be isolated.

For the synthesis of the amino compounds, *p*-dimethylaminophenyllithium, $(CH_3)_2NC_6H_4Li$, was prepared from *p*-bromodimethylaniline. Unlike the Grignard reagent from this bromide,[3] the lithium derivative could be prepared easily and smoothly in good yields. This reagent readily yielded the known *p*-mercuribisdimethylaniline, $[(CH_3)_2NC_6H_4]_2Hg$, when treated with mercuric chloride. By using the required reactant, tetra-(*p*-dimethylaminophenyl)-lead, $[(CH_3)_2NC_6H_4]_4Pb$, triphenyl (*p*-dimethylaminophenyl) - lead, $(C_6H_5)_3PbC_6H_4N(CH_3)_2$, diphenyldi - (*p* - dimethylaminophenyl) - lead, $(C_6H_5)_2Pb[C_6H_4N(CH_3)_2]_2$, and tetra - (*p* - dimethylaminophenyl)-tin, $[(CH_3)_2NC_6H_4]_4Sn$, were prepared. These amino compounds were found to be well-characterized solids with definite melting points and were easily recrystallized from appropriate solvents.

The importance of the nature of the solvent used in the preparation of the amino derivatives was demonstrated when it was found that diphenyllead dichloride or triphenyllead chloride and *p*-dimethylaminophenyllithium did not give the expected products when benzene was used as a solvent, but reacted satisfactorily when a large proportion of ether was present.

The amino compounds, particularly the unsymmetrical ones, were rather sensitive to acids; one or more of the metal–carbon linkages were easily ruptured. In the case of triphenyl-(*p*-dimethylaminophenyl)-lead, acetic acid caused the severing of the dimethylaminophenyl group and the formation of triphenyllead acetate. Tetra-(*p*-dimethylaminophenyl)-tin and -lead dissolved in tenth normal nitric acid were stable for a short time, since they could be reprecipitated by alkali unchanged after about one-half hour. Longer standing in the acid solution caused the gradual decomposition of the compounds.

The lithium derivatives were all easily prepared in much the same manner as the Grignard reagent. Details of the preparation of lithium phenyl have recently been described.[4]

Experimental Part

Preparation of Lithium Aryls.—Fine shavings of lithium were placed in absolute ether and stirred vigorously during the addition of the aryl bromide in ether. To start the reaction a little of the bromide was added and the mixture was heated for a few minutes. The bromide was then added at a rate sufficient to keep the ether refluxing gently. After the addition of the bromide the mixture was refluxed for one-half hour to complete the reaction and the solution was filtered into a graduated separatory funnel. Portions of such a stock solution were then used in subsequent reactions. The solutions, which were from 0.5 to 1.0 molar, were titrated to determine the content of lithium aryl,

[3] Ehrlich and Sachs, *Ber.*, **36**, 4297 (1903).

[4] Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

using the procedure described for the Grignard reagent.[5] Yields of about 90% were obtained. *p*-Lithiumdimethylaniline gave colored solutions which obscured the usual end-point, but by titrating directly with acid in the presence of phenolphthalein, a change from red to green could be observed quite satisfactorily. It was advantageous to carry out this titration in alcohol.

Preparation of Organo-metallic Compounds from Lithium Aryls.—For the preparation of entirely symmetrical compounds (equations I, II and III) an excess of lithium aryl was used. For the replacement of halogen in organo-metallic salts to prepare unsymmetrical compounds (equations IV and V) equimolecular quantities were used. All the reactions (except III) were practically instantaneous and were usually carried out in the cold. When the reactions were complete, the mixture was decomposed with water, the ether layer separated and evaporated and the residue purified by recrystallization from the appropriate solvent.

Table I gives a summary of the compounds prepared by this procedure. The Roman numerals correspond to the equation followed in the preparation and the reactant was the metallic or organo-metallic halide employed on which the yield was based. The yield of product given was usually once-crystallized material. The nitrogen analyses were carried out by Mr. K. W. Eder in this Laboratory using the micro-Dumas method.

TABLE I

ORGANO-METALLIC COMPOUNDS PREPARED FROM LITHIUM ARYLS AND METALLIC HALIDES

Equation	Compound	Reactant, g.	Yield g.	Yield %	M. p., °C.	Previously recorded m. p., °C.	Analyses, % Metal Calcd.	Metal Found	Nitrogen Calcd.	Nitrogen Found
I	$(p\text{-}CH_3C_6H_4)_2Hg$	2.7	3.4	89	237–238	238[a]				
I	$[p\text{-}(CH_3)_2NC_6H_4]_2Hg$	4.0	0.8	12	167–169	169[b]				
III	$(C_6H_5)_4Pb$	7.0	2.5	48	223–225	225[c]				
IV	$(C_6H_5)_3Pb(p\text{-}C_6H_4CH_3)$	1.3	0.6	41	124–125	125.5[d]				
V	$(C_6H_5)_2Pb[p\text{-}C_6H_4CH_3]_2$	4.3	1.9	38	121–122	[e]	38.13	38.18		
III	$[p\text{-}(CH_3)_2NC_6H_4]_4Pb$	2.8	0.6	17	197–198	[f]	30.14	29.97	8.15	8.26
IV	$(C_6H_5)_3Pb[p\text{-}C_6H_4N(CH_3)_2]$	4.7	4.3	77	124–125	[g]	37.11	37.26	2.51	2.65
V	$(C_6H_5)_2Pb[C_6H_4N(CH_3)_2]_2$	4.3	1.0	16	134–135	[h]	34.44	34.32	4.65	4.91
II	$(p\text{-}CH_3C_6H_4)_4Sn$	1.3	2.2	91	233	233.5[i]				
II	$[p\text{-}(CH_3)_2NC_6H_4]_4Sn$	2.6	2.9	58	198–199	[j]	19.82	20.17	9.35	9.24

[a] Zeiser, *Ber.*, **28**, 1670 (1895). The mercuric chloride was dissolved in 100 cc. of ether and the *p*-tolyllithium added in the cold. The product was recrystallized from benzene.

[b] Schenk and Michaelis, *ibid.*, **21**, 1501 (1888). In this preparation the mercuric chloride in ether was added to the lithium derivative and the mixture refluxed for one hour. For purification the product was recrystallized repeatedly from benzene. The yield was based on pure product.

[c] Gilman and Robinson, THIS JOURNAL, **49**, 2317 (1927). The lithium phenyl and lead chloride in 100 cc. of ether and 150 cc. of benzene were refluxed for four hours. Besides the tetraphenyllead there was obtained 1.8 g. of a mixture of triphenyllead and tetraphenyllead. It blackened at about 150° and melted at 216–220°. Triphenyllead decomposes at 155° with the deposition of lead [Krause and Reissaus, *Ber.*, **55B**, 888 (1922)].

[d] Krause and Schmitz, *ibid.*, **52**, 2153 (1919). The triphenyllead chloride in 50 cc. of benzene was treated in the cold with *p*-tolyllithium. The product was recrystallized from alcohol. In another experiment 5.6 g. of triphenyllead chloride was added to a large excess of *p*-tolyllithium and refluxed for two hours. The product was fractionated

[5] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

from benzene–alcohol mixture and the most soluble fraction (0.4 g.) was recrystallized from alcohol; it melted at 124–126° and was therefore triphenyl-*p*-tolyllead. The least soluble fraction (1.3 g.) was recrystallized repeatedly from alcohol–benzene or acetone–benzene mixture and melted at 236–237°. A mixed melting point with an authentic specimen of tetra-*p*-tolyllead showed no depression.

[e] The diphenyllead dichloride was suspended in 50 cc. of benzene and 50 cc. of ether and stirred vigorously during the slow addition of the *p*-tolyllithium. The product was recrystallized from alcohol.

[f] The lead chloride was added to an excess of the lithium derivative in 100 cc. of ether and 150 cc. of benzene and then refluxed for eight hours. The product was recrystallized from a ligroin–benzene or alcohol–benzene mixture which gave cream-colored needles.

[g] The triphenyllead chloride in 100 cc. of benzene and 50 cc. of ether was heated to boiling and then treated with the lithium derivative. The product was recrystallized from alcohol–benzene mixture or from ligroin, which gave a white crystalline powder. When the triphenyllead chloride was dissolved in benzene alone the expected product was not obtained.

[h] The diphenyllead dichloride was suspended in 150 cc. of ether and stirred vigorously and the lithium derivative added dropwise. The product was recrystallized from alcohol–benzene mixture and gave a white crystalline powder. When benzene was used as the solvent the only product was a tarry material.

[i] Krause and Becker, *Ber.*, **53**, 178 (1920). The stannic chloride in 25 cc. of benzene was added to the vigorously stirred solution of *p*-tolyllithium. The tetra-*p*-tolyltin was recrystallized from benzene.

[j] This compound was prepared as described for tetra-*p*-tolyltin and was recrystallized from an alcohol–benzene mixture which gave light brown needles.

Triphenyl-(*p*-dimethylaminophenyl)-lead and Acetic Acid.—Five-tenths of a gram of the lead compound in absolute alcohol was treated with the calculated amount of acetic acid in petroleum ether to form the salt. However, there was isolated only 0.1 g. of original material and 0.1 g. of triphenyllead acetate, m. p. 206–207°. A mixed melting point with an authentic specimen of triphenyllead acetate[6] showed the two substances to be identical.

Tetraethyllead and *p*-Tolyllithium.—An excess of *p*-tolyllithium and 3.2 g. of tetraethyllead in 70 cc. of benzene and 50 cc. of ether were refluxed for eight hours. The product on standing gave a crystalline material in oil. This was filtered and gave 0.2 g. of what was shown to be di-*p*-tolyl. After recrystallization from alcohol it melted at 118–119° and a mixed melting point with an authentic specimen showed no depression. The oily product was not investigated.

The author wishes to express his appreciation to Professor C. S. Marvel for many helpful suggestions.

Summary

Lithium derivatives have been shown to be generally applicable to the preparation of organic compounds of mercury, tin and lead.

p-Bromodimethylaniline readily yields a lithium derivative which has been used in the synthesis of a series of compounds containing the dimethylaminophenyl group.

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[6] Austin, THIS JOURNAL, **53**, 3517 (1931).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE GEORGE WASHINGTON UNIVERSITY]

THE CONDENSATION OF BROMAL WITH THE NITRANILINES[1]

BY D. C. KNOWLES, JR., AND R. P. JACOBSEN

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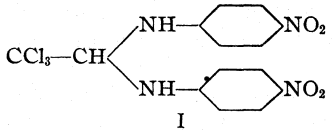
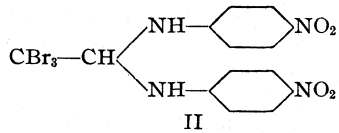
Eibner[2] condensed chloral with *p*-nitraniline to form a Schiff base, N,N′-β,β,β-trichloroethylidene-bis-*p*-nitraniline, of formula (I).



I



II

Wheeler and Weller[3] repeated his experiments and confirmed his results. In addition they condensed ortho and meta nitranilines with chloral to form the corresponding ortho and meta isomers.

It was thought to be of interest to investigate the condensation of bromal, tribromoacetaldehyde, with the three nitranilines. It was found that this condensation takes place as with chloral and there is formed, for example, N,N′,β,β,β-tribromoethylidene-bis-*p*-nitraniline from one mole of bromal and two moles of *p*-nitraniline. The formula (II) is given to the compound on the evidence of the analysis and the analogous behavior of this compound to the chloral condensation product. The ortho and meta isomers have also been prepared.

Treatment of the condensation products with hot, dilute or concentrated hydrochloric acid results in the decomposition of the molecule with the formation of bromal, which can be detected in the vapors, and the corresponding nitraniline, which can be recovered by neutralization of the acid solution with ammonium hydroxide.

Treatment of the ortho and para isomers with cold or hot alcoholic potash results in the formation of an intense red coloration. Wheeler and Jordan[4] report similar behavior for the chloral condensation products and that they prepared hydroxy and alkoxy derivatives by the replacement of one of the chlorine atoms by the hydroxy group by the use of alcoholic potash or alkoxy groups by the use of sodium alkoxides. We were unable to isolate such products. Apparently the treatment with alcoholic potash results in a complete decomposition of the molecule of the condensation product since we were able to isolate considerable amounts of the corresponding nitraniline from the reaction mixture.

[1] A portion of the material in this paper is taken from a thesis submitted to the Faculty of Columbian College, The George Washington University, by R. P. Jacobsen in partial fulfilment of the requirements for the degree of Master of Arts, October, 1931.

[2] Eibner, *Ann.*, **302**, 366 (1898).

[3] Wheeler and Weller, THIS JOURNAL, **24**, 1063 (1902).

[4] Wheeler and Jordan, *ibid.*, **31**, 937 (1909).

Treatment with an excess of bromine in glacial acetic acid results in a decomposition of the condensation product and we obtained various di- and tribromonitranilines which were identified by analysis and mixed melting points.

Experimental

Bromal was prepared by the bromination of paraldehyde in the presence of ethyl acetate according to the method of Pinner.[5]

N,N′,β,β,β-Tribromoethylidene-bis-*p*-nitraniline.—Twenty grams of powdered *p*-nitraniline was suspended in 100 cc. of benzene or ether. Twenty grams of freshly distilled bromal was dissolved in 25 cc. of the solvent and added slowly to the *p*-nitraniline. The mixture becomes warm and almost immediately a light yellow precipitate of the condensation product settles out. The mixture is allowed to stand overnight and then filtered. The light yellow sandy precipitate is washed many times with hot 70% alcohol to remove the unreacted *p*-nitraniline and then recrystallized from anhydrous acetone. It is insoluble in most organic solvents and only slightly soluble in acetone.

The condensation of ortho and meta nitranilines was carried out in the same manner except that the volume of the solvent is reduced since these condensation products are more soluble.

TABLE I

ANALYTICAL AND OTHER DATA FOR THE COMPOUNDS

Substance, N,N′,β,β,β,-tribromo-ethylidene-bis-	M. p., °C.	Needles from acetone	Yield, %	Analysis for Br, % Calcd. for $C_{14}H_{11}Br_3N_4O_4$		Found
o-Nitraniline	106–107	Light yellow	30	44.49	44.20	44.46
m-Nitraniline	117–118	Dark orange	34	44.49	44.71	44.24
p-Nitraniline	127–128	Dark orange	48	44.49	44.64	44.71

Summary

1. Bromal has been condensed with *o*-, *m*- and *p*-nitranilines to form three new Schiff bases.

2. These Schiff bases are decomposed completely by treatment with acids, alcoholic potash and bromine.

WASHINGTON, D. C.

[5] Pinner, *Ann.*, **179**, 68 (1875).

[CONTRIBUTION FROM THE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE CONFIGURATION OF METHYLISOPROPYLCARBINOL WITH A NOTE ON RACEMIZATION

BY PHILIP G. STEVENS

RECEIVED MAY 21, 1932 PUBLISHED SEPTEMBER 5, 1932

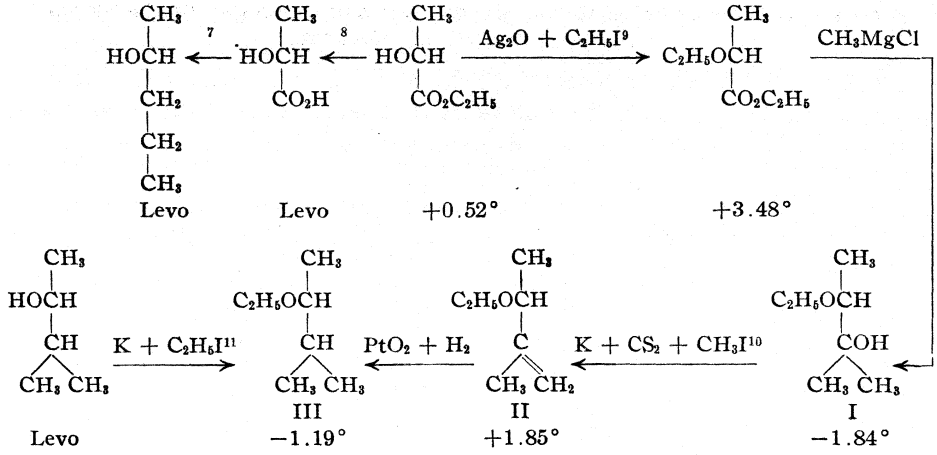
The only carbinols whose configurations have been directly correlated are those having straight chains or those with the branched chain at least one carbon atom removed from the asymmetric carbon atom. The first attempt to correlate carbinols with the branched chain directly attached to the asymmetric carbon atom was made by Levene and Marker,[1] who deduced the configuration of the isopropylcarbinols from their abnormal rotatory powers. They concluded that these carbinols had opposite configurations from those of the corresponding straight chain carbinols; in support of this conclusion, they found that levo methylethylisopropylmethane was configurationally related to dextro methylethylpropylmethane.[2]

However, the first member of the isopropyl series, methylisopropylcarbinol, has a comparatively low rotation. For this reason it is not possible to deduce its configuration with the same degree of certainty that Levene and Marker attained in the case of the higher members of the series. This paper therefore deals with the direct correlation of methylisopropyl- and methylpropylcarbinols. It now seems certain that the two carbinols are configurationally related when both have the same sign of rotation, contrary to the conclusion of Levene and Marker.

The correlation of levo methylisopropyl- and levo methylpropylcarbinol was accomplished by synthesis from dextro ethyl lactate. Fortunately commercial ethyl lactate had a sufficient activity to render a resolution of lactic acid unnecessary.[3] By ethylating this ester, the rotations were increased to such an extent that there could be no doubt that the rotations were real. In no reaction was the asymmetric carbon atom involved. The general scheme of correlation is as indicated.

The dehydration of the ethoxycarbinol I to give the optically active unsaturated ether II was the key to the correlation. Tschugaeff's xanthogenate method of dehydration avoids rearrangements, as is shown so well by the formation of bornylene from borneol,[4] and tertiary-butylethylene from methyl-tertiary-butylcarbinol.[5] The hydrogenation of II caused an inversion of the sign of rotation just as with unsaturated carbinols.[6] Fi-

[1] Levene and Marker, *J. Biol. Chem.*, **90**, 669 (1931).
[2] Levene and Marker, *ibid.*, **91**, 405 (1931).
[3] Compare McKenzie, *J. Chem. Soc.*, **87**, 1373 (1905).
[4] Tschugaeff, *Chem. Centr.*, I, 94 (1905).
[5] Fomin and Sochanski, *Ber.*, **46**, 246 (1913).
[6] Levene and Haller, *J. Biol. Chem.*, **83**, 579 (1929).



nally, the saturated ether III thus obtained was compared with the dextro ethyl ether of methylisopropylcarbinol prepared from the dextro carbinol, and the two were found to be chemically identical.

It is interesting to note that there was no racemization of the ethoxy tertiary carbinol I when heated for ten hours at 190° with metallic potassium, while methylisopropylcarbinol under about the same conditions (180°) was almost completely racemized in four hours. These facts fit in well with the mechanism of racemization and rearrangement of alcoholates proposed recently by Hückel,[12] which involves the loss of hydrogen with the formation of an unsaturated (hence inactive) intermediate, followed by reduction to the rearranged (racemized) substance.

The ethoxy tertiary alcoholate from I has no hydrogen on the carbon atom to which the alcoholate group is attached, and hence cannot lose hydrogen. This case is then similar to the case of those acids which do not racemize because there is no enolizable hydrogen in the α-position. On the other hand, methylisopropylcarbinol alcoholate possesses such a hydrogen and does racemize.

The correlation of levo methylisopropyl- and levo methylpropylcarbinol shows that a change of a propyl to an isopropyl group lowers the optical rotation without reversing the sign. The effect of the branched chain when directly attached to the asymmetric carbon atom is therefore to depress the rotatory power. The other members of the isopropyl series, *viz.*, ethyl-, propyl-, and butyl-isopropylcarbinols have higher rotations than the

[7] Levene and Haller, *J. Biol. Chem.*, **72,** 591 (1927).

[8] Karrer, Escher and Widmer, *Helv. Chim. Acta*, **9,** 303, 323 (1926).

[9] Purdie and Irvine, *J. Chem. Soc.*, **75,** 483 (1899).

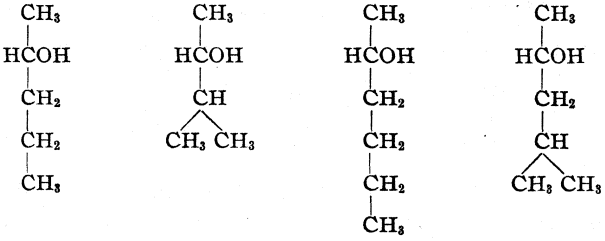
[10] Tschugaeff, *Ber.*, **32,** 3332 (1889); Gandurin, *ibid.*, **41,** 4362 (1908).

[11] The material actually used was dextrorotatory.

[12] Hückel, *Ber.*, **64B,** 2137 (1931).

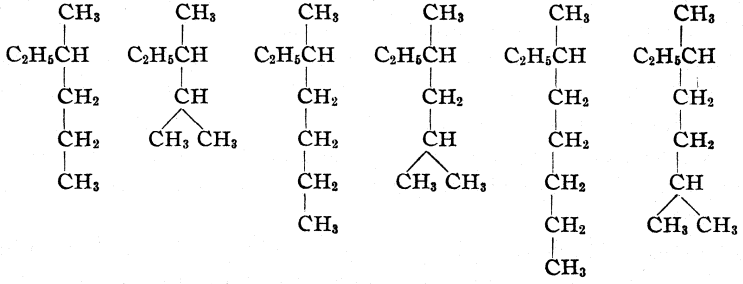
corresponding straight chain carbinols; but as Levene and Marker[1] suggested, they are undoubtedly oppositely configurated, and show the depressing effect of the isopropyl group by a change in the sign of rotation. Therefore, according to the rule of Levene and Haller,[13] the isopropyl radical, while heavier than the methyl, acts as if lighter than the ethyl group.

When, however, the branched chain is once removed from the asymmetric carbon atom, then the rotation is exalted, as Levene and Walti[14] have already shown.



$[M]_D$	$+12.1°$[15]	$+4.3°$	$+11.8°$	$+20.9°$

Levene and Marker[16] found a similar depression and exaltation in the hydrocarbon series, except that the depression caused by the isopropyl group when next to the asymmetric carbon atom was sufficient to invert the sign of rotation. On the other hand, however, they found that when twice removed from the asymmetric carbon atom, the effect of the branched chain was negligible.



$[M]_D$	$+9.9°$	$-15.7°$	$+11.4°$	$+21.3°$	$+12.0°$	$+11.9°$

It may seem strange that the effect of a group should be so different when attached to, and once removed from, the asymmetric carbon atom. A difference in polarities, as suggested by acid dissociation constants at least, does not seem to be the cause, for butyric and isobutyric acids have about the same dissociation constants, while the propyl- and isopropyl-

[13] Levene and Haller, *J. Biol. Chem.*, **79**, 475 (1928).

[14] Levene and Walti, *ibid.*, **94**, 367 (1931).

[15] Maxima by Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

[16] Levene and Marker, *J. Biol. Chem.*, **95**, 1 (1932).

carbinols have very different rotations. Most probably the real cause is a difference in the absorption bands in the ultraviolet, as Kuhn and Freudenberg[17] have already indicated.

There is also a possibility that asymmetry plays an important role. From dissociation constants and absorption spectra, one can reason that the phenyl group should have the opposite effect from the isopropyl and tertiary-butyl groups. The correlation of carbinols containing these groups directly attached to the asymmetric carbon atom should be, therefore, of theoretical value. Work in this direction is now in progress.

I am indebted to Dean Frank C. Whitmore for making available the facilities of this Laboratory; and to the Mallinckrodt Chemical Works which so generously supplied the large quantities of iodine necessary in this work. Part of the funds required for this research were privately contributed.

Experimental Part

In this work all rotations are for the homogeneous state.

Dextro Ethyl Lactate, $CH_3CHOHCO_2C_2H_5$.—Eastman's commercial ethyl lactate $[\alpha]_D$ +0.45°, was fractionated through a 91-cm. adiabatic controlled reflux column (column A); b. p. 151.6–152.2°; $[\alpha]_D^{27}$ +0.52°. Another sample was less active: $[\alpha]_D^{27}$ +0.30°; n_D^{20} 1.4127.

Dextro Ethyl α-Ethoxy Propionate, $CH_3CHOC_2H_5COOC_2H_5$.[6]—To 196 g. of ethyl lactate $[\alpha]_D^{27}$ +0.30°, dissolved in 936 g. (3.6 equiv.) of ethyl iodide, was added gradually with mechanical stirring 696 g. (1.8 equiv.) of dry silver oxide. The reaction started on warming. After all the oxide had been added, the mixture was boiled for several hours and then allowed to stand overnight. The next morning, 460 g. of ethyl iodide was added, and the boiling continued all day. After standing warm overnight, dry ether was added, the silver compounds filtered off, and the resulting solution fractionated directly through column A.

1st fraction: b. p. (731 mm.) 152.0–153.6°; 66.5 g., $[\alpha]_D^{23}$ +1.56°, n_D^{20} 1.4021
2d fraction: b. p. (731 mm.) 153.6–154.3°; 104.5 g., $[\alpha]_D^{23}$ +1.62°, n_D^{20} 1.4015

(Thermometer completely immersed in the vapor)

Forty cc. of the second fraction was shaken thoroughly with water, with 2% aqueous sodium carbonate, dried over anhydrous potassium carbonate and refractionated through a similar 61 cm. column (column B):[18] b. p. (730 mm.) 152.7–152.8°; $[\alpha]_D^{23.5}$ +1.69°; n_D^{20} 1.4011.

The ethoxy ester prepared from the more active lactate of $[\alpha]_D^{27}$ +0.52° had the activity $[\alpha]_D^{24}$ +3.48°.

Levo 2-Ethoxy-3-methylbutanol-3, $CH_3CHOC_2H_5COH(CH_3)_2$.—109 g. of the ethoxy ester, $[\alpha]_D^{24}$ +3.48°, was added to 4–5 equivalents of methylmagnesium chloride in the usual way. After standing at room temperature for two days with intermittent stirring, the reaction mixture was decomposed with ice and ammonium chloride, and the product extracted with ether. The ether was then washed with 10% aqueous potassium

[17] W. Kuhn, *Ber.*, **63,** 199 (1930); W. Kuhn, Freudenberg and Wolf, *ibid.*, **63,** 2368 (1930).

[18] Karvonen reported: b. p. (750 mm.) 153–155°; n_D^{20} 1.40125. *Ann. Acad. Sci. Fennicae,* [6] **10A,** 1 (1916).

hydroxide, dried over sodium sulfate and fractionated through column A. The main fraction, b. p. 140.2–141.7°, weighed 84 g., yield 85%. This material was redistilled in a modified Claisen flask from 8 g. of sodium metal:[19] b. p. 140.0–140.5°; $[\alpha]_D^{29.5}$ −1.84°; n_D^{20} 1.4111.

Anal. (micro). Calcd. for $C_7H_{16}O_2$: C, 63.6; H, 12.1; OC_2H_5, 34.1. Found: C, 63.0; H, 11.8; OC_2H_5, 35.5.

Another sample from the less active ethoxy ester, $[\alpha]_D^{23.5}$ +1.69°, was fractionated through column B: b. p. (728 mm.) 140.1–140.4°; $[\alpha]_D^{27}$ −0.83°. In order to remove any unchanged ester the material was boiled for eight hours with alcoholic potassium hydroxide, steam distilled, refractionated and distilled from sodium metal: b. p. (736 mm.) 140.5–140.8° (bath 200°); $[\alpha]_D^{30.5}$ −0.83°.

Anal. (micro). Calcd. for $C_7H_{16}O_2$: C, 63.6; H, 12.1; OC_2H_5, 34.1. Found: C, 63.1; H, 12.0; OC_2H_5, 37.4. Further attempts to correct the ethoxyl value reduced it to only 36.4%.

Dextro 2-Ethoxy-3-methylbutene-3, $CH_3CHOC_2H_5CCH_3{=}CH_2$.—40.6 g. of the ethoxycarbinol, $[\alpha]_D^{29}$ −1.84°, dissolved in 600 cc. of *p*-cymene[20] was boiled with 20 g. (2 equiv.) of clean, bright potassium metal until no more metal was consumed (±three hours); 50 cc. of the solvent was now distilled off to remove any unreacted carbinol. The almost colorless mixture was cooled, most of the potassium removed mechanically, and 575 cc. of dry ether added. Now 46.8 g. (2 equiv.) of carbon disulfide was added, precipitating the yellow xanthogenate. After one hour at room temperature, 110 g. (2.5 equiv.) of methyl iodide was added, and the mixture put in the hood overnight. The next morning, after boiling gently for five hours, as much as possible of the reaction mixture was distilled off on the steam-bath. Only a small amount of mercaptan had formed up to this point.[21] The distillation was continued, using a free flame. Soon a vigorous fuming occurred as the xanthogenate decomposed. The distillation was continued until the temperature rose to the boiling point of the pure solvent. The distillate was extracted with 5% aqueous potassium hydroxide, and then with a saturated solution of mercuric chloride, until no more mercaptide formed. After washing well with water and drying over sodium sulfate, the ether was fractionated off. During this process, a considerable amount of a white substance precipitated. The ether solution was therefore decanted, washed thoroughly with aqueous sodium carbonate and potassium hydroxide to remove any mercuric compounds, dried over anhydrous potassium carbonate and fractionated through column B

1st fraction, b. p. 90–94°; $[\alpha]_D^{27}$ +1.02°; 4 g.
2d fraction, b. p. 94–99°; 21 g. } 71% yield

The second fraction was refractionated

1st fraction, b. p. (730 mm.), 94.0–97.1°; $[\alpha]_D^{27.5}$ +1.65°
2d fraction, b. p. (730 mm.), 97.1–98.1°; $[\alpha]_D^{25.5}$ +1.85°

Part of this second fraction, b. p. 98.0°, n_D^{20} 1.4039, was dried over calcium chloride.

Anal. (micro). Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.4. Found: C, 73.5; H, 12.2.

Ethoxyl values were too high, due to contamination of diethyl ether.

The new substance was actively unsaturated. It absorbed bromine in cold carbon tetrachloride solution instantly. Likewise, it reduced cold aqueous permanganate in-

[19] Compare Ciamician and Silber, *Ber.*, **44**, 1554 (1911).

[20] The cymene, b. p. 175.0–175.5°, was purified by boiling with potassium metal for five hours.

[21] Gandurin[7] reported tertiary xanthogenates as decomposing at room temperature

stantly. The reduction of permanganate in acetone solution was slow. The compound possessed a clean, strong, peppermint-like odor, there being no trace of any methyl mercaptan.

Levo 2-Ethoxy-3-methylbutane, $CH_3CHOC_2H_5CH(CH_3)_2$.—12.5 g. of the unsaturated ether, $[\alpha]_D^{25.5}$ +1.85°, was reduced in glacial acetic acid with Adams' platinum catalyst and hydrogen at 3 atmospheres pressure. There was a fairly long induction period before the reduction started. Approximately the correct amount of hydrogen was absorbed. The solution was then decanted into a liter separatory funnel, ice added and the mixture neutralized with 20% aqueous potassium hydroxide. When strongly alkaline, the solution was extracted with ether, which was washed with aqueous potassium hydroxide, and water, then dried over calcium chloride and fractionated through column B. The main fraction, b. p. (732 mm.) 99.2–100.0°, weighed 6.5 g. This material showed no unsaturation, giving no reactions with either bromine or permanganate. It had a pleasant camphor-like odor, identical with that of the ethyl ether of methylisopropylcarbinol prepared from the carbinol. The saturated ether was levorotatory, $[\alpha]_D^{27.5}$ −1.21°. The ether was boiled in a small Claisen flask over potassium metal, and then distilled: b. p. 99.0–99.2°, $[\alpha]_D^{26}$ −1.19°, n_D^{20} 1.3873.

Anal. (micro). Calcd. for $C_7H_{16}O$: C, 72.4; H, 13.9. Found: C, 72.5; H, 13.9.

As the substance gave high analyses for ethoxyl, due to contamination of diethyl ether, it was refractionated through column B. The fraction, b. p. 100.0°, was now pure, n_D^{20} 1.3877.

Anal. (micro). Calcd. for $C_7H_{16}O$: C, 72.4; H, 13.9; OC_2H_5, 38.8. Found: C, 72.3; H, 14.0; OC_2H_5, 38.4.

Dextro Methylisopropylcarbinol, $CH_3CHOHCH(CH_3)_2$.—The carbinol, b. p. 110.0–110.1°, prepared from isobutyric aldehyde and methylmagnesium chloride, was converted into the acid phthalate with phthalic anhydride and pyridine, and then resolved with brucine in acetone solution.[22] Four recrystallizations of the salt were sufficient. The carbinol was recovered in the usual way and fractionated through column B: b. p. (734 mm.) 111.6–111.8°, $[\alpha]_D^{24}$ +0.90°, n_D^{20} 1.4090.

Dextro 2-Ethoxy-3-methylbutane, $CH_3CHOC_2H_5CH(CH_3)_2$.—29.3 g. of the carbinol, $[\alpha]_D^{24}$ +0.90°, dissolved in 475 cc. of *p*-cymene was boiled with 16 g. of clean potassium metal. After four hours, as no more potassium seemed to react, the mixture was cooled, and 70 g. of ethyl iodide was added. On warming the iodide reacted, precipitating potassium iodide. The reaction products were now boiled until most of the metal had disappeared, and then allowed to stand overnight. The following morning the products were distilled out directly. The material, b. p. 90–175°, was fractionated through column B. The fraction of b. p. 99.0–99.8° was the desired ether. It was purified by boiling for one hour over metallic potassium, distilling and boiling again over fresh potassium. The final distillate, from a small Claisen flask, b. p. 99.0–99.4°, was dextrorotatory; $[\alpha]_D^{25}$ +0.60°, n_D^{20} 1.3876.

Anal. (micro). Calcd. for $C_7H_{16}O$: C, 72.4; H, 13.9; OC_2H_5, 38.8. Found: C, 72.3; H, 14.1; OC_2H_5, 38.4.

Considerable amounts of unreacted carbinol were recovered. These were refractionated through column B, b. p. 111.0–111.3°, n_D^{20} 1.4097. No optical activity could be detected in a one decimeter tube.

Action of Heat (190°) on the Alcoholate of Levo 2-Ethoxy-3-methylbutanol-3.—Fifteen grams of the carbinol, $[\alpha]_D^{31}$ −0.85°, n_D^{20} 1.4098, dissolved in 340 cc. of decaline (b. p. 188–190°), was treated with 10 g. (2.3 equiv.) of clean potassium metal which was then converted to powder by warming and shaking. After warming to 100–120° for

[22] Pickard and Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

a few hours, shaking frequently, the mixture was allowed to stand overnight, all of the alcoholate remaining in solution. The next day, the solution was boiled for ten hours. The clear solution gradually became black, due to the formation of tarry matter. At the end of the ten hours, all the metal had disappeared. Now after cooling, 35 cc. of methyl alcohol was added, the mixture shaken well, and distilled directly. The material b. p. 65–185° was fractionated through column B twice. About 2 g. of the original carbinol was thus obtained, b. p. 138–143°, n_D^{20} 1.4118. The optical activity was unchanged, $[\alpha]_D^{28}$ −0.82°. There had been, therefore, decomposition apparently but no racemization.

Summary

1. Levo methylisopropyl- and levo methylpropylcarbinols are configurationally related.

2. A tertiary alcoholate was not racemized by heating at 190° for ten hours; this supports Hückel's mechanism of racemization and rearrangement of alcoholates.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TORONTO]

THE FRIEDEL AND CRAFTS REACTION. SOME UNSYMMETRICAL ACID ANHYDRIDES AND THEIR BEHAVIOR WITH BENZENE AND ALUMINUM CHLORIDE

BY J. M. ZEAVIN AND A. M. FISHER

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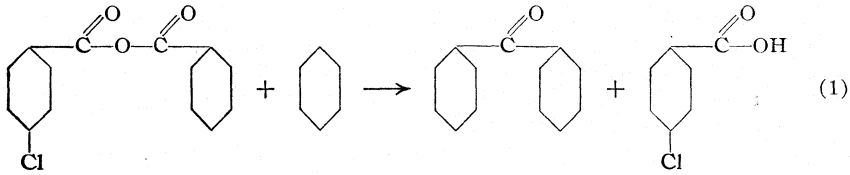
Previous research in this Laboratory on the Friedel and Crafts reaction—the production of acids and ketones from anhydrides, aromatic hydrocarbons and aluminum chloride—has been concerned with anhydrides of single acids. The purpose of the present research was to determine the course of the reaction using anhydrides which would give two acids on hydrolysis. With mono-*p*-chlorobenzoic anhydride, for example, there are three possibilities



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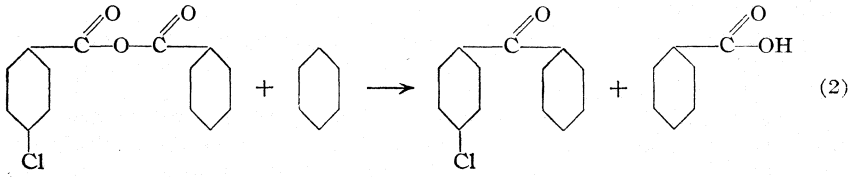


(2)

(3) The ketones might be a mixture of benzophenone and mono-*p*-chlorobenzophenone. In this paper a number of such anhydrides have

been prepared and their behavior with benzene and aluminum chloride has been investigated.

A. Preparation of the Anhydrides.—Attempts were made to prepare the anhydrides from the sodium salts of suitable acids and an acid chloride but this method was found to be satisfactory only in a few cases. Direct bromination of anhydrides failed to give the desired product. A modification of the method of Einhorn and Seuffert[1] for the preparation of anhydrides of substituted salicylic acid was used to prepare most of our anhydrides. A general outline of the modified method is as follows.

The acid required was dissolved in cold ether and pyridine and to this a cold ethereal solution of the molecular quantity of the acid chloride was added slowly. After standing at 0° a precipitate of pyridine hydrochloride was formed. This, together with the excess pyridine, was removed by two washings with 25 cc. of concd. hydrochloric acid and ice and then with 7% sodium hydroxide and ice. The solution was then washed with cold water and dried at 0° with anhydrous sodium sulfate, filtered, the ether evaporated and the anhydride, if impure, recrystallized from suitable solvents.

In some cases it was found more satisfactory to perform the first part of the experiment at room temperature and to shake the mixture instead of keeping it at 0°. Though most of the anhydrides were quite stable when once prepared, still the yield was decreased considerably by hydrolysis during the course of preparation, especially in ethereal solutions, and, therefore, to inhibit hydrolysis, benzene was used instead of ether. In so doing, it was unnecessary to dry the solution with anhydrous sodium sulfate. Also, when benzene was a better solvent for the anhydride, it was used instead of ether. Details concerning each of the anhydrides are given in the table.

Stability of the Anhydrides.—α-Naphthoicacetic anhydride and β-naphthoicacetic anhydride decompose very readily at room temperature.

Some of the anhydrides are unstable when heated to their melting points. When mono-*p*-chlorobenzoic anhydride was first heated, it melted at 66.5–70.0°. Cooling this molten material produced another solid which melted at 126–144°. It seems probable that the decomposition indicated in the change of the melting point may account for failure to obtain a sharper melting point for some of the anhydrides. Another example of similar instability is the behavior of mono-*p*-bromobenzoic anhydride. This anhydride melted at 82–83°, began to solidify at 86° and melted again at 165–182°. A sample of it was heated to its melting point and precipitated fractionally from benzene with petroleum ether. It was found to consist of benzoic anhydride and *p*-dibromobenzoic anhydride. A similar transformation took place when a concentrated solution of the anhydride in benzene was heated to boiling. This was not evident in dilute solutions.

B. The Friedel and Crafts Reaction. The Acid Anhydrides with Benzene and Aluminum Chloride.—Working with phthalic anhydride, benzene and aluminum chloride, Rubidge and Qua[2] found that maximum yields of *o*-benzoylbenzoic acid were obtained when the anhydride and aluminum chloride were used in amounts proportional to their formula weights (using Al_2Cl_6 for aluminum chloride). In all experiments in the present research, this practice was followed. Excess benzene was used both as a reagent and as a solvent.

[1] Einhorn and Seuffert, *Ber.*, **43**, 2993 (1910).

[2] Rubidge and Qua, THIS JOURNAL, **36**, 732 (1914).

TABLE I

PREPARATION AND PROPERTIES OF THE ANHYDRIDES

	Anhydride	Reactants: Acid	Chloride	Solvent	Yield, %	M. p., °C.	Remarks
1	Mono-*o*-benzoxybenzoic	Salicylic	Benzoyl	Benzene	88	67.0–67.8	Recryst. warm Bz[a]
2	Mono-*o*-methoxybenzoic	*o*-Methoxybenzoic	Benzoyl	Ether	77	76.3–77.2	Recryst. large plates, warm Bz
3	Mono-*p*-chlorobenzoic	*p*-Chlorobenzoic	Benzoyl	Ether	69	66.5–70.0	See "Stability of the Anhydrides"
4	Mono-*p*-bromobenzoic	*p*-Bromobenzoic	Benzoyl	Benzene	80	82.0–83.0	[b]
5	Mono-*o*-nitrobenzoic	*o*-Nitrobenzoic	Benzoyl	Ether	75	65.0–65.5	Recryst. Bz and pet. ether[c]
6	Mono-*m*-nitrobenzoic	*m*-Nitrobenzoic	Benzoyl	Benzene	75	101–103	Diff. method by Gerhardt[d]
7	Mono-*p*-nitrobenzoic	*p*-Nitrobenzoic	Benzoyl	Benzene	65	130–130.5	Diff. method by Kahn,[e] m. p. 130°
8	3,5-Dinitrobenzoic	3,5-Dinitrobenzoic	Benzoyl	Benzene	60	115.5	.....
9	α-Naphthoicbenzoic	α-Naphthoic	Benzoyl	Ether	69	89.5–90.3	Recryst. Bz and pet. ether
10	β-Naphthoicbenzoic	β-Naphthoic	Benzoyl	Benzene	..	54.0–57.5	[f]
11	α-Naphthoicacetic	α-Naphthoic	Acetyl	Benzene	85	.....	Clear brown oil, dec. readily
12	β-Naphthoicacetic	β-Naphthoic	Acetyl	Benzene	83	50.5–51.0	.....
13	Dibenzoicphthalic	Sodium phthalate and benzoyl chloride heated at 120° for twelve hours gave better results. The mixture was shaken with warm benzene and filtered hot. Addition of petroleum ether to the cooled filtrate produced long white needles which melted at 131.0–132.0°; yield, 75%.					

[a] *Anal.* Calcd. for $C_{21}H_{14}O_5$: C, 72.8; H, 4.08. Found: C, 72.7; H, 4.21. Einhorn and Seuffert report m. p. 74–75°.

[b] *Anal.* Calcd. for $C_{14}H_9O_3Br$: Br, 26.20. Found: Br, 26.14.

[c] *Anal.* Calcd. for $C_{14}H_9O_5N$: N, 5.17. Found: N, 5.16.

[d] Gerhardt, *Ann.*, **87**, 158 (1853).

[e] Kahn, *Ber.*, **36**, 2536 (1903).

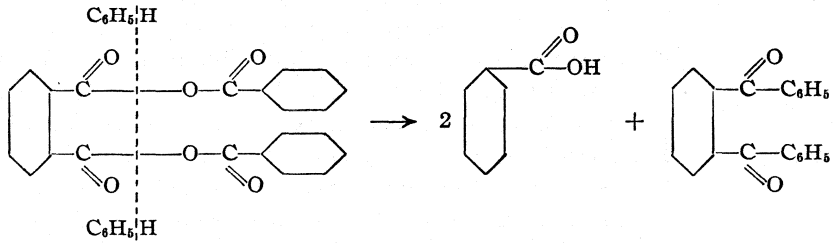
[f] An oily residue which formed crystals when precipitated from cold benzene with petroleum ether.

With the anhydrides listed above as numbers 2, 3, 4, 6, 7, 8, 9 and 10 the procedure was as follows.

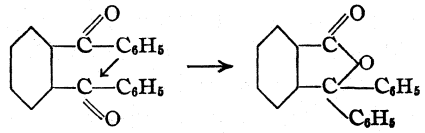
Five grams of the anhydride was dissolved in 50 cc. of benzene and the molecular quantity of aluminum chloride was added slowly. After standing for about one hour, the mixture was heated on a steam-bath in a flask fitted with a reflux condenser and calcium chloride tube until evolution of hydrogen chloride ceased (usually between eight and ten hours); 75 cc. of 5% hydrochloric acid was added slowly and the benzene removed by steam distillation. The contents of the distilling flask were cooled and filtered and the residue was warmed with 7% sodium hydroxide solution, cooled and filtered. The acids were recovered from the filtrate on the addition of concd. hydrochloric acid. Benzophenone was obtained from the portion insoluble in sodium hydroxide by steam distillation or by recrystallization from alcohol or ether. In the case of mono-*m*-nitrobenzoic anhydride, a slight trace of mono-*m*-nitrobenzophenone was found.

With α-naphthoicacetic anhydride and β-naphthoicacetic anhydride the only ketone produced was acetophenone.

With dibenzoicphthalic anhydride the products of the reaction were benzoic acid and diphenylphthalide, whereas *o*-benzoylbenzophenone was expected.



This is probably due to a rearrangement, as



In working with the nitro derivatives of benzoic anhydride, it was found that a tarry material was produced if the mixture was not kept at room temperature for at least twenty hours before heating on the steam-bath.

The authors' thanks are due to Mr. F. E. Beamish for the analyses recorded and to Professor F. B. Allan under whose direction this investigation was performed.

Summary

1. Ten new anhydrides have been prepared, *viz.*, mono-*o*-methoxybenzoic anhydride, mono-*p*-chlorobenzoic anhydride, mono-*p*-bromobenzoic anhydride, mono-*o*-nitrobenzoic anhydride, 3,5-dinitrobenzoic anhydride, α-naphthoicbenzoic anhydride, β-naphthoicbenzoic anhydride, α-naphthoicacetic anhydride, β-naphthoicacetic anhydride and dibenzoicphthalic anhydride.

2. A new method of preparation for mono-*m*-nitrobenzoic anhydride and for mono-*p*-nitrobenzoic anhydride has been described.

3. The stability of some of these anhydrides has been discussed.

4. The behavior of eleven of the anhydrides with benzene and aluminum chloride has been investigated and the products of the reaction identified.

TORONTO, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

REARRANGEMENTS IN THE CONDENSATION OF METHYLATED DERIVATIVES OF α-NAPHTHOYL-2-BENZOIC ACID

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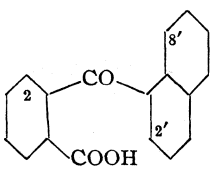
While 1,2-benzanthraquinone is the sole condensation product formed by the action of sulfuric acid on α-naphthoyl-2-benzoic acid (I), the quinone is accompanied by about 10% of an isomeric substance when molten sodium aluminum chloride is used as the condensing agent.[1] The isomer, which has the properties of a lactone, is probably formed either by a Scholl benzanthrone condensation between positions 2 and 8′ or by intramolecular addition of position 8′ to the carbonyl group to give a substance of the type formed by 2′-hydroxy-1-naphthoyl-2-benzoic acid.[1b] In order to study this matter further and to determine if possible which type of *peri* condensation actually takes place, we have investigated the behavior of a few substituted acids with which it seemed reasonable to expect a higher proportion of the abnormal reaction product.



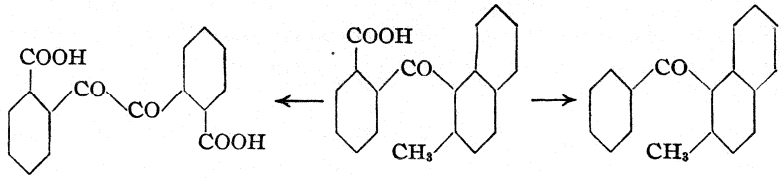
I

By blocking position 2′ with a methyl group we hoped to prevent entirely the formation of an anthraquinone, but this expectation was not realized. On heating 2′-methyl-1-naphthoyl-2-benzoic acid (III) in sodium aluminum chloride at 150°, there was produced a yellow substance having the composition and the properties of a methyl-1,2-benzanthraquinone. Such a compound could be formed from an acid of the structure indicated only as the result of a rearrangement. In view of the unexpected results, it seemed advisable to establish beyond question the structure of the starting material. There can be little doubt on this point, for Scholl and Tritsch, who prepared the acid by condensing phthalic anhydride with β-methylnaphthalene, noted that the substance is not converted into an anthraquinone by concentrated sulfuric acid.[2] More positive evidence was

[1] (a) I. G. Farbenind., English Patent 303,375 (1930); (b) Fieser, THIS JOURNAL, **53**, 3546 (1931).

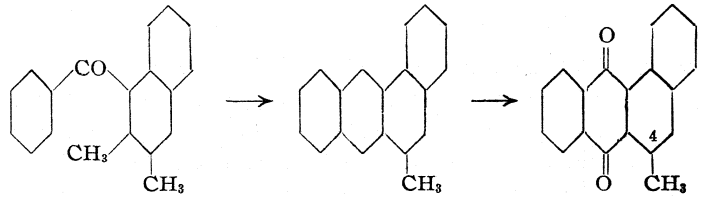
[2] Scholl and Tritsch, *Monatsh.*, **32**, 997 (1911).

found on the one hand in the oxidation of the acid to diphthalylic acid, II, and on the other hand by decarboxylation to the known ketone IV.



II III IV

Though the yellow condensation product obtained from III gave well-formed crystals, it did not melt sharply and after repeated fractionation it was separated into two isomeric quinones melting at 185 and 167°. Since all of the known methyl-1,2-benzanthraquinones melt in this same range, the melting temperature in itself is hardly characteristic and it was necessary to secure samples for comparison. The simplest course for the reaction to take would involve a displacement of the methyl group of III from the 2′ to the 3′ position, giving 4-methyl-1,2-benzanthraquinone, VII. We therefore synthesized the latter compound by carrying out an Elbs condensation on 1-benzoyl-2,3-dimethylnaphthalene, V, and oxidizing the product. The quinone, VII, melted at 167° but it was not identical with the lower melting isomer described above. It is a matter of interest that



V VI VII

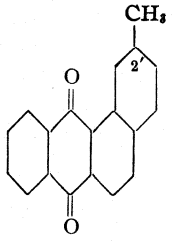
the product obtained by heating the ketone was found to contain both the hydrocarbon VI and the corresponding anthrone. The formation of an anthrone in the Elbs reaction has been observed only in rare instances.[3] The present synthesis is of further interest in connection with the recent observations of Cook.[4] It might be inferred from his statements that the cyclization of the ketone V could not be accomplished without the loss of a methyl group. Our results show that there is no such elimination of the alkyl group from this particular α-position (4) of the resulting benzanthracene. The generalization of Cook thus should be modified as follows: elimination of an alkyl group in the course of the Elbs reaction is to be expected when the group occupies an α-position in the naphthalene nucleus of the ketone.

[3] Morgan and Coulson, *J. Chem. Soc.*, 2551 (1929).

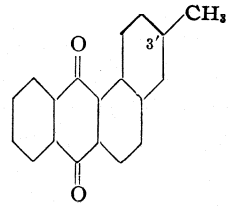
[4] Cook, *ibid.*, 456 (1932).

A second possible course of the rearrangement of the acid III would involve a displacement of the methyl group to the 4′ position. This would give 3-methyl-1,2-benzanthraquinone, a compound described by Scholl and Tritsch[2] as melting at 175°. This compound was likewise prepared for comparison but it was not identical with either of the two condensation products.

It thus seems evident that the methyl group of the benzanthraquinones in question is not attached to the anthraquinone nucleus but to the fused-on ring. Cook[4] recently has described 2′-methyl and 3′-methyl-1,2-benzanthraquinone (formulas VIII and IX) and their melting points are close to those of the compounds obtained in the present work. A comparison of our compounds with those prepared by Cook's method indeed proved the two pairs of compounds to be identical. The quinone melting at 185° has the structure of VIII, the isomer melting at 167° is IX.



VIII



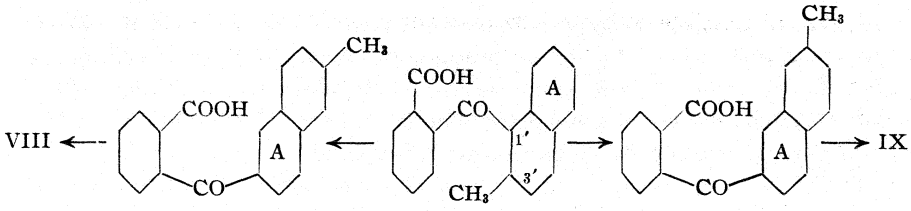
IX

The formation of the quinones VIII and IX could of course be the result of a migration of the methyl group in the starting material (III) to the unsubstituted ring of the naphthalene nucleus. Methyl migrations, though not of such an extensive kind, have been observed by Mayer, Fleckenstein and Günther in studying the Scholl condensation of aroylmethylnaphthalenes.[5] There is, however, a much more plausible way of accounting for the reaction, namely, that the rearrangement involves a migration of the aroyl rather than the methyl group. The mobility of an acyl or aroyl group in the α-position of naphthalene has been adequately demonstrated by Cook, both by direct[6] and by indirect[7] evidence. The migration is always from an α- to a β-position. In the present case the migration of the phthalic acid residue cannot be to a β-position of the ring which it originally occupied (position 1′ $\longrightarrow$ position 3′ in III, below) for this would give 4-methyl-1,2-benzanthraquinone instead of the 2′ and 3′ derivatives, VIII and IX. The formation of these quinones must be the result of a migration to both of the β-positions in the unsubstituted ring (A), in the following manner

[5] Mayer, Fleckenstein and Günther, *Ber.*, **63**, 1464 (1930).

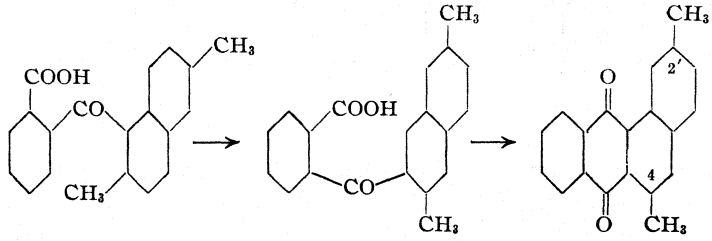
[6] Cook and Galley, *J. Chem. Soc.*, 2012 (1931).

[7] Cook, *ibid.*, 487, 489 (1931).



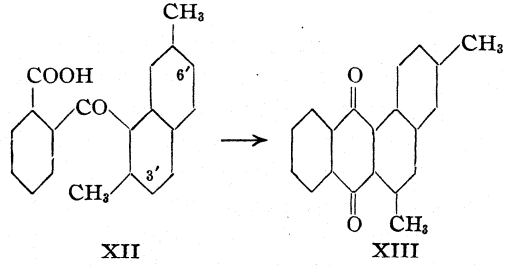
III

In order to test further this conception of the reaction, the condensation of three dimethylnaphthoylbenzoic acids was investigated. With the acid X, obtained from phthalic anhydride and 2,6-dimethylnaphthalene,



X XI

there are only two free β-positions to which the phthalic acid residue could migrate and these are identical. It is thus evident that if the reaction follows the course indicated it should yield only one product. This was found to be the case; dehydration with sodium aluminum chloride yielded a single, pure substance. We regard the product as 2′,4-dimethyl-1,2-benzanthraquinone (XI), and consider it to be formed by the rearrangement indicated. Starting with 2,7-dimethylnaphthalene, which is likewise symmetrical in structure, we next prepared the acid XII and carried out a dehydration. Here again the aroyl group can migrate in only one way, to



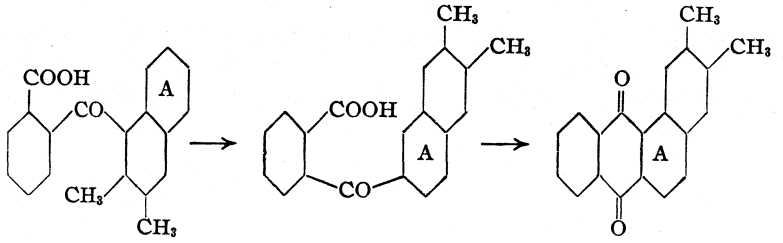
XII XIII

the identical β-positions 3′ and 6′. The condensation thus should give a single substance, XIII, and this should be an isomer of the dimethylbenzanthraquinone, XI, from 2,6-dimethylnaphthalene. The results were found to be in accord with both of these predictions.

It should be pointed out that it is quite impossible to predict the struc-

tures of these condensation products on the basis of the alternate hypothesis that the formation of the benzanthraquinones is the result of the migration of a methyl group. It does not appear likely, however, that the acids X and XII would each give a single quinone and that these quinones would be different, if a methyl migration were involved.

A further interesting application of the mechanism suggested for the reaction is found in the condensation of the 2′,3′-dimethyl derivative, XIV.



XIV XV

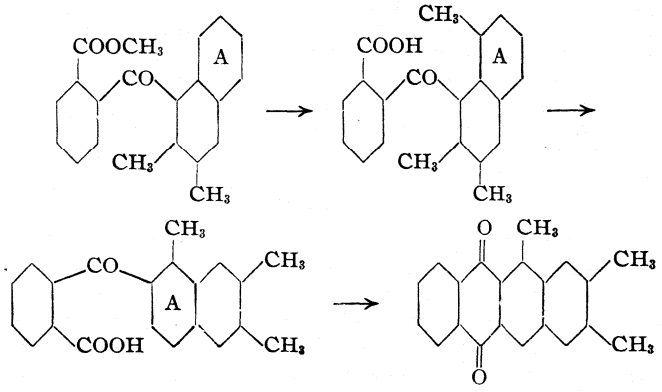
Here a rearrangement to a β-position in the ring originally carrying the aroyl group is not possible without the displacement of a methyl group. Any such displacement would probably lead to a mixture of substances. On the other hand, the migration to the unsubstituted ring, A, could give rise to only one compound, the dimethyl quinone, XV. In the reaction product actually obtained we found only one substance and it corresponded in properties to a substance having the structure of XV.

From the observations which have been made it seems clear that the reaction may be described in the following general terms. Under the influence of sodium aluminum chloride an α-naphthoylbenzoic acid carrying an alkyl group in such a position as to prevent direct quinone formation rearranges in such a way that the phthalic acid group migrates to any free β-position of the ring which does not contain the blocking alkyl group.

One other interesting observation was made in the course of this work. The intramolecular condensation of the aroyl benzoic acids was usually brought about by using the free acid in question, but in one or two cases an attempt was made to improve the yield by using the methyl ester. When the ester of 2′,3′-dimethyl-1′-naphthoyl-2-benzoic acid (XIV) was so employed the reaction mixture was found to contain in addition to the dimethyl-1,2-benzanthraquinone, XV, a substance having the composition and properties of a trimethylbenzanthraquinone. It differed, however, in a striking manner from the other methylated quinones which have been described or discussed in this paper, for it did not form the characteristic hyposulfite vat. Such a behavior is a highly characteristic property of the linear tetracyclic quinones and it is an indication that the compound in question is a derivative of naphthacenequinone rather than of the angular

1,2-benzanthraquinone. As for the source of the third methyl group it is significant that the trimethyl compound was obtained from the ester but not from the free acid. This suggests that the alkylation is brought about by the action of methyl chloride formed by the hydrolysis of the ester group. The ethyl ester was investigated but it yielded only the dimethyl quinone, XV. In view of the decreased reactivity of ethyl as compared with methyl chloride the result is not surprising.

The yield of the trimethyl derivative is so low that it seemed impractical to attempt to establish its structure. In view of this difficulty we may record here what we regard as the probable course of the reaction even though this is based upon very meager evidence (see formulas). The rearrange-



XVI

ment here postulated is in accord with the transformations observed above. The assumption that α-alkylation in Ring A precedes the migration is the only way of accounting for the formation of a linear, rather than an angular, quinone.

Experimental Part

1. Preparation of the Naphthoylbenzoic Acids

The methyl and dimethyl naphthalenes used for the condensation with phthalic anhydride were the highly purified products supplied by the Gesellschaft für Teerverwertung. As the solvent, both nitrobenzene and carbon disulfide proved less satisfactory than tetrachloroethane, and the best results were obtained by working at a low temperature. The general procedure adopted was as follows. A solution of 0.1 mole of the hydrocarbon and 0.11 mole of phthalic anhydride in 100 cc. of tetrachloroethane (warmed) was stirred mechanically in an ice-bath and 0.22 mole of aluminum chloride was added in the course of one hour. Stirring was continued for about five hours and the mixture was allowed to stand overnight. The product was worked up in the usual manner and precipitated from a cold soda solution. The crude acid in most cases separated in the form of an unstable hydrate and the product was best dried by heating it on the steam-bath, cooling and pouring off the water. The yield usually was quantitative and the crude product pure enough for most reactions. The acids do not form particularly good crystals and they are most conveniently purified through the esters,

where this is possible. The properties and analyses[8] of the acids are recorded in Table I, the corresponding esters are described in Table II. The methyl ester of 2′-methyl-1′-naphthoyl-2-benzoic acid was obtained only as an oil.

TABLE I

ALKYL DERIVATIVES OF 1′-NAPHTHOYL-2-BENZOIC ACID

Positions of substituents	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Melting point, °C.
2′-Methyl[2]	78.60	78.40	4.86	4.91	193
2′,6′-Dimethyl	78.92	78.12	5.30	5.42	238
2′,7′-Dimethyl	78.92	79.09	5.30	5.45	210
2′,3′-Dimethyl	78.92	79.06	5.30	5.40	205

TABLE II

ESTERS OF THE DIMETHYL-1′-NAPHTHOYL-2-BENZOIC ACIDS

Positions of substituents	Ester group	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Melting point, °C.
2′,6′	Methyl	79.23	79.02	5.70	5.80	162
2′,7′	Methyl	79.23	78.88	5.70	5.82	131
2′,3′	Methyl	79.23	79.18	5.70	5.85	170
2′,3′	Ethyl	79.49	79.58	6.07	6.11	165

2. Proof of Structure

2′-Methyl-1′-naphthoyl-2-benzoic acid (2.9 g.) was oxidized in alkaline solution with potassium permanganate (13 g.) in essentially the manner described by Graebe for the unmethylated acid.[9] In working up the product, however, it was found convenient to take advantage of the sparing solubility of the manganese salt of the oxidation product. At the end of the reaction the mixture was treated with sulfur dioxide until the manganese dioxide was dissolved and the manganese salt referred to had separated as a white precipitate. This was boiled with alkali, the solution was filtered and acidified and the diphthalylic acid (1 g.) precipitated at this point in nearly pure condition. Crystallized from nitrobenzene it melted at 277°.

Anal. Calcd. for $C_{16}H_{10}O_6$: C, 64.42; H, 3.38. Found: C, 63.98; H, 3.64.

The acid was definitely identified by the preparation of the colorless and the yellow methyl derivatives described by Graebe and Juillard,[10] which were found to melt at 276 and 192°, respectively. The yellow ester was prepared with diazomethane instead of through the silver salt.

The decarboxylation of 2′-methyl-1′-naphthoyl-2-benzoic acid was accomplished by heating it with a trace of copper powder at 300°, and quickly distilling the product in vacuum in order to avoid an Elbs condensation. The resulting ketone had to be seeded but it then crystallized well, melted at 71°, and showed no depression on admixture with an authentic sample of 1-benzoyl-2-methylnaphthalene (m. p. 71°).[11]

A further derivative of the keto acid may be described. *2′-Methyl-1′-naphthylmethyl-2-benzoic acid*, prepared by reducing the keto acid with zinc dust in alkaline solution, melted at 187° after crystallization from benzene–ligroin.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.44; H, 5.93.

[8] The analyses (semi-micro) reported in this paper were all carried out by Mr. C. L. Bickel.

[9] Graebe, *Ann.*, **340**, 249 (1905).

[10] Graebe and Juillard, *ibid.*, **242**, 214 (1887).

[11] Mayer and Sieglitz, *Ber.*, **55**, 1851 (1922).

The structure of 2′,3′-dimethyl-1′-naphthoyl-2-benzoic acid was established by oxidation in the manner described above to a product which was identified as diphthalylic acid.

3. Condensation to the 1,2-Benzanthraquinones

The condensations were all carried out in much the same manner. Thus for the reaction of 10 g. of 2′-methyl-1′-naphthoyl-2-benzoic acid a melt was made by heating a mixture of 12.5 g. of sodium chloride and 62.5 g. of aluminum chloride over a free flame until fusion was complete. The melt was allowed to cool until it began to crystallize (about 100°), and the acid was slowly added with good stirring. The mixture was then heated for one-half hour with continued stirring in an oil-bath at 150°. The mixture changed from a bright red color at the beginning to brown. On pouring the hot melt onto ice the quinone separated as a greenish-yellow solid. The material did not filter well and became somewhat oily on being heated and it was found expedient to extract the quinone by shaking the suspension with ether. The material left on evaporation of the ether did not crystallize well until after it had been distilled *in vacuo*. Crystallization from glacial acetic acid then gave a very good product; yield, 6.6 g. (71%).

No separation of the isomers present was accomplished by repeated crystallization from glacial acetic acid or from alcohol, the melting point remaining at 168–170°. The composition was that of a methylbenzanthraquinone.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.45. Found: C, 83.39; H, 4.62.

After further purification by vatting, the product gave extremely well-formed crystals but the melting point remained unsharp and variable. A separation was finally accomplished by fractional crystallization from methyl ethyl ketone, the higher melting isomer crystallizing first. There is very little difference in the solubilities, and the amounts of the two pure components isolated were small. One isomer after further repeated crystallization from glacial acetic acid melted at 185° and showed no melting-point depression with 2′-methyl-1,2-benzanthraquinone, which we prepared according to Cook[4] and for which we found a melting point of 186°. The other isomer, crystallized from benzene–ligroin, melted at 167° and was identical with an authentic sample of 3′-methyl-1,2-benzanthraquinone which melted at 168°.

The condensation of the dimethylbenzoic acids was carried out in exactly the manner described above. The yields of material which had been extracted, distilled and crystallized were all about 70% of the theoretical amount, and we found no sign of the presence of isomers. The quinones all crystallized from glacial acetic acid in the form of good yellow needles, and the melting points were sharp. The properties are recorded in Table III.

TABLE III

DIMETHYL-1,2-BENZANTHRAQUINONES, $C_{20}H_{14}O_2$

Positions of substituents	Formula	Color in H_2SO_4	Melting point, °C.	Analyses, % C Calcd.: 83.89	H Calcd.: 4.93
2′,4	XI	Blue	190	83.68	5.12
3′,4	XIII	Dull red	195	83.74	5.08
2′,3′	XV	Purple	236	83.70	4.96

The condensation product obtained from the methyl ester of 2′,3′-dimethyl-1′-naphthoyl-2-benzoic acid was worked up in a somewhat different manner. The suspension obtained on pouring the melt onto ice gave a good solid product on being digested at the boiling point. This was extracted with successive portions of boiling glacial acetic acid from a small amount of residue and the quinone was precipitated with water, dried and distilled. This was crystallized repeatedly from glacial acetic acid until the crystals no longer gave a red vat with alkaline hyposulfite solution. The crystals were those of

the trimethyl quinone described below, yield 4%. The dimethyl quinone present in the mother liquors was easily isolated in pure form by taking advantage of the fact that, unlike the trimethyl derivative, it forms a characteristic red hyposulfite vat. After crystallization of the vatted material, 2',3'-dimethyl-1,2-benzanthraquinone melting at 236° was obtained in 60% yield.

1,2',3'-Trimethyl-2,3-benzanthraquinone, XVI.—The first product obtained from the condensation formed long, orange-yellow needles, melting at 275°. The solution in concentrated sulfuric acid is bluish-green in color.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.97; H, 5.37. Found: C, 83.83; H, 5.62.

The compound is distinctly less soluble and higher melting than the dimethyl-1,2-benzanthraquinones. In these properties and in the appearance of the crystals it strongly resembles naphthacenequinone. A further striking resemblance is in the behavior toward reducing agents. The new substance is not affected by boiling with alkaline hyposulfite solution, it forms a green vat on adding this reducing agent to an alcoholic suspension of the quinone, and a red color, which is rapidly discharged by shaking with air, is produced by the action of zinc dust in glacial acetic acid solution.

4. Synthesis of 4-Methyl-1,2-benzanthraquinone

1-Benzoyl-2,3-dimethylnaphthalene (V).—The ketone was prepared both by the usual synthesis and by the Perrier method of carrying out the Friedel and Crafts reaction. The latter method was found to be much more rapid and to give a better yield of the pure product. To a suspension in carbon disulfide of the addition compound from 14.1 g. of benzoyl chloride and 14.0 g. of aluminum chloride, 15.6 g. of 2,3-dimethylnaphthalene was added in the course of a few minutes. After heating on the steam-bath for ten minutes to complete the reaction, the mixture was cooled and the crystalline addition product was collected and washed with carbon disulfide. It was decomposed by stirring it into ice and the ketone formed in this operation was obtained as a good solid by crushing the lumps and washing with a little ether; yield, 18 g., 79%. One crystallization from alcohol gave a pure product melting at 126°. It crystallizes well from alcohol as stout colorless needles.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.65; H, 6.15. Found: C, 87.46; H, 6.26.

The Elbs condensation was carried out by heating the ketone at the temperature necessary to maintain gentle boiling for three to four hours. On distillation in vacuum a considerable residue was left and the distillate was an oil which did not solidify. The hydrocarbon and the anthrone were isolated from this oil only in small amounts and in separate experiments. The corresponding quinone is easily obtained by oxidizing the crude distillate, but the yield from the ketone was only 16%. The anthrone was isolated by dissolving the oil in ligroin; the solution slowly deposited a small crop of yellow crystals. The hydrocarbon was separated from an alcoholic solution as the picrate. This was purified to a constant melting point and converted into the hydrocarbon.

4-Methyl-1,2-benz-9-anthrone forms yellow leaflets melting at 150° from ligroin. The solution in alcoholic alkali is yellow with a green fluorescence.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.09; H, 5.45.

4-Methyl-1,2-benzanthracene (VI) forms colorless microscopic clusters of needles from alcohol, m. p. 107°. The picrate crystallizes from alcohol as fine dark red needles, melting at 119–120°.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.83. Found: C, 94.05; H, 5.88.

4-Methyl-1,2-benzanthraquinone (VII) crystallizes from glacial acetic acid as well-formed yellow needles, melting at 167°. It is dull green in concentrated sulfuric acid. It forms a hydroquinone diacetate melting at 220°.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.45. Found: C, 83.42; H, 4.53.

Summary

It was expected that the substitution of a methyl group in the 2′-position of 1′-naphthoyl-2-benzoic acid would prevent the formation of an anthraquinone on subjecting this substance to condensation in the sodium aluminum chloride melt. It was found, however, that two isomeric methyl-1,2-benzanthraquinones are produced and a study has been made of the rearrangement obviously involved in the course of the reaction. Through the identification of the methylbenzanthraquinones and a study of the condensation of various dimethyl-1′-naphthoyl-2-benzoic acids it has been found that the rearrangement involves the migration of the phthalic acid residue to a β-position of the originally unsubstituted ring.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. CXXX. SYNTHESIS OF 2-KETO-1,2,3,4-TETRAHYDROPYRIMIDINES

BY KARL FOLKERS,[1] H. J. HARWOOD[1] AND TREAT B. JOHNSON

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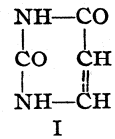
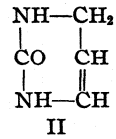
This paper is presented as a preliminary contribution dealing with methods of synthesis and the chemistry of 2-keto-1,2,3,4-tetrahydropyrimidine compounds. The structural relationship between uracil and the mother substance of such a series (acroleinharnstoff) is expressed by formulas I and II, respectively. Theoretically the pyrimidine II should



I



II

be formed by the action of acrolein on urea, but, thus far, all attempts to prepare this compound by interaction of these reagents have been unsuccessful.[2,3,4]

A practical procedure for preparing derivatives of this pyrimidine II was first described by Biginelli[5] in 1893. This is based on that investigator's discovery that an aldehyde will combine with a β-keto ester and urea in alcohol solution with smooth formation of a tetrahydropyrimidine. With benzaldehyde and ethyl acetoacetate, for example, he was able to

[1] Squibb and Sons Research Fellows in Organic Chemistry, 1931–1932.

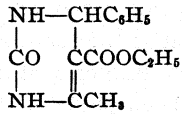
[2] Schiff, *Ann.*, **151**, 203 (1869); *Ber.*, **15**, 1393 (1882).

[3] Leeds, *Ber.*, **15**, 1159 (1882).

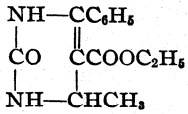
[4] Lüdy, *Monatsh.*, **10**, 300 (1889).

[5] Biginelli, *Gazz. chim. ital.*, **23**, 360 (1893); *Atti. accad. Lincei*, [5] **3**, 195 (1894); *Chem. Zentr.*, **65**, 823 (1894); *Ber.*, **24**, 1317 (1891).

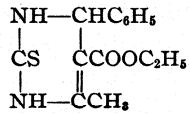
prepare 2-keto-6-methyl-5-carbethoxy-4-phenyl-1,2,3,4-tetrahydropyrimidine III, and he also applied the reaction successfully with several dif-



III



IV



V

ferent aldehyde combinations. Biginelli showed, furthermore, that the same pyrimidine III is also formed by interaction of benzaldehyde with β-carbamidocrotonic ester, by combining benzylidene-diureide with ethyl acetoacetate and by the action of ethyl α-benzalacetoacetate on urea.

Apparently no further attention was paid to the Biginelli condensation until 1929, when Hinkel and Hey[6] took up his work and introduced changes in experimental technique which they considered favorable for the production of dihydropyridines according to the Hantzsch reaction. These investigators did succeeed in demonstrating the formation of dihydropyridines by using Biginelli's reagents, but they found that in every case examined, the main product of the condensation was still a tetrahydropyrimidine derivative as originally formulated by Biginelli. The authors became interested in the chemistry and application of the Biginelli condensation for the following reasons: (a) the necessity of acquiring additional evidence in support of the constitution assigned to the products of reaction described by Biginelli: (b) the need of a clearer conception of the mechanism of the change leading to these pyrimidine formations, and (c) the possible application of the reaction for the synthesis of a large number of new organic substances for pharmacological research, in which constitutional changes of great variety could be incorporated. In fact, this series of pyrimidines offers unusual possibilities for evaluating and determining the influence of definite changes in molecular structure on physiological action.

If Biginelli's conclusion of cyclic structure as represented in formula III is correct, one is compelled to take under consideration also the isomeric forms as represented in formula IV. In tetrahydropyrimidines of this type we are dealing with cyclic allyl constructions and from our past experience it is known that such unsaturated groupings are theoretically prone to isomeric change, in this case with shifting of a double bond in the pyrimidine ring. This interesting question of isomerization is now receiving attention by us, and will be discussed in a future paper. Hinkel and Hey obtained evidence of isomerization when they examined the behavior of thio-urea toward benzaldehyde, ethyl acetoacetate and urea. The introduction of a mixture of urea or thiourea, a β-keto ester and an aldehyde together into a common solution like alcohol constitutes an or-

[6] Hinkel and Hey, *Rec. trav. chim.*, **48**, 1280 (1929).

ganic system which presents the possibility of a variety of chemical reactions taking place. It would be predicted, therefore, that different organic combinations would be capable of formation depending upon the experimental conditions employed. Biginelli observed no evidence of the formation of any product except a tetrahydropyrimidine, while Hinkel and Hey working under different conditions report the formation also of small amounts of a pyridine derivative. In fact, Hinkel and Hey conclude that the fundamental difference between the pyridine condensation of Hantzsch and that of Biginelli would appear to be due to the fact that in the former the first reaction is between ethyl acetoacetate and ammonia, whereas in the Biginelli reaction the first action consists undoubtedly in the formation of the aldehyde diureide. In the opinion of the authors it is not yet established conclusively that the correct explanation of the mechanism of the Biginelli condensation has been given and the authors are now engaged in a study of this problem.

We have now extended the application of Biginelli's condensation by utilizing a common β-keto ester—ethyl acetoacetate—and by varying the constitution or type of aldehyde combination. Both aliphatic and aromatic aldehydes have been used. As a result we have been able to synthesize several new pyrimidine representatives belonging to Biginelli's series of condensation products. In every case which we have examined we have employed hydrochloric acid to catalyze the condensation reaction. The pyridine condensation of the Hantzsch type apparently does not take place under such experimental conditions. The various 2-keto-1,2,3,4-tetrahydropyrimidines which have been prepared are registered in Table I in the Experimental Part of this paper. All of these pyrimidines will be examined to ascertain their physiological behavior.

After six months' experience with the study of this tetrahydropyrimidine class of compounds, the directions of Hinkel and Hey have again been carried out in an effort at a duplication of them, but in every case the results were negative. With purified ethyl acetoacetate, which did not show the slightest acidity to litmus paper, the reaction mixture was poured into 300 ml. of water and allowed to stand for twenty-four hours, when a yield of only 0.77% was obtained. Redistilled ethyl acetoacetate which had stood for two months and showed a slight acidity to litmus paper gave a yield of pyrimidine equal to 2.3%. Again using the acid-free ester and adding (a) four drops of glacial acetic acid and (b) twenty-five drops of glacial acetic acid to the solution, yields of 3.8 and 16.9%, respectively, were obtained. With these same reagents, and using four drops of concentrated hydrochloric acid as catalyst, the yield of pyrimidine was raised to 78.5%. These experiments demonstrate that the three components react in the Biginelli condensation at a very slow rate unless catalyzed by acid. It appears that the reason for Hinkel and Hey ob-

taining the Hantzsch condensation as a side reaction was because the amount of acid impurities was not sufficient to prevent it.

Experimental Part

Application of Biginelli's Condensation. Preparation of 2-Keto-6-methyl-5-carbethoxy-4-phenyl-1,2,3,4-tetrahydropyrimidine. III

In Ethanol.—A careful study of the experimental conditions influencing Biginelli's reaction has led to the following procedure for preparing this pyrimidine in maximum yield. Fifty-three grams of benzaldehyde, 30 g. of urea, 97.5 g. of ethyl acetoacetate, 200 ml. of absolute ethanol and 40 drops of concentrated hydrochloric acid were refluxed for three hours. The reaction mixture was then cooled to 0°, and the pyrimidine filtered and dried at 50°. The yield here was 93.6 g. The filtrate was then refluxed for two hours longer and finally distilled until 155 ml. of alcohol was collected. On cooling the residue we obtained an additional 21.3 grams of the pyrimidine or a total yield of 88.4% of the theoretical. To purify this substance it was divided into two equal portions, and each fraction dissolved in 800 ml. of 95% boiling alcohol. On cooling, the pyrimidine III separated in colorless crystals melting at 202–204°. The yield of purified material was 102 g. The loss on recrystallization may be materially decreased by distilling the solvent to incipient crystallization, since the pyrimidine dissolves in alcohol slowly and an excess of solvent is generally used.

In Glacial Acetic Acid.—Biginelli's condensation can be applied successfully in glacial acetic acid solution. In order to determine whether this solvent or ethanol was more favorable for the condensation, three experiments were conducted as follows. One-tenth mole each of benzaldehyde and urea, 0.15 mole of ethyl acetoacetate, and eight drops of concentrated hydrochloric acid were taken in individual experiments and treated for three hours as follows: (a) refluxed at 85° in 40 ml. of absolute ethanol; (b) heated at 85° in 40 ml. of glacial acetic acid, and (c) refluxed at 112–125° in 40 ml. of glacial acetic acid. The reaction product in each experiment was obtained by pouring the cooled reaction mixture into 400 ml. of water, filtering and drying. The pyrimidine was recrystallized by dissolving in 400 ml. of boiling ethanol and then distilling 250 to 285 ml. of the solvent. The yields of pyrimidine were (a) 70% (m. p. 201.5–203°); (b) 68.1% (m. p. 201–203°); (c) 63.5% light yellow crystals (m. p. 201.5–203°). Thus the tetrahydropyrimidine may be prepared in similar yield and purity in either ethanol or glacial acetic acid at 85°.

Hinkel and Hey's Modification of Biginelli's Condensation Reaction.—The procedure of Hinkel and Hey for the preparation of the tetrahydropyrimidine III in ethanol was repeated but without success after four trials. However, if four drops of concentrated hydrochloric acid for each 0.05 mole of urea were added before refluxing, the Biginelli condensation was accomplished successfully and the tetrahydropyrimidine III was obtained in better yields than those reported by Hinkel and Hey. Their directions for carrying out the condensation with thiourea, ethyl acetoacetate and benzaldehyde to obtain the thiopyrimidine V were also repeated, but without success, unless a few drops of concentrated hydrochloric acid were added as a catalyst. In this connection it is also important to note that Biginelli did not specify the use of hydrochloric acid when he prepared his pyrimidine III, but he did mention its use in the application of the condensation reaction between benzaldehyde and β-carbamidocrotonic ester.

Hinkel and Hey postulated that the Biginelli condensation first involves the formation of an aldehyde-diureide as an intermediate and introduced two equivalents of ethyl acetoacetate, believing that this extra equivalent was necessary to convert the diureide into ethyl β-carbamidocrotonate, thus leading to an improved yield of the pyrimidine III.

TABLE I

2-KETO-6-METHYL-5-CARBETHOXY-4-R-1,2,3,4-TETRAHYDROPYRIMIDINES

R-	Aldehyde RCHO	Moles Urea	Ester	Solvent, ml.	Drops concd. HCl	Reflux time, hrs.	Solvent	Yield, %	M. p. uncorr., °C.	Analyses, % N Calcd.	Found	
Phenyl- (1)	0.5	0.5	0.75	EtOH 200	40	3	EtOH	78.5	202.4	..	..	..
4-Hydroxyphenyl- (2)	.2	.2	.3	EtOH 50	12	3	EtOH	66.5	227–229	10.14	9.97	9.98
4-Methoxyphenyl- (3)	.2	.2	.3	EtOH 80	16	3	EtOH	61.2	201–202	9.65	9.37	9.41
4-Nitrophenyl-	.066	.066	.1	AcOH 100	8	3	EtOH	58.4	207–208.5	13.77	13.57	13.61
4-Nitrophenyl-	.072	.072	.108	EtOH 40	6	4	Aq-EtOH	31.3	207–208.5	..	..	..
3-Nitrophenyl-	.3	.3	.3	EtOH 75	12	6	BuOH	56.6	226–227.5	..	..	..
Styryl- (4)	.5	.5	.75	AcOH 350	0	0	BuOH	71.4	238–239.5	..	..	..
2-Phenylethyl- (5)	.1	.1	.15	AcOH 70	0	0	Aq-EtOH	13.5	179.2–180.2	9.71	9.60	9.53
n-Hexyl- (6)	.5	.5	.75	EtOH 100	40	5.5	Aq-EtOH	7.6	151–152	10.44	10.54	10.55
Hydrogen- (7)	..	..	.45	AcOH 150	20	5	EtOH	17.9	253.8–256	..	..	..
Methyl-	.15	.10	.15	EtOH 20	8	3	Aq-EtOH	25.8	189–190	..	..	..
Methyl- (8)	.15	.10	.15	Dioxane 40	5	2	.....	46.9	181–184	..	..	..
4-Aminophenyl- (9)	..	..	..	.....	..	..	Aq-EtOH	..	220–221	15.27	14.99	14.99
3-Aminophenyl- (9)	..	..	..	.....	..	..	Aq-EtOH	51.6	208.2–209.5	15.27	14.97	14.91
3-Methoxy-4-hydroxyphenyl-	.1	.1	.15	EtOH 40	8	3	EtOH	42.5	232–233	9.15	9.14	8.96
3,4-Dimethoxyphenyl-	.1	.1	.15	EtOH 40	8	2	EtOH	46.9	178–178.5	8.75	8.71	8.70
3,5-Diiodo-4-hydroxyphenyl- (10)	.025	.025	.037	AcOH 30	2	2.25	Gl-AcOH	11.5	216	5.31	5.11	5.10
2,4,6-Trimethoxyphenyl- (11)	.015	.015	.022	EtOH 10	1	2	EtOH	38.1	185–185.5	8.00	7.94	7.99
2-Hydroxyphenyl- (12)	.1	.1	.15	EtOH 40	5	3	EtOH	19.0	201–202	..	..	..
2,4-Dihydroxyphenyl- (13)	.05	.05	.075	AcOH 20	..	..	EtOH	34.2	225.5–226.5	9.59	9.33	9.33
Furyl- (14)	.1	.1	.15	AcOH 40	..	..	EtOH	36.0	204.5–205	..	..	..
3,4-Methylene-dioxyphenyl-	.1	.1	.15	EtOH 40	8	3	EtOH	49.0	187–188	9.21	9.08	9.10
2,6-Dimethyl-1,5-heptadienyl- (15)	.5	.5	.75	AcOH 100	..	5	EtOH	..	150.5–151.5	9.15	904	8.99

COMMENTS ON TABLE I

(1) The actual manipulation of this preparation is described above.

(2) After refluxing the mixture was allowed to stand three days for crystallization.

(3) An additional 3.1 g. of reaction product was obtained by refluxing the filtrate and concentrating the solution.

(4) The components were mixed and allowed to stand for forty-three hours at 25°. During this time 71.4% of the reaction product crystallized out in pure form. The filtrate and washings were allowed to stand for forty-two hours and then poured into water. This gave 12.8 g. more of condensation product, m. p. 236–238°; total yield, 80.3%.

(5) Components allowed to stand for nineteen days at 25° and then poured into 300 ml. of water; the yield was not improved by refluxing in absolute ethanol. *Anal.* Calcd.: C, 66.62; H, 6.99. Found: C, 66.88; H, 6.89.

(6) Was made in two runs of 0.2 mole each and one of 0.1 mole. The reaction mixtures were poured into water and allowed to stand overnight, after which they were combined and the solid separated from oil by filtration. *Anal.* Calcd.: C, 62.64; H, 9.02. Found: C, 62.52; H, 9.16.

(7) 21.3 g. of methylene urea[7] was refluxed with the ketone ester in acetic acid. The suspension of methylene urea gradually dissolved and after filtering, the solution was cooled and poured into 500 ml. of water.

(8) In using dioxane the hydrochloric acid was not added until after one hour of refluxing. When this was added at the beginning, 3.3 g. of alcohol-insoluble material was obtained which melted at 235.5–236.5°. By allowing acetaldehyde and urea to interact in an acidified (hydrochloric acid) water solution at room temperature for several days, a precipitate was obtained which melted at 236.5–237.5°. A mixture of the two products melted at 232–233°.

(9) These two amino derivatives were prepared by hydrogenation of the corresponding nitro compounds with platinum catalyst in glacial acetic acid under three atmospheres of hydrogen. The only loss was that of recrystallization.

The 3-amino compound was also made by reduction of the nitro compound with zinc dust and hydrochloric acid as follows: 15 g. of nitro compound was dissolved in 200 ml. of glacial acetic acid at 75°. After adding 75 g. of zinc dust, 160 ml. of concentrated hydrochloric acid was added in the course of an hour. The solution was then filtered, concentrated *in vacuo* at 75°, cooled, made ammoniacal and filtered. The precipitate was leached twice with concentrated ammonium hydroxide solution, filtered, washed and dried to yield 11.5 g. (85%) of product of m. p. 202.5–206°. After three recrystallizations from aqueous ethanol it melted at 208.5–209.5°. This melting point was not depressed when the material mixed with the 3-amino derivative obtained by catalytic hydrogenation.

(10) The cooled reaction mixture was poured into 350 cc. of cold water. The precipitate was crystallized once from 200 cc. of ethanol and then from glacial acetic acid with the addition of norite.

(11) After filtering the crystals which separated from the cooled reaction mixture, the filtrate was poured into water, a small amount of additional product being thus obtained.

(12) Previously prepared by Biginelli. The cooled reaction mixture was treated with 40 cc. of water and distilled until two phases began to appear. Upon cooling an oil separated which partially crystallized. The product was best purified by dissolving in a minimum of boiling ethanol and distilling to about one-third the volume.

(13) The mixture was allowed to stand at room temperature for four days. The

[7] Dixon and Taylor, *J. Chem. Soc.*, **109**, 1244 (1916).

precipitate was filtered and the filtrate allowed to stand for several weeks, additional material gradually separating. The product was purified by dissolving in a minimum of boiling ethanol and distilling to incipient crystallization.

(14) Previously prepared by Biginelli. The mixture was allowed to stand at room temperature for six days. The precipitate was then filtered and the filtrate poured into water yielding additional product.

(15) The cooled mixture was poured into 1500 cc. of water. An oil separated which partially crystallized upon standing overnight. This was washed with 100 cc. of 65% ethanol in two portions and was then treated with about 500 cc. of petroleum ether. After working well with a spatula, the insoluble material was filtered and washed with petroleum ether. A yield of 40.5 g. or 26.5% of crude product, m. p. 95–110°, was obtained. Fractional crystallization of this material from ethanol yielded in addition to the pyrimidine described in Table I a second product melting at 110–111.5°. *Anal.* Calcd. for $C_{17}H_{26}O_3N_2$ (m. p. 150.5–151.5°): C, 66.63; H, 8.56; N, 9.15. Found: C, 66.91; H, 8.74; N, 9.04, 8.99. Found for compound (m. p. 110–111.5°): C, 66.97; H, 8.69; N, 9.05, 9.05. The apparent isomerism of these two products is being investigated.

In order to determine what amount of β-ketone ester was necessary for producing a maximum yield of pyrimidine III in ethanol in the presence of hydrochloric acid, four experiments were carried out as follows: 0.05 mole each of urea and benzaldehyde were refluxed for two hours in 20 ml. of absolute ethanol with four drops of concentrated hydrochloric acid and with 1.0, 1.25, 1.5 and 2.0 equivalents of ethyl acetoacetate. The yield of the pyrimidine III crystallizing out on cooling was 58.5, 61.5, 67.7 and 64.6%, respectively. Evidently two equivalents of ethyl acetoacetate as used by Hinkel and Hey are excessive and in our condensations reported in this paper where ethyl acetoacetate was employed, 1.5 equivalents of the reagent were used.

As stated above, Hinkel and Hey detected small quantities of a pyridine derivative (4-phenyl-3,5-dicarbethoxy-dihydro-lutidine) by decomposition of the pyrimidine derivative formed in the Biginelli condensation with dilute nitric acid and precipitating the lutidine by addition of alkali. In order to determine whether there was any evidence of a Hantzsch condensation taking place under the experimental conditions used in our work, we performed the following experiment. One-tenth mole each of benzaldehyde, urea, and 0.15 mole of ethyl acetoacetate were refluxed for four hours in 40 ml. of absolute ethanol in the presence of six drops of concentrated hydrochloric acid. The cooled mixture was distinctly acid to litmus paper. It was made alkaline with 10% sodium hydroxide solution and poured into 200 ml. of water. The dried precipitate weighed 21.5 g. This was then decomposed by refluxing for four hours with 300 ml. of dilute nitric acid. The filtered solution was cooled. On making alkaline there was no precipitation of the lutidine derivative. From this result we conclude that the Hantzsch condensation does not take place to any appreciable extent by applying the Biginelli condensation in the presence of hydrochloric acid.

In Table I are recorded data from the preparations of the tetrahydropyrimidines by application of the Biginelli condensation. These substances were desired for pharmacological work, and therefore the condensation mixture was examined solely for these products. Undoubtedly the yields could be improved by variations in experimental technique. Several of these condensations are now being studied more critically in order to obtain a better understanding of the reaction mechanism and also to determine the possibility of isomerization. Details of manipulation in addition to the notes under Table I are not given, for the sake of brevity. The drops of hydrochloric acid were measured from a 5 ml. pipet. Practically all the recrystallizations were carried out by dissolving the pyrimidine in the solvent under a reflux condenser and then distilling to

incipient crystallization. Absolute ethanol and glacial acetic acid were the solvent media used for the condensation reactions.

Summary

1. The authors have reëxamined the condensation reaction described originally by Biginelli, which involves a combination between urea, a β-ketone ester and an aldehyde.

2. We have extended the application of this condensation reaction and find that the change is accelerated by the use of hydrochloric acid.

3. The condensation can be applied in either absolute alcohol or glacial acetic acid solutions.

4. Several new aldehydes have been incorporated in the reaction and several new 2-keto-1,2,3,4-tetrahydropyrimidines have been described.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS AND COMPANY]

OPTICAL PROPERTIES OF SOME DERIVATIVES OF LOWER ALIPHATIC ALCOHOLS AND ALDEHYDES

BY W. M. D. BRYANT

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Among physical methods of identifying closely related organic compounds, those of optical crystallography offer great promise both from the standpoint of speed and sensitivity.[1] The members of homologous series of organic compounds, because of their gradual changes in chemical and ordinary physical properties with increasing molecular weight, place great obstacles in the way of the chemist attempting their identification. A number of optical crystallographic properties can be observed by means of the polarizing microscope, many of which are, for all practical purposes, independent physical constants, and greatly increase the possibility of a precise identification of closely related compounds.

The scheme of optical identification employed in this research is one successfully used by Wright,[1] Wherry,[2] Keenan[3] and others,[4] and depends upon the determination of such properties as refractive index, optic axial angle, extinction angle, optical character, dispersion, together with the orientation of the optical ellipsoid within the crystal. This characteriza-

[1] Wright, THIS JOURNAL, **38**, 1647 (1916).

[2] Wherry, *U. S. Dept. Agr. Bull.*, No. 679 (1918); Wherry and Yanovsky, THIS JOURNAL, **40**, 1063 (1918).

[3] Keenan, *J. Biol. Chem.*, **62**, 163 (1924); Keenan and Weisberg, *J. Phys. Chem.*, **33**, 791 (1929); Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).

[4] Poe and Sellers, *ibid.*, **54**, 249 (1932); Kofler and Mayrhofer, *Mikrochemie*, **10**, 460 (1932); Takahashi and Yaginuma, *J. Soc. Chem. Ind. Japan, Suppl.*, **33**, 370 (1930).

tion is usually carried out upon detached crystals and only rarely with crystals from fused preparations. Chamot and Mason[5] describe a procedure of obtaining crystals by fusion of substances directly on the microscope slide under a cover glass. Such a procedure naturally gives rise to better plane parallel crystal plates, thus facilitating the determination of the optic axial angle as well as examination with immersion objectives of high numerical aperture. This method has been used together with the others in the present investigation.

More stress is laid upon the optic axial angle in this paper than is usual in the recent literature. This property is a function of differences of the three refractive indices of biaxial crystals. It can be determined independently and is in many cases practically an independent physical property.

The technique outlined above was adopted in characterizing members of two series of aliphatic compounds, the lower saturated alcohols and aldehydes. The alcohols were converted into their 3,5-dinitrobenzoyl esters, and the aldehydes into the corresponding 2,4-dinitrophenylhydrazones. Both series of derivatives crystallize easily from solvents and melt without decomposition, hence are well suited for examination with the polarizing microscope.

Experimental

Materials.—Reagents: *2,4-dinitrophenylhydrazine* was an Eastman Kodak Company product. *3,5-Dinitrobenzoyl chloride* was prepared from the corresponding acid obtained from Eastman, according to Berend and Heymann,[6] and boiled at 194–196° at 10 mm. pressure. *Methanol* was a J. T. Baker special grade. *Ethanol* (absolute) was obtained from the U. S. Industrial Chemical Co. *n-Propanol* and *isobutanol* were du Pont products of boiling ranges, respectively, 97.1–97.3° and 107.5–107.7°. *Isopropanol, normal, secondary* and *tertiary butanol* were all obtained from the Eastman Kodak Company. *2-Methyl-butanol-2* was from the Sharples Solvents Corporation. *Formaldehyde* (37%) solution and *acetaldehyde* were Mallinckrodt products. *Propionaldehyde, normal* and *isobutyraldehyde* were again Eastman products. All of these substances were of the best grade available.

Preparation of the Derivatives.—The 3,5-dinitrobenzoates of the alcohols were prepared as directed by Reichstein.[7] The products were recrystallized twice from petroleum ether. The melting points of these derivatives were in satisfactory agreement with the literature as shown in Table I.

The 2,4-dinitrophenylhydrazones of the aldehydes were prepared by the method of Brady.[8] The derivatives were crystallized twice from hot aqueous alcohol. The melting points of some of these compounds are

[5] Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley and Sons, Inc., N. Y., 1930, Vol. I, p. 354.

[6] Berend and Heymann, *J. prakt. Chem.*, [2] **65**, 291 (1902); *ibid.*, **69**, 455 (1904).

[7] Reichstein, *Helv. Chim. Acta*, **9**, 799 (1926).

[8] Brady, *J. Chem. Soc.*, p. 756 (1931).

TABLE I

MELTING POINTS OF 3,5-DINITROBENZOYL ESTERS

Derivative	Melting point (observed), °C.	Melting point (literature), °C.	
Methanol	108	110 –110.5[7]	107.8[9]
Ethanol	93	93 – 94[7]	92.7[9]
n-Propanol	74	74 – 75[7]	73.0[9]
Isopropanol	123	121 –122[7]	122.1[9]
n-Butanol	64	61 – 63[7]	62.5[9]
Isobutanol	87	87 – 88[7]	86.5[9]
Sec.-butanol	76		75.6[9]
Tert.-butanol	142	141.5–142.5[7]	
2-Methyl-butanol-2	116	117 –118[7]	

higher than those in the literature, especially in the case of the formaldehyde derivative, for which there are no recent data. These results are given in Table II.

TABLE II

MELTING POINTS OF 2,4-DINITROPHENYLHYDRAZONES

Derivative	Melting point (observed), °C.	Melting point (literature), °C.
Formaldehyde	167	155[11]
Acetaldehyde	167	162[10]147[11]
Propionaldehyde	156	155[10]
n-Butyraldehyde	123	122[10]
Isobutyraldehyde	187	182[10]

Melting Points.—Melting points were determined potentiometrically by means of an electrically heated copper bar similar to that of Dennis and Shelton.[12] The bar was checked by the capillary tube method using calibrated short scale thermometers. The melting points in Tables I and II should be correct to ±0.5°.

Optical Equipment.—The petrographic microscope used in this investigation was the LCH model of Bausch and Lomb, specially equipped with a 1.40 N. A. immersion condenser. The principal source of light was the green line (5461 Å.) of the mercury arc isolated by means of Corning filters Nos. G-555-Q and G-34-Y. A few observations were made in red light from a Wratten No. 70 filter used in conjunction with an incandescent lamp.

A 7X Huyghenian eyepiece micrometer with a fixed linear scale was used for axial angle determinations. The angular equivalent of the micrometer scale was evaluated empirically with the aid of a Zeiss Abbe apertometer, hence the calibrations are independent of the Mallard relation.[13] These calibrations were further checked by comparison with a

[9] Malone and Reid, THIS JOURNAL, **51**, 3424 (1929).

[10] Brady and Elsmie, *Analyst*, **51**, 77 (1926).

[11] Purgotti, *Gazz. chim. ital.*, **24**, 569 (1894).

[12] Dennis and Shelton, THIS JOURNAL, **52**, 3128 (1930).

[13] Wright, "The Methods of Petrographic-Microscopic Research," Carnegie Bull. No. 158, p. 148 (1911).

carefully standardized cleavage of muscovite. The two standards agreed within the observational error. In this connection the writer wishes to thank F. E. Wright of the Geophysical Laboratory in Washington both for the mica and for the use of his axial angle apparatus in standardizing the specimen.

Refractive indices were determined by the immersion method and have been reported only where the optical orientation could be verified by interference figures. The immersion liquids used were prepared in intervals of 0.01 in refractive index extending from 1.36 to 1.72. Above 1.72 solutions were prepared only as required. The liquids of low refractive index were standardized by means of the Abbe refractometer. Liquids above 1.60 were determined by the method of minimum deviation using a spectrometer with hollow prisms. The dispersion of the liquids was also determined for sodium and several mercury lines. The following mixtures of liquids were used in the present investigation

n_D = 1.36–1.40 glycerol–glycol–water
n_D = 1.40–1.72 potassium mercuric iodide–glycerol–water
n_D = 1.74–1.78 methylene iodide–sulfur
n_D = 1.85–2.10 methylene iodide–arsenic trisulfide

Determination of Optical Properties

The optical characteristics of the fourteen crystalline derivatives of alcohols and aldehydes were determined by the conventional methods in use among petrographers and are given in Tables III and IV.

All refractive index measurements were carried out at 25 ± 3° using liquids standardized at 25°. In the alkyl dinitrobenzoate series the refractive index γ is not reported. This is because of the thin plate-like character of the crystals which makes the determination of the edgewise γ index extremely difficult. Likewise the optical data for formaldehyde 2,4-dinitrophenylhydrazone are extremely meager due to the peculiar habit of the crystals.

"Hydrazone" crystals presenting the β-γ index plane were obtained by sublimation from a cover glass, followed by cautious fusion upon the slide. Tabular forms of the desired orientation result from the crystallization of the minute fused droplets.

The third decimal place of the refractive index has been approximated by proportional mixing of adjacent immersion liquids. In the ester series the refractive indices should be correct to ±0.003. In the case of the "hydrazones" the error should not exceed ±0.005, but is probably greater than in the preceding series, due in part to the extremely strong double refraction which magnifies errors of optical orientation and to the instability of the more highly refracting solutions. Work is now under way to improve the precision of the measurements and to supply the missing refractive indices.

TABLE III

OPTICAL PROPERTIES OF 3,5-DINITROBENZOYL ESTERS

Derivative	Methanol	Ethanol	*n*-Propanol	Isopropanol	*n*-Butanol	Isobutanol	*Sec.*-butanol	*Tert.*-butanol	2-Methyl-butanol-2
Habit	Elongated plates	Prismatic needles	Elongated plates	Prismatic needles	Plates, needles	Plates, needles	Elongated plates	Elongated plates	Elongated plates
Probable crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Elongation	Elongation inclined 45° from β	Elongation = β	Elongation inclined 35° from α	Elongation = β	Elongation = β	Elongation = β	Elongation = β	Elongation = β	Elongation = β
Refractive indices α	1.382	1.560	1.486		1.488	1.558	1.486	1.484	1.491
λ = 5461 Å. at 25 ± 3° β	1.780	1.576	1.603	1.609	1.621	1.558	1.578	1.585	1.588
Precision ± 0.003									
Birefringence	Very strong	Medium	Strong	Strong	Strong	Medium	Strong	Strong	Strong
Optical character	Negative	Positive	Negative	Negative	Negative	Positive	Negative	Negative	Negative
Optic axial angle, $2E$	74 ± 5° (Calcd.)[b]	74 ± 2° (Calcd.)[b]	Large	126 ± 3° (Calcd.)[b]	107 ± 4° (Calcd.)[b]	15 ± 2°[a]	126 ± 6° (Calcd.)[b]	Large	Large
λ = 5461 Å.									
$2V$	40°	45°		67°	59°	10°	70°		
Remarks	Extinction inclined	Extinction parallel	Extinction inclined	Extinction parallel	Extinction parallel	Extinction parallel	Extinction parallel	Extinction parallel	Extinction parallel

[a] Microscope system calibrated directly with aid of the angle scale of the Abbe apertometer.

[b] Calibration as in (*a*), but using the numerical aperture scale of the apertometer, and converting the readings to $2E$ by means of the relation sin E = N. A.

TABLE IV

OPTICAL PROPERTIES OF 2,4-DINITROPHENYLHYDRAZONES

Derivative	Formaldehyde	Acetaldehyde		Propionaldehyde	*n*-Butyraldehyde	Isobutyraldehyde
Habit	Elongated prisms	Elongated prisms and tablets		Prisms	Elongated prisms	Elongated prisms
Probable crystal system	Monoclinic	Monoclinic		Monoclinic	Orthorhombic	Orthorhombic
Optical orientation		$b = \beta$ $b = \gamma$ (red)		$b = \gamma$	$c = \alpha$	$c = \alpha$
Refractive indices for α		1.412 1.410 (red)		1.426	1.426	1.426
λ = 5461 Å. at 25 ± 3°. β	1.901	2.078 1.938 (red)		1.917	1.869	1.906
Precision ± 0.005 γ		2.078 1.948 (red)		1.959	1.965	2.002
Birefringence	Very strong	0.666 0.538 (red)		0.533	0.539	0.576
Optical character	Negative	Negative		Negative	Negative	Negative
		I	II			
Optic Axial Angle $2E_{5461}$[a]	Large	16 ± 2°	5 ± 2°	44 ± 1°	80 ± 1°	78 ± 1°
Optic Axial Angle $2E_{6800}$[a]		42.5 ± 1°	45 ± 1°	58 ± 1°	88 ± 1°	87 ± 1°
Optic Axial Angle $2V_{5461}$		8°	2.5°	24°	40°	38.5°
Remarks	Extinction oblique in prisms from alcohol	Crossing of axial planes between 5461 and 5780 Å. Elongation inclined 51–56° from α in prisms from alcohol		Elongation inclined 54° from α in prisms from alcohol	Extinction parallel or symmetrical	Extinction parallel or symmetrical

[a] Microscope calibrated directly with aid of the angle scale of the Abbe apertometer.

The apparent optic axial angle in air, $2E$, was measured directly from interference figures of which both melatopes were visible, using an eyepiece micrometer calibrated with the angle scale of the Abbe apertometer. Where the angular field of a dry objective did not include both melatopes, or the crystal grains were too small to produce clear interference figures in the ordinary manner, a homogeneous oil immersion objective was used. In this case the ocular micrometer was calibrated by means of the numerical aperture scale of the apertometer and $2E$ calculated from the relation, N. A. $= \sin E$. If the optic axial angle in air is very large, the angle in oil, $2H$, may be calculated, using the expression, $\sin H =$ N. A./n, where n is the refractive index of the immersion oil. Rough estimates were obtained by other methods[14] where suitable interference figures were lacking. The estimated precision of the observations varies, becoming less for greater angles. Other factors[15] may affect the results to some extent but need not be considered here. For the sake of completeness the axial angle measurements have been reduced to the true angle $2V$ by means of the intermediate index β.

The 2,4-dinitrophenylhydrazones exhibit strong dispersion of the optic axes, and in one instance a crossing of the axial planes. The optic axial angles of these substances have therefore been reported for both the green mercury line at 5461 Å. and a narrow band in the red (6500–7000 Å.). They are practically opaque to the blue and violet mercury lines.

The crossed axial plane dispersion of the acetaldehyde derivative is particularly valuable for identification because of the comparative rarity of this phenomenon. Two samples of the derivative have been prepared which show slightly different axial angles, the difference being more marked in the green. Both preparations have the same melting point with no noticeable depression on mixing. It was further ascertained that the difference is not caused by either decomposition during fusion or a noticeable temperature coefficient. There is some indication of slight contamination since such an effect would increase $2E$ for green. Additional experiments are being carried out to clear up this uncertainty.

The probable crystal systems to which the two series of crystalline compounds belong were deduced from elementary symmetry considera tions. In the less certain cases, optical properties are referred to the elongation of the crystal.

Metastable Modifications.—Very little interference has been encountered from metastable forms resulting from the crystallization of fused preparations. A negative uniaxial tabular form of both the normal and isobutyraldehyde "hydrazone" has been observed on rare occasions. Isobutyl 3,5-dinitrobenzoate sometimes remains for several hours as a negative modification optically isomorphous with the other butyl esters.

[14] Wright, Carnegie Bull. No. 158, p. 152; *Am. J. Sci.*, [4] **20**, 285 (1905).

[15] Wright, *J. Opt. Soc. Am.*, **7**, 779 (1923).

Conclusions.—The results of the present investigation indicate that optical methods of identification are entirely feasible for differentiating between closely related substances, particularly when used in conjunction with the melting point. In the aldehyde series gratifying differences in refractive index and optic axial angle were observed. On the other hand, the differences in properties between the adjacent and isomeric alcohol derivatives were not as great as had been hoped, yet taken collectively there is little doubt that identification could be satisfactorily accomplished.

It seems likely that reagents could be selected which would yield compounds exhibiting greater variations in optical properties. Such a property might be encouraged by increasing the structural asymmetry of the reacting molecule. However, it is reasonable to believe that, ascending in an homologous series, the differences in physical properties would continually become less, and a point be reached where the ordinary precision of optical measurement would not be sufficient to distinguish between isomers. Such an effect might to some extent be offset by increasing the precision of the work.

The writer gratefully acknowledges the valuable advice and encouragement of Drs. F. E. Wright and H. E. Merwin of the Geophysical Laboratory in Washington, and extends his thanks to Dr. Edgar T. Wherry of the University of Pennsylvania, and Mr. G. L. Keenan in the Bureau of Chemistry for useful suggestions.

Summary

1. Optical properties of fourteen crystalline organic compounds have been determined. The compounds investigated include the 3,5-dinitrobenzoates of nine alcohols, and the 2,4-dinitrophenylhydrazones of five aldehydes, all of the saturated aliphatic series.

2. Acetaldehyde 2,4-dinitrophenylhydrazone is reported as a new example of crossed axial plane dispersion in crystals.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF THE OZARKS]

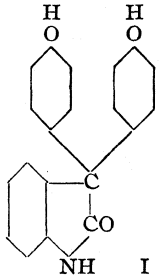
THE PREPARATION OF CERTAIN IODINATED DERIVATIVES OF PHENOLISATIN

BY WARD C. SUMPTER

RECEIVED MAY 31, 1932 PUBLISHED SEPTEMBER 5, 1932

Especial interest is attached to compounds of the oxindole series because of their possible use as therapeutic agents. While but little is known concerning the physiological effects of compounds of this series, such information as is available indicates that the further study of the chemical and pharmacological properties of such compounds may well lead to the discovery of valuable therapeutic agents.

Kendall has shown that certain synthetic oxindole derivatives[1] cause an increase in basal metabolism as well as in respiration rate. Oxindole and some of its derivatives[2] have been reported to possess antipyretic and antineuralgic properties. Phenolisatin (3,3-bis-(4'-hydroxyphenyl)-oxindole), I, and its diacetyl derivative[3] (Isacene) are finding use as mild purgatives.



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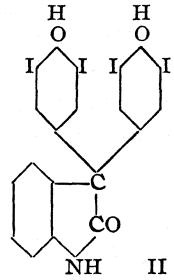

II

In view of the general interest attached to derivatives of oxindole, the similarity in the physiological properties of phenolisatin and phenolphthalein, and the fact that tetraiodophenolphthalein (Nosophen) possesses powerful antiseptic properties, it seemed desirable to undertake the preparation of a series of iodinated derivatives of phenolisatin.

5-Iodophenolisatin and 5,7-di-iodophenolisatin were prepared by condensing 5-iodoisatin and 5,7-di-iodoisatin with phenol. When heated with acetic anhydride for two hours at 130–135°, 5-iodophenolisatin yielded the triacetyl derivative while 5,7-di-iodophenolisatin on similar treatment gave the diacetyl derivative. This is in accord with the findings of Liebermann and Danaila[4] in the preparation of the acetyl derivatives of the corresponding chloro- and bromophenolisatins.

[1] Kendall, *Ind. Eng. Chem.*, **17**, 525 (1925).

[2] German Patent 218,477.

[3] Bergell, *Z. Mediz. Chem.*, **4**, 65 (1926); *Chem. Abstracts*, **21**, 3708 (1927); Christensen, *Archiv. Pharm. Chem.*, **88**, 47–56, 69–78 (1931); *Chem. Abstracts*, **25**, 4264 (1931).

[4] Liebermann and Danaila, *Ber.*, **40**, 3588–3597 (1907).

Derivatives of the type of II were prepared by iodinating phenolisatin, 5-iodophenolisatin, and 5,7-di-iodophenolisatin by the method of Datta and Prosad.[5] These highly iodinated derivatives are very insoluble in organic solvents and cannot be purified satisfactorily. Heating with acetic anhydride gave the corresponding triacetyl derivatives except in the case of the compound with iodine in position 7. In this case the diacetyl derivative was obtained.

Pharmacological tests of the compounds described in this paper are being made by Dr. T. H. Rider of the Wm. S. Merrell Co. and will be reported elsewhere by him.

Experimental

5-Iodophenolisatin (3,3-Bis-(4'-hydroxyphenyl)-5-iodo-oxindole).—Five cc. of concentrated sulfuric acid was added a drop at a time to a solution of 5 g. of 5-iodoisatin in 20 g. of molten phenol. After standing for ten minutes the reaction mixture was poured into one liter of water and the mixture stirred for one hour with a mechanical stirrer. The precipitate was filtered off and purified by crystallization from glacial acetic acid. The compound separated from this solvent in the form of colorless plates. When heated slowly from room temperature the substance seemingly undergoes a change at about 220° and melts with decomposition at 264–265°. When the melting point tube is introduced into the heating bath at 220°, the substance melts, solidifies and melts again at 264–265°. The lower melting point can be realized only by introducing the melting point tube into the heating bath at 220°. The yield was 5.7 g. or 70% of the theoretical.

Anal. Calcd. for $C_{20}H_{14}O_3NI$: N, 3.16. Found: N, 2.98, 2.98.

5,7-Di-iodophenolisatin (3,3-Bis-(4'-hydroxyphenyl)-5,7-di-iodo-oxindole).—The procedure was identical with that described above. The yield from 5 g. of 5,7-di-iodoisatin was 5.3 g. or 74% of the theoretical. The substance separated from glacial acetic acid in colorless plates; m. p. 239–240°.

Anal. Calcd. for $C_{20}H_{13}O_3NI_2$: N, 2.46. Found: N, 2.54, 2.42.

Iodination Procedure.—Iodination of phenolisatin, 5-iodophenolisatin, and 5,7-di-iodophenolisatin. The procedure in the case of phenolisatin is typical. One gram of phenolisatin was dissolved in 150 cc. of concentrated ammonium hydroxide and 25.2 cc. of a normal iodine–potassium iodide solution (four molecular proportions) slowly added. A colorless precipitate began to separate when about two-thirds of the iodine solution had been added. The reaction mixture was poured into an excess of dilute hydrochloric acid and the precipitate filtered off. In all three iodinations the products were very insoluble in organic solvents and could be purified only superficially by washing with acetic acid and water. None of the products melted on heating to 265°. The yields averaged 80% of the theoretical. The analyses indicate that the products were not obtained in a pure state.

Anal. (3,3-Bis-(3',5'-di-iodo-4'-hydroxyphenyl)-oxindole). Calcd. for $C_{20}H_{11}O_3NI_4$: N, 1.70; I, 61.85. Found: N, 1.69, 1.45; I, 58.38.

Anal. (3,3-Bis-(3',5'-di-iodo-4'-hydroxyphenyl)-5-iodo-oxindole). Calcd. for $C_{20}H_{10}O_3NI_5$: N, 1.47; I, 67.05. Found: N, 1.54, 1.52; I, 65.49.

Anal. (3,3-Bis-(3',5'-di-iodo-4'-hydroxyphenyl)-5,7-di-iodo-oxindole). Calcd. for $C_{20}H_9O_3NI_6$: N, 1.30; I, 71.00. Found: N, 1.41, 1.42; I, 68.08.

[5] Datta and Prosad, THIS JOURNAL, **39**, 441 (1917).

Acetyl Derivatives.—These derivatives were obtained by heating the appropriate phenolisatins with acetic anhydride at 130–135° for two hours.

TABLE I

Oxindole	Formula	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Iodine, % Calcd.	Iodine, % Found
A. 1-Acetyl-3,3-bis-(4′-acetoxyphenyl)-5-iodo-	$C_{26}H_{20}O_6NI$	169–170°[a]	2.46	2.51, 2.47	22.31	22.13
B. 3,3-Bis-(4′-acetoxyphenyl)-5,7-di-iodo-	$C_{24}H_{17}O_5NI_2$	256–257°[b]	2.29	2.09, 2.18	38.89	38.93
C. 1-Acetyl-3,3-bis-(3′, 5′-di-iodo-4′-acetoxyphenyl)-	$C_{26}H_{17}O_6NI_4$	267–268°[c]	1.47	1.31, 1.34	53.64	53.99
D. 1-Acetyl-3,3-bis-(3′, 5′-di-iodo-4′-acetoxyphenyl)-5-iodo-	$C_{26}H_{16}O_6NI_5$	272–273°[d]	1.30	1.24, 1.19	59.17	59.07
E. 3,3-Bis-(3′, 5′-di-iodo-4′-acetoxyphenyl)-5,7-di-iodo-	$C_{24}H_{13}O_5NI_6$	255–256°[e]	1.21	1.11, 1.25	65.86	66.04

[a] Colorless prisms from glacial acetic acid. [b] Colorless plates from glacial acetic acid. [c] Colorless prisms from acetic anhydride. [d] Colorless prisms from acetic anhydride. [e] Colorless plates from acetic anhydride.

The writer is indebted to Messrs. Lee Graves and Thell C. Woods for assistance in making the analyses reported herein, to Dr. S. H. Con'é of Wilmington, Delaware, for financial assistance and to the Dow Chemical Co. for the gift of a generous supply of indigo from which the isatin, iodoisatin, and di-iodoisatin used in this work were prepared.

Summary

Several iodinated derivatives of phenolisatin have been prepared.

CLARKSVILLE, ARKANSAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTICALLY ACTIVE DIAZO COMPOUNDS. VI. DIAZOCAMPHOR

BY WILLIAM ALBERT NOYES AND ERICH MEITZNER

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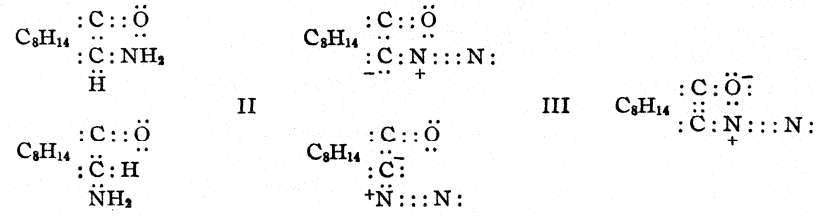
This is a continuation of a study of the question whether diazo compounds of the type, $R:\ddot{C}(\ddot{R}_2):N:::N:$, may occur in optically active forms.[1] Some of the previous investigations have not been satisfactory because the instability of some of the diazo compounds has prevented their isolation in a state of sufficient purity to demonstrate conclusively that the small rotations observed were not due to optically active impurities. The fact that in many of them the diazo group was attached to a carbon atom adjacent to a carbonyl group, may also have been an important factor (see below).

[1] Fifth paper, W. A. Noyes and Ulrich Heubaum, THIS JOURNAL, **52**, 5070 (1930). Further references will be found in that paper.

Diazocamphor (II) has been prepared by Schiff[2] by the action of nitrous



acid on an aminocamphor (I) which had not been resolved into active constituents. The compound is reported as comparatively stable and its study seemed to be of especial interest for our purposes. The same diazocamphor was obtained from each of the stereomeric aminocamphors. This excludes the formulas (II), which represent optically active forms. Formula (III) seems possible.

Experimental Part

Resolution of Amino-*d*-camphor.—*d*-Camphor was converted into isonitroso-*d*-camphor by treatment with ethyl nitrite in the presence of sodium.[3] The mixture of α- and β-oxime obtained was reduced with zinc and alkali according to Duden and Pritzkow.[4] The freshly distilled aminocamphor was converted into the neutral oxalate by addition of an equivalent of oxalic acid. The properties of the salt agreed with those given by Duden and Pritzkow for the acid oxalate. We found the acid salt much more easily soluble. The melting point of the neutral salt prepared from the unresolved aminocamphor was 135°.

Anal. (micro-Dumas). Calcd. for the neutral salt, N, 6.6; for the acid salt, N, 5.5. Found: N, 6.56.

The first crop of crystals consisted mostly of the low rotating oxalate and gave a constant rotation after three or four crystallizations. This salt was converted into the benzoate and further crystallized, but the amine recovered from the oxalate and benzoate showed no difference in rotation.

It may be remarked that as amino-*d*-camphor has two asymmetric carbon atoms besides the one connected with the amino group, the use of an optically active acid is not necessary for its resolution.

The mother liquor from the first crystallizations contained the high rotating oxalate still in mixture with the low rotating salt. The solution was evaporated under diminished pressure, to avoid decomposition by long boiling. The separated crystals were filtered off from time to time and crystallizations, with constantly increasing rotations, were obtained in this way. The last fractions were recrystallized to constancy.

Amino-*d*-camphor 1. $[\alpha]_D$ +17.5° in alcohol (p = 1.6492). Oxalate: m. p. 212°. $[\alpha]_D$ +8.49°; 8.22° in water (p = 1.4520; 1.4908). Amino-*d*-camphor 2. $[\alpha]_D$ 55.5° in alcohol (p = 1.6700). Oxalate: m. p. 203°; $[\alpha]_D$ 43.3°; 43.7° in water (p = 1.3588; 0.6456).

Preparation of Diazocamphor.—Attempts to prepare diazocamphor by the method of von Pechmann were without success. The urethan, which we obtained from aminocamphor and ethyl chlorocarbonate by means of the Schotten–Baumann reaction,

[2] Schiff, *Ber.*, **14**, 1375 (1881); Angeli, *ibid.*, **26**, 1715 (1893).

[3] Claisen and Manasse, *Ann.*, **274**, 73 (1893).

[4] Duden and Pritzkow, *Ber.*, **32**, 1539 (1899).

could be converted into a rather unstable nitroso derivative, which on treatment with sodium methylate at low temperatures gave the yellow solution of diazocamphor. Every attempt to free the solution from alkali resulted in a rapid evolution of nitrogen. We therefore reverted to the method already employed by Schiff and by Angeli.[2]

The oxalate of the aminocamphor obtained by the resolution was suspended in an ice-cold solution of sodium nitrite and placed in a separatory funnel with some petroleum ether. The calculated amount of dilute acetic acid was added while shaking. The yellow solution of diazocamphor in the petroleum ether was separated and then washed with water. The diazocamphor separated on cooling to $-80°$ and was recrystallized by dissolving in petroleum ether at room temperature and subsequent cooling until the melting point was 74°. Such preparations were proved by combustion to be pure and were used exclusively for the determination of the rotation.

Anal. Calcd.: N, 15.76. Found: N, 15.7.

The measurements were made with a sensitive Schmidt and Haensch half-shade polarimeter with a monochromater. The source of light was a 1000-watt lamp and the readings were taken with the usual precautions. Ether was used as a solvent.

SPECIFIC ROTATION OF DIAZO-*d*-CAMPHOR

	From aminocamphor 1			From aminocamphor 2		
λ	0.8306	0.4012	0.6856	0.3984	0.8290	g/100 cc.
620	87.6	87.4	87.6	86.9	...	
589	100.1	99.6	99.7	100.3	100.0	
565	107.7	110.0	108.1	109.1	108.7	
545	116.1	115.7	115.9	115.0	115.7	
510	119.1	121.2	120.6	119.4	120.5	

Discussion

These results demonstrate that the carbon atom attached to the diazo group has lost the asymmetry characteristic of the same carbon atom in the two aminocamphors from which the diazocamphor was prepared. This may be due to the fact that the diazo group has the cyclic structure, $C_8H_{14}\begin{array}{l}:C::O\\ \quad :N:\\ :C\ ::\\ \quad :N:\end{array}$, which has usually been assumed for aliphatic and alicyclic diazo compounds. Another explanation is that it has the structure (III) given at the beginning of the paper. In this formula the carbon atom bearing the diazo group is represented as forming a double covalence with the adjacent carbon atom, while the oxygen atom of the carbonyl group becomes semipolar. This structure is closely related to that of the diazo derivative of sulfanilic acid, $C_6H_4\begin{array}{l}:SO_2:\ddot{O}^-:\\ \quad\ \ \ddot{}\\ :\underset{+}{N}:::N:\end{array}$, in which the semi-polar oxygen atom of the sulfonic ion balances the positive ammonium ion of the diazonium group.

Weissberger and Haase[5] and Weissberger and Bach have recently prepared a crystalline, optically inactive, diazo compound from *d*-aminosuccinic ester and have shown that a diazo compound prepared by the

[5] Weissberger and Haase, *Ber.*, **64**, 2896 (1931); Weissberger and Bach, *ibid.*, **65**, 265 (1932).

methods used by Chiles and Noyes, Levene and Mikeska, and by Lindemann, Wolter and Groger, contained enough *d*-hydroxysuccinic ester to account for the activity of the diazo compound observed by the others. They seem to imply that optically active aliphatic diazo compounds are improbable. They make no reference to the evidence for the existence of such compounds, which has been accumulated in this and other American laboratories. They explain the well-known reactions of optically active aliphatic amines with nitrous acid, which often give active derivatives, by assuming an active diazohydroxide, $\begin{matrix} R: & :\ddot{N}::\ddot{N}:\ddot{O}:H \\ & C \\ R': & :H \end{matrix}$, as an intermediate. This would imply the structure, $\begin{matrix} R: & :N::N \\ & C \\ R': & : \end{matrix}$, as an intermediate in the formation of the ketazine (see below).

We understand Weissberger and his co-workers to imply that all aliphatic diazo compounds have a cyclic arrangement of the nitrogen atoms. The diazo derivative of aminosuccinic ester may have the structure, $C_2H_5:\ddot{O}:C::C:N:::N:$ with $:\ddot{O}:$ and $CH_2CO_2C_2H_5$ similar to the structure suggested for diazocamphor.

We wish, especially, to call attention to studies of aminolauronic acid, $C_8H_{14}\begin{matrix}CO_2H\\NH_2\end{matrix}$, which have been carried on, at intervals, for nearly thirty years. Noyes and Taveau[6] obtained a ketazine derived from the ethyl ester of aminolauronic acid by treating the nitroso derivative, $C_8H_{14}\begin{matrix}CO\\|\\NNO\end{matrix}$ with sodium hydroxide and dilute alcohol. They did not succeed in determining the structure of the compound.

Oppé[7] obtained the methyl ester of diazomethyl-*o*-benzoic acid, $C_6H_4\begin{matrix}CO_2CH_3\\CHN_2\end{matrix}$, by treating the nitroso derivative of phthalimidine, $C_6H_4\begin{matrix}CO\\|\\NNO,\end{matrix}$ with sodium methylate. Noyes and Coss[8] obtained the corresponding ethyl ester and showed that it decomposes to form a ketazine (called a "bishydrazone"), $(C_2H_5CO_2C_6H_4CH{=}N{-})_2$, and that by boiling with alcohol it gives ethoxytoluic ester, just as diazomethane gives anisole with phenol. This reaction is most simply interpreted by the electronic formula proposed by one of us

$$C_2H_5CO_2C_6H_4:\ddot{\underset{\ddot{H}}{C}}:\overset{+}{N}:::N: + C_2H_5OH = C_2H_5CO_2C_6H_4:\ddot{\underset{\ddot{H}}{\overset{H}{C}}}:OC_2H_5 + N_2$$

The course of the reaction is not, however, quite so simple as these

[6] Noyes and Taveau, *Am. Chem. J.*, **32**, 290 (1904).

[7] Oppé, *Ber.*, **46**, 1095 (1913).

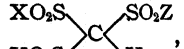
[8] Noyes and Coss, THIS JOURNAL, **42**, 1280 (1920).

formulas indicate. There is a Walden inversion and the ethoxy group takes the place of the unshared electrons of the diazo compound, these electrons shifting to the place of the diazo group to receive the hydrogen ion from the alcohol.[9] It may be objected that this indicates a cyclic arrangement for the nitrogen atoms of the diazo group, but such a structure will not account for the asymmetry of the carbon atom which is retained in this and in many other decompositions of active amino compounds by nitrous acid.

Noyes and Coss also demonstrated that the compound described by Noyes and Taveau is a ketazine, the bis-hydrazone of camphononic acid, $(C_2H_5OCOC_8H_{14}{=}N{-})_2$, and obtained very definite indications that a diazo compound is an intermediate step in the formation of the ketazine. Kendall and Noyes[10] succeeded in preparing the intermediate diazo compound in a crystalline form and showed that it decomposes almost quantitatively to give the ketazine. This demonstrates that the diazo compound is an intermediate step in the formation of the ketazine from the nitroso derivative. Kendall and Noyes also prepared a crystalline diazo compound from the *trans*-aminolauronic acid, which differs from the *cis*-aminolauronic acid only in the asymmetry of the carbon atom to which the amino group is attached. These compounds were so unstable that it was impossible to show any difference in their optical rotations.

Ray[11] has prepared these two diazo compounds from the *cis*- and *trans*-aminolauronic esters and has shown that their decomposition gives, in part at least, the same decomposition products which were obtained by Noyes and Skinner[9] and by Skinner[12] by treatment of the esters with nitrous acid. This demonstrates that the two diazo compounds are different and that the carbon atoms to which they are attached are asymmetric. It also gives almost conclusive evidence that when an aliphatic or alicyclic amine is decomposed by treatment with nitrous acid the first step in the process is the formation of a diazo compound, which retains the asymmetry of the amine.

Noyes and Heubaum[1] have prepared diazo compounds from the two bornylamines. These showed apparent differences in their rotary dispersion curves and one gave a dextrorotatory bornyl chloride and the other a levorotatory chloride.

Gibson[13] has been unable to resolve trisulfonylmethanes of the type,  , in which the hydrogen is capable of ionization, leaving

[9] Noyes and Potter, THIS JOURNAL, **34**, 1067 (1912); Noyes and Skinner, *ibid.*, **39**, 2692 (1917).

[10] Kendall and Noyes, *ibid.*, **48**, 2404 (1926).

[11] Ray, *ibid.*, **52**, 3004 (1930).

[12] Skinner, *ibid.*, **45**, 1498 (1923).

[13] Gibson, *J. Chem. Soc.*, 2637 (1931).

a negative carbon atom, with two unshared electrons, a condition similar to that supposed above for the aliphatic diazo compounds. Gibson suggests that ionization may have rendered the activity too fugitive to be observed. This indicates that active compounds of this type are difficult to isolate but, in the light of the evidence given above, is not conclusive against the possibility of such structures.

Summary

1. Amino-*d*-camphor, which had not previously been resolved, has been separated into two amines with specific rotations $[\alpha]_D$ 17.5 and 55.5°, respectively.

2. The diazocamphors prepared from the two amines were proved to be identical.

3. The theoretical aspect of this fact is discussed.

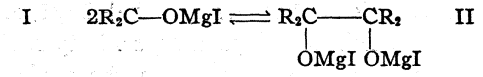
URBANA, ILLINOIS

COMMUNICATIONS TO THE EDITOR

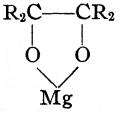
THE MECHANISM OF THE PINACOL SYNTHESIS BY THE SYSTEM Mg + MgI_2

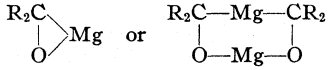
Sir:

In a recent paper [THIS JOURNAL, **54,** 2112 (1932)] Bachmann criticizes adversely the arguments brought by Bergmann and Schuchardt [*Ann.*, **487,** 225 (1931)] in favor of their interpretation of the reduction of aromatic ketones by Mg + MgI_2. In the considerations advanced by Bachmann, there are two erroneous assumptions to which I intend to draw attention. In the first place, it is impossible to ascribe to the equation



more than only a formal meaning, because the ketyls—and the left-hand compound belongs, to all appearances, to the ketyls—are practically monomeric, as was pointed out by Schlenk and Thal [*Ber.*, **46,** 2840 (1913)]. In contrast to Bachmann's opinion, we are far from denying that the iodomagnesium pinacolate (II) is capable of dissociation into radicals, but we may almost deny that it is capable of existence in its dimeric form. It is very probable that molecules of the formula I can be formed, for instance by the action of a Grignard reagent on a pinacol, and come in equilibrium with the five-membered compound (III), but as it is impossible to obtain pinacols from the sodio-ketyls, we shall not make the "MgI-ketyls" responsible for the formation of the pinacols. In the paper criticized by Bachmann it was assumed, therefore, that the five-membered ring compound III is formed and, on hydrolysis, yields the pinacols.

III 

IV 

Secondly, it is impossible to attribute the colors formed in the Gomberg–Bachmann reaction to the ketyl-like compound I. The colors observed are never those of the ketyls, but of the di-alkali or analogous compounds. In a great number of experiments we have verified this statement. When on addition of a Grignard reagent to the solution of a pinacol the color in question appears, we must conclude that by any means the compound IV is formed, for instance because it is very difficult to free a Grignard solution from finely divided magnesium. It is a well-known fact that not only the ketyls, but also the ketone disodium compounds, regenerate the ketones under the influence of oxygen in iodine. These reactions also, therefore, do not prove the formation of ketyls (I). I may believe that the mechanism proposed by Bergmann and Schuchardt for the excellent method of Gomberg and Bachmann is right.

FRIEDRICH WILHELM UNIVERSITY
BERLIN, GERMANY
E. BERGMANN

RECEIVED JUNE 6, 1932
PUBLISHED SEPTEMBER 5, 1932

THE REDUCTION OF KETONES BY MAGNESIUM + MAGNESIUM IODIDE AND BY SODIUM

Sir:

In the preceding communication, E. Bergmann has presented a defense of his criticisms of the mechanism proposed by Gomberg and Bachmann, according to which reduction of ketones by Mg + MgI_2 to pinacols involves the intermediate formation of iodomagnesium ketyls, R_2C—OMgI. He insists that a vast difference exists between the sodium ketyls and our proposed equilibrium system, 2 R_2C—OMgI $\rightleftharpoons$ $R_2C(OMgI)(IMgO)CR_2$; and he concludes that we cannot be dealing with iodomagnesium pinacolates in equilibrium with a very small amount of iodomagnesium ketyls because ketyls are practically monomolecular.

I shall not stop now to point out why Professor Bergmann has arrived at erroneous conclusions, although the reasons are indicated partly in what follows. At this time I wish to say only that in a communication which will appear shortly in THIS JOURNAL, I shall present experimental evidence which will show definitely not only that our interpretation with respect to the magnesium compounds is correct, but also that the corresponding sodium compounds are like the magnesium derivatives. To be more specific, in the reaction between sodium and aromatic ketones, the sodium ketyl radicals persist as such *to a small extent only*, so that there

exists at the end of the reaction an equilibrium mixture of sodium ketyl and sodium pinacolate

$$2R_2C{-}ONa \leftrightarrows R_2C(ONa)(NaO)CR_2$$

in which the equilibrium is preponderantly in favor of the *right-hand* side of the formulation. In other words, the products obtained by addition of sodium to aromatic ketones are *not radicals existing in the monomolecular state, as has been commonly supposed for nearly twenty years,* but consist for the most part of the *dimolecular form,* namely, sodium pinacolate.

In addition, the forthcoming publication will point out the reason why Schlenk, E. Bergmann and others were misled in interpreting as they did the reaction and the structure of the compounds.

CHEMISTRY LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN
W. E. BACHMANN

RECEIVED JUNE 11, 1932
PUBLISHED SEPTEMBER 5, 1932

THE ELECTRODEPOSITION OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

Sir:

The possibility of the electrodeposition of molybdenum and tungsten from aqueous solutions is suggested by their position below hydrogen in the electromotive series. Acidic solutions of these elements in various valence states may be prepared with citric acid, glucose or other hydroxyl compounds. Since the procedure for the electrodeposition of molybdenum and tungsten should resemble to a certain extent the methods applicable to chromium, some studies were first made using solutions of tervalent chromium salts and citric acid.

Britton and Westcott [*Trans. Faraday Soc.*, **27**, 809 (1931)] have suggested, subsequent to the completion of these experiments, that chromium may be deposited from solutions containing chromium in the form of complexes with organic acids.

The following procedure was found to give bright, adherent deposits of chromium: 2 g. of hydrated chromic chloride and 4 cc. of 2.5 *M* monopotassium citrate solution are diluted in 20 cc., heated to boiling and cooled. A carbon anode is contained in a porous cup and a sheet of copper serves as cathode. Metal is deposited at a current density of 3 amp. per sq. dm. and a voltage drop of 4.5 to 7.5 volts. Too high current density and voltage will cause the deposition of black powder. Chromium was also deposited from a bath in which tartaric acid was employed.

Molybdenum may be deposited from an acid solution: 2 g. of molybdic acid and 15 cc. of 34% hydrobromic acid are evaporated almost to dryness. The dark red-brown residue is dissolved in 6 cc. of 2.5 *M* dipotassium citrate

and diluted to 20 cc. After neutralizing with potassium hydroxide, 1 cc. of 2.5 *M* citric acid is added. A current density three or four times greater than for chromium is used. Tartaric acid and glycerol were substituted for citric acid with less satisfactory results. Molybdenum has also been deposited from solutions of molybdic acid in citric and tartaric acids, but the results have also been less satisfactory.

Tungsten has been deposited from aqueous media [Fink and Jones, *Trans. Am. Electrochem. Soc.*, **59**, 461 (1931)] of alkaline nature. It may also be deposited from acid solutions in bright coherent form. Two grams of tungstic acid is dissolved in potassium hydroxide, 5 cc. of 2.5 *M* citric acid is added, then potassium hydroxide to neutrality and 1 cc. of 2.5 *M* citric acid. The solution is diluted to 20 cc. A platinum foil (5 sq. cm.) is the anode and a copper sheet is used as cathode. Similar results may be obtained if sodium hydroxide and tartaric acid are substituted for potassium hydroxide and citric acid, respectively. Tungsten may also be obtained from solutions containing acetic acid and glycerol or glucose.

Work now in progress has shown the possibility of the electrodeposition of columbium and tantalum by similar methods.

More complete data as to optimum conditions of procedure, current efficiencies and the properties of the deposits will be published at a later date.

DEPARTMENT OF CHEMISTRY
ST. LOUIS UNIVERSITY
ST. LOUIS, MISSOURI
L. F. YNTEMA

RECEIVED JULY 5, 1932
PUBLISHED SEPTEMBER 5, 1932

THE DISSOCIATION CONSTANT OF ACETIC ACID

Sir:

The new conductivity measurements on acetic acid of MacInnes and Shedlovsky [MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932)] lead to a dissociation constant that falls off rapidly at concentrations above 0.01 *N*, and the authors are inclined to attribute the effect to a change in the dielectric constant of the solvent. This seems unlikely, if only because such a change would affect both the mobilities and the activity coefficients of the ions, and the resultant effect upon *K* would be extremely small. On the other hand, there are good grounds for thinking that a viscosity correction of some sort should be applied to data such as these, and I have accordingly recalculated the degree of dissociation using the simple viscosity correction, *i. e.*, by employing in place of Λ the value $\Lambda\eta/\eta_0$; values for the relative viscosity were taken from "International Critical Tables," Vol. V, p. 20. The results are reproduced in the figure, where the open circles represent the viscosity corrected values, the solid dots are

MacInnes and Shedlovsky's points, and the line e' is their "theoretical" line.

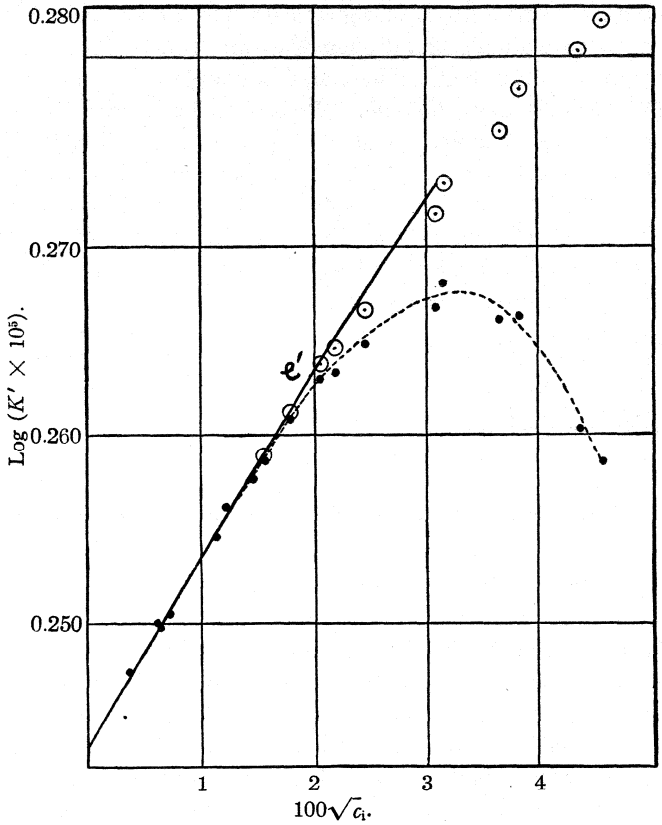


Fig. 1.—⊙, Viscosity-corrected value; ●, uncorrected values.

It appears that, at the concentrations considered, the mass action expression $f_{\pm}^2\Lambda^2c/f_u\Lambda_x(\Lambda_x-\Lambda)$ will give constant values, provided that Λ is a viscosity-corrected conductivity.

BATTERSEA POLYTECHNIC CECIL W. DAVIES
LONDON, S. W. 11, ENGLAND

RECEIVED JULY 5, 1932
PUBLISHED SEPTEMBER 5, 1932

DERIVATIVES OF DIOXANE

Sir:

In view of the recent article by Butler and Cretcher [THIS JOURNAL, **54**, 2987 (1932)] a brief preliminary report of work now completed in this Laboratory seems desirable. We have obtained the symmetrical tetra-

chlorodioxanes described by Butler and Cretcher and have confirmed their findings. In addition, we have obtained several new derivatives. The dichlorodioxane reacts with the Grignard reagent to produce disubstituted dioxanes. As an example, 2,3-diphenyldioxane (m. p. 49°) was prepared and its structure established. This reaction should be a general method of preparing the homologs of dioxane. We are now extending it to the symmetrical tetrachlorodioxanes. Catechol reacts with dichlorodioxane to give a derivative similar to 1,4,5,8-naphthodioxane [Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50,** 909 (1931)]. Only one isomer could be isolated. The evidence is inconclusive regarding the *cis–trans* isomers which Böeseken reported in this class of compounds. We expect to submit evidence in the near future on this point.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
ROBERT K. SUMMERBELL
ROBERT CHRIST

RECEIVED JULY 14, 1932
PUBLISHED SEPTEMBER 5, 1932

THE DECOMPOSITION OF DIETHYL ETHER AT LOW PRESSURES

Sir:

We have made experiments on the decomposition of diethyl ether at 525° with initial pressures ranging from about 0.15 mm. to 200 mm. and at 462° with initial pressures ranging from about 0.8 mm. to 450 mm. These experiments have been made in a Pyrex vessel immersed in a salt-bath the temperature of which can be controlled within 0.1°, using ether which had been dried over sodium and purified by distillation in vacuum. Runs have also been made with a bulb packed with Pyrex tubing in order to test the homogeneity of the reaction. At the lower pressures it is necessary to correct the runs with packed bulbs for gas, probably water vapor, which is continuously distilled out of the apparatus, whether the ether is there or not; when this is done it appears that the reaction is homogeneous throughout the pressure ranges reported. The results have been compared with the results previously obtained by Hinshelwood [*Proc. Roy. Soc.* (London), **A114,** 84 (1927)] in the more limited range of pressures in which he worked. Our rates at 525° are somewhat faster, corresponding to a difference in the absolute temperature scale of about 7°; our activation energy is about 60,000 calories compared to Hinshelwood's 53,000; the cause of these discrepancies is not clear. It will be seen that this means that we agree, roughly, with Hinshelwood, and with Steacie [*J. Phys. Chem.*, **36,** 1562 (1932)] at the lower temperature.

When we plot the logarithm of the rate constant against the logarithm of the pressure, we get a curve which does not fall off nearly as fast in the lower pressure region as one would expect on the basis of the usual theory.

In fact, it appears to have a very slight concave upward curvature. This suggests, though we cannot be quite certain, that it is approaching a second unimolecular region at low pressures, a possibility previously discussed by one of us [*Z. physik. Chem.*, **B7**, 226 (1930)]. The temperature coefficient appears to be slightly greater at the lower pressures. We hope to be able to give a more thorough discussion of these phenomena at a later time, when the experimental results will also be presented in full.

It may be well to note that we have verified the effect of hydrogen in increasing the reaction rate. It appears to have the same effect within the limit of error—which is rather large in the presence of excess hydrogen—at the two temperatures, a point which is of some importance in connection with the question of whether hydrogen is really an inert gas, or whether its effect is due to reaction with the ether. We see no reason at present to believe that it is not inert, as far as the decomposition of the ether is concerned—it may, of course, react with the products of the decomposition.

CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

O. K. RICE
D. V. SICKMAN

RECEIVED JULY 12, 1932
PUBLISHED SEPTEMBER 5, 1932

ACTIVITY COEFFICIENTS OF BARIUM CHLORIDE

Sir:

In a communication from the Laboratory of Yale University [Harned and Nims, THIS JOURNAL, **54**, 423 (1932)], it was presented that the evidence obtained indicates a maximum in the activity coefficient–temperature curve for sodium chloride. Direct confirmation of this phenomenon was lacking, however.

Studies in progress at this Laboratory on the activity coefficients of barium chloride from electromotive force data at different temperatures indicate that this phenomenon certainly exists for barium chloride.

Electromotive forces have been measured very satisfactorily using barium amalgam cells of special construction. Activity coefficients calculated from the data at 0 and 45° coincide fairly closely while those at 25° are appreciably higher for the same concentration.

With complete electromotive force data the heats of dilution may be calculated. When experimental work has been completed the data will be submitted for publication.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

ROY F. NEWTON
EMERSON A. TIPPETTS

RECEIVED JULY 23, 1932
PUBLISHED SEPTEMBER 5, 1932

INFLUENCE OF GASEOUS THERMAL DIFFUSION ON EQUILIBRIUM MEASUREMENTS ON THE Fe–O–H SYSTEM

Sir:

In a previous publication [THIS JOURNAL, **52,** 4268 (1930)] the authors have pointed out that equilibrium constants for the reaction $FeO + H_2 = Fe + H_2O$ reported by various authors [see Eastman and Evans, THIS JOURNAL, **46,** 888 (1924)] for static systems are about 40% higher than those obtained by a flow system. Furthermore, the flow system values are in good agreement with the constants calculated indirectly with the help of known Fe–C–O equilibrium data and equilibrium constants for the reaction $CO + H_2O = H_2 + CO_2$. Up to the present no conclusive explanation of the cause of the discrepancy has been presented. It is the purpose of the present letter to point out a source of error that seems to explain the high H_2O–H_2 ratio obtained in previous static experiments for both the Fe–H–O system and other metal–metallic oxide systems such as Sn–SnO_2.

It has long been recognized [S. Chapman, *Phil. Trans. Roy. Soc.*, **217A,** 115–147 (1918)] that if a mixture of two gases of different molecular weights such as H_2O–H_2 or CO_2–H_2 is placed in a tube one end of which is hot and the other cold, the ratio of the heavy gas to the lighter gas will rapidly become and remain larger in the cold portion of the tube than in the hot portion because of thermal diffusion. The purely static experiments on Fe–H_2O–FeO–H_2, SnO_2–H_2–Sn–H_2O or similar equilibria permit this diffusion factor to come into play; the H_2O–H_2 ratios obtained in such experiments are always those existing in the part of the apparatus that is at about room temperature and not necessarily in the hot part of the reaction tube. Accordingly H_2O–H_2 ratios determined in static experiments for heterogeneous equilibria will in general be higher than the true steam–hydrogen ratios existing in the hot end of the reaction tube in contact with the metal–metal oxide sample, unless some continuous and rapid circulation of the gas mixture is effected.

Preliminary calculations of the maximum difference in the "hot end" and "cold end" H_2O–H_2 ratios for the temperature differences existing in the above equilibrium experiments have been made using formulas developed by Chapman (*loc. cit.*). The results indicate that the thermal diffusion factor may easily account for the observed high H_2O–H_2 values of the static experiments. To establish definitely that at least in the case of the Fe–H–O system thermal diffusion actually does account for the high H_2O–H_2 values, the authors have set up a standard Deville type static apparatus and arranged to analyze samples of the steam–hydrogen mixture taken by a quartz capillary from the hot part of the reaction tube adjacent to the Fe–FeO or FeO–Fe_3O_4 samples. Simultaneously the usual "cold end" steam–hydrogen ratios were determined by observing the total pressure in the system and the temperature of the water thermostat regulating the

vapor pressure of water in the cold part of the apparatus. The average results obtained for the Fe–H–O system may be summarized as follows:

Furnace temp., °C.	Solid phases	Steam–hydrogen ratio: In "cold end" (by pressure readings)	In "hot end" by analysis	In static expts. of Eastman and Evans	In flow expts. of Emmett and Shultz
700	Fe–FeO	0.57	0.41	0.584	0.422
800	Fe–FeO	.71	.48	.706	.499
900	Fe–FeO	.82	.55	.822	.594
1000	Fe–FeO	.97	.67	.937	.669
700	FeO–Fe_3O_4	1.50	1.19	1.45	1.181
800	FeO–Fe_3O_4	3.18	2.35	2.98	2.372

The obvious agreement between the "cold end" values (column 3) and the previous static results (column 5) on the one hand, and the "hot end" analysis (column 4) and the previous flow results (column 6) on the other, seems to show definitely that the principal cause of discrepancy between the various steam equilibrium constants for the Fe–H–O system is the factor of thermal diffusion. Since the magnitude of the steam–hydrogen ratios in the Sn–H_2O–H_2–SnO_2 system is about the same as for the Fe–FeO–H_2O–H_2 system, it is evident that the same diffusion factor will also account for the static experiments on the Sn–H–O system in which the steam–hydrogen equilibrium ratios are apparently about 40% high [THIS JOURNAL, **50**, 1106 (1928)].

BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

P. H. EMMETT
J. F. SHULTZ

RECEIVED JULY 25, 1932
PUBLISHED SEPTEMBER 5, 1932

A FILM WHICH ADSORBS ATOMIC H AND DOES NOT ADSORB H_2

Sir:

We report the following brief study, which we shall discontinue for the present, because of its bearing on the subject of "activated adsorption."

A lamp had two pure tungsten filaments and one filament of Elinvar wire which contained 35% nickel and 12% chromium, the remainder being probably iron. The lamp was sealed to a vacuum system having liquid-air traps, and the Elinvar filament heated to a bright red heat in vacuum for fifteen minutes. The amount of metal thus evaporated was too small to be visible on the walls or to produce a change in resistance of the wire. Pure hydrogen was then admitted at a pressure of 0.250 mm. and one of the tungsten filaments was lighted at 2700°K., at which temperature 3.5% of the hydrogen molecules which strike a tungsten surface are dissociated. The hydrogen disappeared at an exponential rate, decreasing from 210 cu. mm. to 170 cu. mm. in 6.5 minutes.

The lamp was next evacuated and torched at about 450° for ten minutes,

during which time water vapor given off by the glass walls presumably oxidized the metallic deposit. A second clean-up run then showed a much more rapid disappearance from 210 cu. mm. to 35 cu. mm. in 2.5 minutes, with log pressure varying linearly with time. The evaporation of a fresh film from the Elinvar wire, covering up previous films, always reduced the rate of clean-up to a low value, and subsequent torching of the tube restored the high value. In one run enough hydrogen disappeared in the film to form a layer 20 atoms deep while the rate of clean-up remained undiminished.

When the tungsten filament was turned off the pressure started immediately to rise. In one experiment 10% of the adsorbed hydrogen reappeared in ten minutes at 25°, and 90% in two minutes at 450°. Owing to this tendency of the gas to leave the film at a slow rate, the net rate of disappearance diminished markedly as the pressure fell below 0.020 mm. If the lamp was cooled in liquid air, the clean-up stopped instantly, showing that the catalytic effect of the cold film caused recombination of all impinging atoms. If H was adsorbed at 25° and the lamp then cooled in liquid air, there was no escape of hydrogen on turning off the filament. It is known that hydrogen evaporates as atoms from glass surfaces at 25° but recombines on cold glass, so it probably diffused as atoms to the deeper layers of our film at 25°. The film never showed any tendency to adsorb molecular hydrogen.

The recombination of atomic hydrogen at a *tungsten* surface is promoted by cooling the lamp in liquid air, due probably to the removal of water vapor. The H generated by a filament at 2700°K. delivered 0.63 watt to a neighboring tungsten filament with the lamp at 25°, and 1.48 watts with the lamp in liquid air, although cold walls lower the concentration of H in the gas phase by catalyzing recombination.

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, NEW YORK

KATHERINE B. BLODGETT
IRVING LANGMUIR

RECEIVED AUGUST 10, 1932
PUBLISHED SEPTEMBER 5, 1932

NEW BOOKS

The Life and Work of Charles James, 1880–1928. Edited by WALTER C. SCHUMB, HAROLD A. IDDLES, LYMAN C. NEWELL and AVERY A. ASHDOWN. Published by the Northeastern Section of the American Chemical Society, A. A. Ashdown, Custodian, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1932. 26 pp. Illustrated. 15.5 × 23.5 cm. Price, $0.50.

This memorial volume to Charles James contains, first, the Resolutions passed by the Northeastern Section on the occasion of his death; second, three essays, one on Charles James, the Man, by Melvin M. Smith, one on Charles James, the Teacher, by Lester A. Pratt, and one on Charles James,

the Chemist, by B. S. Hopkins; and third, a List of the Scientific Papers of Charles James. There are also included several excellent portraits of James, photographs of the famous gardens of the Jameses and a photograph of the new chemical laboratory at the University of New Hampshire that has been named in his memory the Charles James Hall.

This carefully edited and beautifully printed brochure is a fitting and graceful tribute from the Northeastern Section to the memory of one of its most distinguished members. The essays are excellent; together they give a vivid picture of James, his lovable personality, his high-minded idealism, his outstanding ability. The bibliography shows meticulous care. The book will be read with interest and pleasure by the many friends and admirers of Charles James.

ARTHUR B. LAMB

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. XII. By FRANK C. WHITMORE, Editor-in-Chief, ROGER ADAMS, W. H. CAROTHERS, H. T. CLARKE, J. B. CONANT, HENRY GILMAN, C. S. MARVEL, C. R. NOLLER, C. F. H. ALLEN, Secretary. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. vii + 96 pp. 15.5 × 23.5 cm. Price, $1.75.

Volume XII gives methods for preparing the following compounds: acetyl benzoin, *d*-arginine hydrochloride, benzyl phthalimide, *p*-chlorobenzaldehyde, desoxybenzoin, desyl chloride, dibenzalacetone, 1,2-dibromocyclohexane, 2,6-diiodo-*p*-nitroaniline, 2,4-dinitrobenzaldehyde, 4,5-diphenylglyoxalone, ethyl α,β-dibromo-β-phenylpropionate, ethyl-N-methylcarbamate, hippuric acid, iodothiophene, mercury di-β-naphthyl, methyl isopropyl carbinol, S-methyl isothiourea sulfate, β-naphthylmercuric chloride, nitrobarbituric acid, phenylpropiolic acid, phenyl thienyl ketone, propionaldehyde, succinic anhydride, β-thiodiglycol, thiophene, thiosalicylic acid, *p*-tolualdehyde, uramil, diethyl zinc.

The list contains many substances which are important intermediates, including some which are difficult to prepare without specific directions; it also includes a few that seem hardly worthy of a place in the collection. The name of the first preparation is misleading, because the substance is really benzoin acetate.

E. P. KOHLER

BOOKS RECEIVED

July 15, 1932–August 15, 1932

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AN ADIABATIC METHOD FOR THE PRECISE ELECTRICAL CALIBRATION OF THERMOMETERS

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The continuous maintenance of precise adiabaticity in calorimetric systems, like thermostatic control, makes possible not only the exact measurement of a variety of thermal effects otherwise undeterminable, and a significant improvement of accuracy in other calorimetric measurements, but also the development of procedures not practicable under other conditions whereby a number of familiar types of experimental procedure may be methodically improved. In an earlier paper[1] the precautions which must be observed in order to establish and maintain a measurably invariable adiabatic condition for ten hours or more were discussed at length, and procedures were described by which this condition had been closely approached. More recent experiences in this Laboratory having more precisely defined the observations there recorded, and suggested improvements of method by which the desired end was at length attained, a few of the possibilities just referred to have been developed.

Among these are procedures for the minute calibration and for the standardization of thermometers, the first of which it is the purpose of this paper to describe. These procedures are easy, and are known from the results of several intercomparisons of data to be dependable. They insure the calibration and standardization of calorimetric thermometers to an exactitude of $\pm 0.0002°$ or less on a centigrade scale of equal energy increments,[2] at points $0.01°$ apart on any selected temperature intervals within the lower physiological range (*ca.* $0°$ to $25°$). The complete procedure is applicable to any type of thermometer, but has been thus far applied only to the standardization of mercury instruments. In the present paper, attention will be confined to a method recommended for primary calibrations of standard calorimetric instruments of this type.

[1] F. Barry, THIS JOURNAL, 44, 899 (1922).

[2] The particular centigrade thermodynamic scale adopted as the standard in these operations is that defined by Joule's law in terms of the international electrical units and the mean specific heat of water in the fundamental temperature interval.

The method of primary calibration depends, as has already been implied, upon the possibility of maintaining for several hours in a calorimetric system a condition of practically complete adiabaticity or, alternatively, one of small and measurably constant thermal leakage.[3] These conditions are now habitually established in all calorimetric work carried on in this Laboratory with condensed (solid–liquid) systems. By the employment of installations similar to the most efficacious of those described in the paper cited,[4] the maximal total uncompensated thermal leakage or variability from constant leakage during ten hours or more in a system roughly equivalent to a liter of water is reduced to less than 0.1 calorie—that is, to a change in temperature of less than 0.0001°—and since this leakage is determinable with a somewhat greater precision, the temperature correction for incomplete adiabaticity is thus made, with reference to the present limit of thermometric precision, quite negligible.[5] Moreover, the consistency of numerous varied results seems to show that the other errors in this type of measurement[6] are no greater. If this is so, the heat developed by any influx of energy into a calorimetric system thus controlled will be, within the limits of accuracy of any calorimetric measurement now possible, completely conserved; so that, if adequate provision can be made to prevent significant lag in effecting its uniform distribution,[7] it may be determined, with respect to both its total quantity and its rate of evolution, with a precision limited only by that of the means adopted for its generation and control, or by that of its thermometric measurement.

[3] The condition of constant thermal leakage, which may be established by the same means that establish a strictly adiabatic condition, is convenient for many purposes, most obviously for the determination of thermal conductivity (Ref. 1, p. 914 and footnote 26; p. 931, footnote 42—last paragraphs. See also, in the present paper, Table IV, footnote *d*). It may be called, consistently with current usage and in contrast with the *adiabatic* and *merodiabatic* conditions which are those of common practice, the *isodiabatic* condition. Measurements made under this condition may be corrected to the strictly adiabatic standard by application of a leakage modulus similarly determined under the largest temperature gradients that cause no measurable convection. This defines for any calorimeter its characteristic change of temperature by conduction and radiation under a definite gradient sufficiently larger than those established in isodiabatic measurements to make error in the reduction of data so obtained negligible. (Ref. 1, pp. 918 *ff.*, Table V and Fig. 3.) For instance, the leakage modulus of the calorimeter used in the present measurements is ±0.00011° per minute per 0.1° thermal gradient, determined by a measurement of leakage under this head during an hour or more. Its uncertainty (±0.00001°) is therefore the same as that of a corresponding correction for a head of 0.01° continuously maintained for ten hours.

[4] Ref. 1, pp. 901–909.

[5] *Cf.* below, p. 3792. The data given in the tables (see Table IV, p. 3796) are affected by a larger uncertainty from incomplete adiabaticity, the higher precision of control having been more recently established.

[6] Listed in Ref. 1, pp. 899–900.

[7] *Cf.* below p. 3788, lines 7 *ff.*

For the direct thermal calibration of thermometers, two means at once suggest themselves: the introduction of an accurately measured electrical heating current into a calorimeter of known heat capacity, or the initiation and completion within it of some chemical process the reaction heat of which is precisely known. The first of these procedures is advantageously employed at present for determining the heat capacities of calorimeters with reference to a standard thermometric scale.[8] The second has found a limited use for the calibration of thermometers in a standard calorimeter.[9]

Of the two, the electrical method is superior because it permits the development of energy within the calorimeter at a constant rate, and thus makes possible under continuous adiabatic control a calibration by continuous process. It is conceivable that a slow chemical process or a quick reaction frequently repeated (as by the dripping of one liquid into another) could be substituted for the electrical current; but practical difficulties at present insuperable stand in the way of such alternative procedure, which in any case would be awkward. The efficacy of the chemical method, therefore, is restricted to the determination of single temperature intervals (or at best two or three) for every separate assemblage of apparatus and material, and it thus remains insufferably laborious. The procedure herewith presented, therefore, is electrical; its novelty and demonstrable advantages over other methods of thermometric calibration are wholly due to the possibility of continuous adiabatic control.

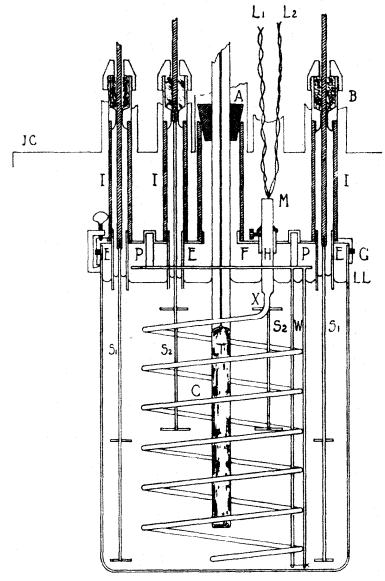

Fig. 1.

Apparatus

Within an adiabatic calorimeter of the uniform type adopted for all protracted determinations (Fig. 1) an electric current, held constant within necessary limits, is passed through a heating coil of constant resistance, and raises the temperature of water in which the thermometer is immersed. The thermometer is placed axially, and is surrounded by the heating coil, which is a cylindrical helix of doubled manganin wire, silk-insulated, thickly shellacked. and embedded in Wood's metal within a copper tube of about 5 mm.

[8] See W. P. White, "The Modern Calorimeter," A. C. S. Monograph, 1928, pp. 132 *ff.*, and references there given.

[9] Richards and Thorvaldsen, THIS JOURNAL, **37**, 81 (1915).

external diameter.[10] The diameter of the helix is such that, when the calorimeter water is still, and a current is passed through the coil, the heat developed is distributed as nearly as possible uniformly, so that in practice the necessary stirring of the system will be minimal; and for the same reason its axial length is such that it traverses all levels of the calorimeter water.

Provision is made for vertical reciprocating stirring by two two-stage stirrers, one within the coil, the other outside it, which may be operated independently, or together in the same or in opposite phases.[11] In practice the system is stirred at the rate of twelve strokes a minute; a measurably complete thermal homogeneity is thus quickly established, while the heat of stirring remains negligible during two hours or more.[12] The Wood's

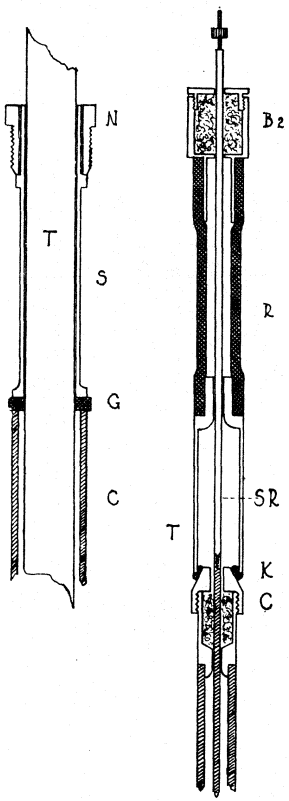

Fig. 2.—Insulations of thermometer and stirrer-rods for use when the air thermostat is not installed. The loose nut, N, engages the jacket chimney.

[10] The shellacked wire was first drawn through the straight copper tube, which then was wound by hand upon a cylindrical block of wood of the required diameter held in the free chuck of a lathe, and was there pulled out to the requisite axial length, and evenly spaced. One open end of the tube—that near which the wire was doubled upon itself—was then fitted into the cap of a brass cartridge full of Wood's metal which was afterward sealed air-tight, and while held vertically with the tube above in a bath of boiling water, was slowly evacuated. The melted metal thus rose not too rapidly about the enclosed wires, and the results of comparative weighings later showed that only very minute air spaces could have been left in the tube. The coil was finished by pinching and soldering the casing-tube at a point about 3 cm. beyond the doubled end of the wire, fashioning the head (Fig. 1) at the other end, and gold-plating the whole. The manganin resistance was closely 13 ohms (*ca.* 260 cm. of No. 27 wire) and its insulation resistance was 9 megohms. Other forms of heating coils, in which, to reduce lag, the thinly insulated wires were not encased, had been previously tested; but though it seems not impossible to utilize dispositions of this sort, they are very fragile, and electrical leakage even if temporarily obviated may at any time be caused either by the fracture or by the chemical deterioration of the insulation.

[11] Rotary stirring is equally possible, of course, and has the advantage that it permits a complete closure of the system. The insulation of the reciprocating stirrers here described, however, had been found adequate to prevent measurable evaporation during the time occupied by the process, and the heat absorbed by it was negligible. It is obvious that in calibration of this sort, as in any precise measurement of a protracted process, the possible errors due either to evaporation or to irregularity of stirring must be shown by test in advance to be negligible.

[12] Ref. 1, pp. 909–916.

metal which surrounds the heating wire ensures a very slight lag in the coil itself: the total lag of the whole system is only a few seconds, and has no measurable calorimetric effect. The leads from the coil are so disposed that the very slight conduction of the wires will be practically constant under adiabatic control (Fig. 1). Two leads of very fine wire are attached to the current leads midway of the gap—that is, at the extremities of the heating wire—so that the potential drop across the heater may be measured while the current is flowing. Both these and the leads from the coil pass through the bath in thermal contact with it, and thus conduct very little heat either into or out from the system.

The electrical system consists of an 8-volt storage battery with control resistance, the calorimeter heater and a standard 10-ohm coil. The control resistance is made up of a 10-ohm fixed resistance and two variable resistances of 100 and 1000 ohms, respectively, all in parallel to permit rapid approximate and precise adjustments. The current through the calorimeter heater is determined by measuring the potential drop across the 10-ohm standard coil with a Wolff potentiometer. The same instrument can be used to check the constancy of the resistance of the heater and of the current by measuring the potential drop across it through the fine wire leads that are soldered to its ends.

By these means it is possible to keep the heating current constant with only negligible occasional fluctuations, to 1 part in 50,000 during any necessary interval of time: in the measurements here discussed it is customarily held constant to 1 part in 30,000. Since the calibration of 1 degree to ten-thousandths necessitates only about one-third this constancy, the calibration is quite unaffected by variability of the power transmitted. Within similar limits of fluctuation, also, the coil resistance remains constant during measurement; it follows, therefore, that all the significant errors of the calibration are calorimetric errors.[13]

Procedure

With these dispositions, a calibration is made by observing at any convenient intervals the temperatures indicated by the thermometer while the actual temperature of the calorimeter rises continuously and uniformly. To distinguish this type of measurement from those employed heretofore it may be called a calibration by continuous process, or, more briefly though inexactly, a *continuous calibration*. Since the thermal leakage of the system heated is negligible, and the influx of energy more than suf-

[13] According to past experiences in this type of measurement, a safe and convenient rate of energy supply is about 5 calories a minute, or 0.35 watt, which in a calorimetric system of the usual heat capacity (approximately 1000 gram-calorie units) causes a temperature rise of about 0.01 degree in two minutes. If a rate somewhat less than this is established, the conduct of the measurement will be quite unhurried, and its duration not unduly prolonged.

ficiently uniform, and since the heat capacity of the system remains sensibly constant, or subject to slight and adequately determinable correction for change in its specific heat as the temperature rises, the only significant errors in actual measurement are those of thermometric registration and reading.

To reduce these errors, readings are made, not of temperatures, but of times. When the standardization is that of a mercury thermometer, the slowly rising meniscus of the thread is closely watched through a telescope while it is occasionally agitated by an attached electrical tapper of ordinary type, and as it approaches a graduation mark the vibration is made continuous. By this means capillary friction (which with a good instrument seldom significantly interferes with fairly correct reading on a rising thread) is reduced to its smallest probable magnitude for the instrument being tested, even if it is not actually eliminated from consideration.[14] The times of the occultation of the meniscus with the graduation marks (which are usually very sharply defined) or those of its emergence from behind them, or both series of times, are taken by stop watches. These determinations may be made with such precision that, under favorable conditions of illumination and magnification after a little practise, and when the rate of energy supply is adjusted so as to cause a 0.01° rise of temperature in from two to three minutes,[15] the temperature reading error is less than ±0.0002°.[16] At the end of the operation, the total time is taken with the same precision, that is, with quite negligible error; and from these data, after they have been corrected in the usual manner for the time equivalents of superimposed effects, the thermometric corrections are readily derived by any convenient method of calculation—which is not excessively laborious if multiplication tables of 60's are used, and is simple when calculating machines are available. These yield the relative values of the indicated 0.01° intervals, expressed as fractions of an indicated degree or other convenient range taken as an arbitrary standard temperature interval. The determination of the absolute value of this interval on a scale of equal energy increments is left for another similar operation—that of standardization. A fragment of an experimental record is here included, which explains the whole procedure very clearly, and illustrates a convenient form of tabulation (Table I).

[14] The consistency of readings for identical repetitions of measurement indicates the maximal possible effect of capillary friction. In the calibration of the calorimetric thermometers used in this Laboratory it is usually not greater than ±0.0003 degree; but there occur, even in these highly perfected instruments, points at which the discrepancies of reading are greater than this, although nothing indicates that for any imaginable reason the other experimental controls are less precise at these indicated temperatures. All experience still points to capillary friction as the most significant defect of mercury thermometers as instruments of precision.

[15] *Cf.* above, footnote 13.

[16] It is worth noting that the precision of such readings will depend very largely upon the fineness of the scale engraving, the importance of which is thus emphasized.

TABLE I

IMMEDIATE DATA OF A CALIBRATION[a]

A. Data of Measurement

1	2	3	4	5	6	7	8	9	10	11
Environment Thermometer C		Bath Thermometer B. S. No. 8961 (twin of P. T. R. No. 54854)					Calorimeter Therm.			
Corrected Temp.[b] °C.	Head of Envt. [1 − 8]	Observed temp. and interpolated means		Apparent head of bath Observed [4 − 8]	At actual equilibrium[c]	Actual head of bath [5 − 6]	P. T. R. No. 54854 Indicated temp. of instrument being calibrated	Observed times In hours, minutes, seconds	In seconds from 6:0:0 P.M.	Criticism
21.50	+1.95	19.544	0.552	−0.002	−0.017	+0.015	19.55 (T_1)	6:33:28	2008	Good: ±<3 secs.
21.52	+1.96	0.560	.551	− .019		− .002	0.56	36:00	2160	Good: ±<3 secs.
	(+1.95)	.542	.547	− .023		− .006	.57	38:30	2310	Excellent. ±<2 secs.
	+1.94	.552	.561	− .019		− .002	.58	Missed	..	Capillary Friction!
21.53	+1.94	.570								
		.775								
21.76		.780	.777	− .013	(− .015)	+ .002	.79	7:34:00	5640	Cap. Frict.! *after:* Good.
	+1.95	.780	.780	− .020	− .014	− .006	.80	36:30	5790	Cap. Frict.! *before:* Fair.
	(+1.90)	(.790)	.785	− .025	− .013	− .012	.81	39:13	5953	Fair: Etching defective.
21.68	+1.85	19.800	.795	− .025	− .012	− .013	19.82 (T_2)	41:45	6105	Very good: ±<2 secs.

B. Derived Data

12	13	14	15	16	17	18	19	20	21	22	23	24
Corrections for superimposed effects in degrees							Corrected times in seconds					
Indicated temp., °C.	Direct leakage to environment	Exposure of thermometer stem	Imperfect isothermal condition[e]	Leakage to the bath	Fluctuation of heating current (reduced)	Sum of corrections in degrees	in seconds	Counted from 6:0:0 P.M. [10 + 18]	From time of first observation	Value of arbitrary 0.01° interval,[f] sec.	Values of summated arbitrary intervals, sec.	Calibration corrections in seconds [20 − 22]	in degrees
19.55	± 0[d]	+0.0012	± 0	± 0	±0	+0.0012	+18	2026	0 (t_1)	152		[0]	[0]
0.56	± 0	+ .0012	± 0	± 0	±0	+ .0012	+18	2178	152		152	± 0	± 0
.57	± 0	+ .0012	± 0	+0.0001	±0	+ .0013	+19	2329	303		304	− 1	−0.0001
.58	+0.0001	+ .0012	± 0	+ .0001	±0	+ .0014	+21	..	..		456	..	....
.79	+ .0004	+ .0012	−0.0001	+ .0002	±0	+ .0017	+25	5665	3639		3648	− 9	− .0006
.80	+ .0004	+ .0012	− .0001	+ .0001	±0	+ .0016	+24	5814	3788		3800	−12	− .0008
.81	+ .0005	+ .0012	− .0002	+ .0002	±0	+ .0017	+25	5978	3952		3952	± 0	± 0
.82	+ .0005	+ .0011	− .0002	+ .0001	±0	+ .0015	+23	6128	4102 (t_2)		4104	− 2	− .0001
Extreme values of corrections	+ .0005	± .00005	− .0002	± .0004	±0								

[a] B. & W.: Calibration No. 8, Part IV (March 27, 1922), in part. [b] By comparison with Baudin Standard Bur. P. et M. No. 18537. [c] From adiabatic comparison of P. T. R. No. 54854 with B. S. No. 8961. [d] ±0 here means less than 0.00005°. [e] Drift, as shown by initial and final tests of the isothermal condition. [f] Mean within the range (19.55° to 19.82°) chosen for repeated tests: = (t_2 − t_1) ÷ 27.

Facility in both measurement and calculation, and precision also perhaps (though certainly to a minor degree), is dependent upon the elimination of as many corrections for experimental error as possible. In the first measurements made by this method (Barry and Webb, 1923), the leakage corrections were far from negligible, and their application tedious; the results were accurate enough, but their determination, which required as a precautionary measure the simultaneous attention of two observers, was protracted, and the work lacked, in consequence, a certain persuasive elegance. In later measurements (Smith, 1925) advantage was taken of a close control of the temperature of the air surrounding the calorimeter, which was made possible by the installation of an enveloping chamber within which this temperature could be and was kept continuously within $\pm 0.02°$ of that indicated by the thermometers, by a quickly adjustable thermostatic mechanism.[17] This control made it necessary to carry out all observations and manipulations from the outside, without awkwardness, however, since the readings in any case were telescopic and since with this additional insulation all fluctuations of external temperatures were so slow and regular that they required much less attention. The consequently minute and uniformly periodic fluctuation of the bath, the minimal conduction of heat through projecting parts, and the very slight effects of thermometer-thread exposure made possible the reduction to negligible magnitude of all calorimetric errors, and therefore the elimination of all corrections whatever. It also facilitated measurement by making it safe for a complete calibration to be carried out by one observer. With a convenient disposition of telescope, galvanometer and mechanisms of control, the maintenance of adiabaticity and constancy of the development of heat required only occasional and momentary interruption of thermometric observations when the work was thus conducted; but the testing of the constancy of the coil resistance and of the constancy of the

[17] This air thermostat was so constructed that the outer air, at a temperature a degree or more below that of measurement, drifted in slowly from below, was heated by lamps placed behind radiation screens and, ascending, was distributed by small fans before it found its way out from the top. Its temperature was regulated by a bimetallic strip suspended from light springs, one terminal of which was a screw adjustable through small gearing by a rod which pierced the wall. By means of a needle attached to this rod, which traversed a graduated dial on the outside of the wall, the position of the regulator terminal could be read with some precision, and adjusted nicely enough to make easy the stepwise regulation of the air temperature to within $\pm 0.02°$ of that of the calorimeter. Telescopic readings were made through a window of plane plate glass, tested by a comparison of micrometer measurements of the thermometric intervals carried out with the window open and closed. Incidental manipulations were made through two elastic cloth sleeves set into apertures in the front wall. This apparatus improves both the facility and the precision of adiabatic measurements of all sorts so remarkably that it has been adopted as an essential part of all calorimetric installations here.

potentiometer system necessitated the omission of one or two 0.01° interval readings in the course of a determination.

There follow two records of calibration, by this method, of calorimetric thermometers of different types: the one, an instrument similar to the familiar Beckmann thermometer, with separate flat porcelain scale; the other, one of the normal thermometer type with scale etched upon the curved surface of the solid stem. Both scales had been made for convenience in reading with a hand lens to 0.001 or 0.0005°, and were, consequently, not as finely etched as that of a normal instrument; they were graduated in 0.01° intervals, which in each case were about 0.7 mm. apart. The first record shown (Table II) is that of a calibration of the flat-scale instrument, made in a constant-temperature closet with customary care,[18] but without the accessory control of the air thermostat (Barry and Webb). The second (Table III) is taken from a later calibration of the solid-stem instrument in which this control was employed (Smith). It will be noted that the precision of these two calibrations is the same.

Criticism

The close consistency of the results obtained in repeated calibrations by this method indicates a very high precision of measurement, and thus justifies a critical examination of the errors which are characteristic of the procedures adopted. The results of a comprehensive survey of this sort, recently made, are typified by the data shown in Table IV, which apply to the particular calibrations here discussed. By exhibiting the relative magnitudes of all errors of control, these data yield the assurance that by nicer regulation of certain of these controls—an easily practicable matter—the precision of the method, which now closely approaches the present accepted limit of thermometric sensitivity for the usual calorimetric ranges (±0.0001°) may with certainty attain it, if the instruments tested are capable of a correspondingly precise consistency of registration.

In the effort to reach this precision, the inconstancy of the heating current need, obviously, cause no concern, since its constancy within one part in thirty thousand—as in these measurements—is adequate, and three or four times this constancy attainable, without excessive care. By use of the adjustable air thermostat, the influence of the external environment in causing leakage through the projecting parts of the calorimeter, and in affecting the temperature of the thermometer stem, may easily be made negligible also, when as here air temperatures are read to 0.01°. The control of the calorimeter bath, however, should be closer; for the error involved in the correction for its fluctuation when its thermal head is determined—as in these measurements—by a comparison of the corrected readings of twin mercury instruments read by estimation to ±0.0005°,

[18] THIS JOURNAL, 42, 1918–1920 (1920); 44, 900–902 (1922).

may be large enough to affect the evaluation of any whole temperature interval greater than half a degree, though it would probably not affect the ratios of the calibrated 0.01° intervals within ranges of less than two degrees. It is, however, by no means certain that the fluctuation of calorimeter temperature is more than approximately calculable from the

TABLE II

COMPARISON OF INDEPENDENT CALIBRATIONS OF A CALORIMETRIC THERMOMETER WITH SEPARATE FLAT SCALE[a]

1 Calorimeter temperatures indicated by P. T. R. No. 54854	2	3	4	5	6	7	8	9	10
	Corrected times in seconds (*Cf.* Table I, Column 20)					Calibration corrections[b] for P. T. R. No. 54854 in degrees	Errors		
	I	II	III	IV	Mean values		a. d. in sec.	A. D. in sec.	A. D. in degrees × 10^4
19.55	0	0	0	0	0	± 0			
19.56	153	159	155	152	155	−0.0001	2.3	1.2	0.8
19.57	304	308	302	303	304	± 0	1.8	0.9	0.6
19.58[c]	474	472	460	..	469	−0.0009[c]	5.7	3.3	2.1
19.59	..	612	613	..	613	− .0003	(0.5)	(0.4)	(0.3)
19.60	752	753	752	751	752	+ .0006	0.5	0.3	0.2
19.61	908	905	907	903	906	+ .0004	1.8	0.9	0.6
19.62[c]	(1076)	1057	1055	1052	1055[d]	+ .0006	1.7[d]	1.0[d]	0.7[d]
19.63[c]	1212	1216	(1227)	1207	1212[d]	+ .0005	2.7[d]	1.6[d]	1.0[d]
19.64	1377	1386	1366	1369	1375	− .0001	7.0	3.5	2.3
19.65	1514	1515	1518	1510	1514	+ .0004	2.0	1.0	0.7
19.66	1666	1668	1670	1671	1669	+ .0002	1.8	0.9	0.6
19.67	1825	1819	1823	1819	1822	+ .0001	3.3	1.7	1.1
19.68	1968	1971	1971	1967	1969	+ .0005	1.8	0.9	0.6
19.69	2111	2115	(2130)	2116	2114[e]	+ .0009	2.0[e]	1.2[e]	0.8[e]
19.70	2268	2271	2278	2268	2271	+ .0006	3.3	1.7	1.1
19.71	2421	2424	(2439)	2419	2421[e]	+ .0006	1.7[e]	1.0[e]	0.7[e]
19.72	2571	2576	2576	2574	2574	+ .0007	1.8	0.9	0.6
19.73	2733	2728	2730	2726	2729	+ .0005	2.3	1.2	0.8
19.74	2884	2887	2881	2888	2885	+ .0002	2.5	1.3	0.8
19.75	3028	3033	3024	3034	3030	+ .0007	3.8	1.9	1.2
19.76	3204	3195	3189	3193	3195	− .0002	4.3	2.2	1.4
19.77	3350	3358	3339	3344	3348	− .0003	6.2	3.1	2.0
19.78	3500	3492	3490	3489	3493	− .0005	3.8	1.9	1.2
19.79	3643	3635	..	3639	3639	+ .0006	2.7	1.6	1.0
19.80[e]	3793	(3818)	3788	3788	3790[e]	+ .0007	2.3[d]	1.4[d]	0.9
19.81	3950	..	3945	3952	3949	+ .0002	2.0	1.2	0.8
19.82	4098	4103	4108	4102	4103	+ .0001	2.8	1.4	0.9

[a] B. & W.: Calibration of a Mueller calorimetric thermometer: Series VIII complete (1922). [b] The mean 0.01° interval of this range, taken as an arbitrary standard, is traversed in 152 seconds. Each mean value (column 6) is here subtracted from the proper multiple of 152 seconds and the difference converted into degrees × 10^4 by the corresponding factor 0.658. The corrections are thus made independent of one another. [c] Capillary friction noted, undependable points (*cf.* Table I). [d] Single values (in parentheses) aberrant beyond twice the reading error, excluded for cause; these values alone were affected by noted uncertainties of reading due to capillary friction. [e] Arbitrary exclusion of grossly aberrant values (in parentheses): scale etching was obscured here, and the readings involved estimations.

TABLE III

COMPARISON OF INDEPENDENT CALIBRATIONS[a] OF A THERMOMETER OF "NORMAL" TYPE WITH SCALE ETCHED ON SOLID STEM

Indicated Temp., °C.	Corrected times in seconds[b] (*Cf.* Table I, Column 20) I	II	III	IV	Arith. mean	Calib. corr. for C. U. No. 1 in degrees	Errors in seconds, or in degrees × 10^4 a. d.	A. D.
20.50	0	0	0	0		± 0		
.51	99	..	97	..	98	+0.0002	(1.0)	(0.7)
.52	196	188	193	198	194	+ .0006	3.3	1.7
.53	295	290	300	297	296	+ .0004	3.0	1.5
.54	397	385	402	..	395	+ .0005	6.3	3.7
.55	..	..	..	494	..	....	...	...
.56	594	584	..	591	590	+ .0010	3.8	2.2
.57	..	..	699	690	695	+ .0005	(4.5)	(2.3)
.58	791	786	794	..	790	+ .0010	3.0	2.1
.59	891	887	898	890	892	+ .0008	3.3	1.7
.60	..	991	..	992	992	+ .0008	(0.5)	(0.3)
.61	1093	1090	1097	1094	1094	+ .0006	4.3	2.2
.62	..	1196	1201	1196	1198	+ .0002	2.3	1.6
.63	1302	..	1302	1294	1299	+ .0001	3.7	2.2
.64	1398	1394	1403	1396	1398	+ .0002	2.8	1.4
.65	..	1492	1504	..	1498	+ .0002	(6.0)	(4.3)
.66	1586	1595	1606	..	1596	+ .0004	7.0	4.1
.67	..	1696	1707	1696	1700	± 0	5.0	2.9
.68	1801	1799	..	1795	1798	+ .0002	2.3	1.4
.69	1903	1896	1909	1892	1900	± 0	6.0	3.0
.70	2001	2001	2007	1996	2001	− .0001	2.8	1.4
.71	2102	2100	2104	2095	2100	± 0	2.8	1.4
.72	2201	2200	2207	2196	2201	− .0001	3.0	1.5
.73	..	2297	2305	2297	2200	± 0	3.7	2.2
.74	..	2406	2408	2396	2403	− .0003	5.0	2.9
.75	2499	..	2504	2492	2498	− .0002	4.3	2.5

Indicated Temp., °C.	Corrected times in seconds (continued) I	II	III	IV	Arith. mean	Calib. corr. for C. U. No. 1 in degrees	Errors in seconds or in degrees × 10^4 a. d.	A. D.
20.76	..	2598	..	2589	2594	+0.0006	4.5	3.2
.77	2694	2694	2691	2689	2692	+ .0008	2.0	1.0
.78	..	2798	2796	2789	2794	+ .0006	3.7	2.2
.79	2891	2893	2898	2892	2894	+ .0006	2.3	1.2
.80	2995	2996	2996	2985	2993	+ .0007	4.0	2.0
.81	..	..	3096	3082	3089	+ .0011	(7.0)	(5.0)
.82	3194	3193	..	3185	3191	+ .0009	4.3	2.5
.83	3295	3293	3291	3286	3291	+ .0009	2.8	1.4
.84	3395	3399	3396	3388	3395	+ .0005	3.3	1.7
.85	3496	3497	3496	..	3496	+ .0004	0.4	0.2
.86	3596	..	3595	3592	3594	+ .0006	1.7	1.0
.87	3699	3692	3700	3697	3697	+ .0003	2.5	1.3
.88	3796	3790	3796	3789	3793	+ .0007	3.3	1.7
.89	3897	3894	3899	3891	3895	+ .0005	2.8	1.4
.90	3997	3995	4000	3993	3996	+ .0004	2.3	1.2
.91	4096	4092	4102	4095	4096	+ .0004	2.8	1.4
.92	4195	4193	..	4195	4194	+ .0006	0.9	0.5
.93	4293	4292	4295	4291	4293	+ .0007	1.3	0.6
.94	4393	4393	4397	4391	4394	+ .0006	1.8	0.9
.95	4494	4494	..	4494	4494	+ .0006	0	0
.96	4595	4596	4594	4594	4595	+ .0005	0.8	0.4
.97	4698	4699	4701	..	4699	+ .0001	1.0	0.6
.98	..	4802	4799	4797	4799	+ .0001	1.7	1.0
.99	4900	..	4899	4898	4899	+ .0001	1.0	0.6
21.00	5000	5000	5000	5000		[±0]		

Average divergence from the mean (a. d.) = 0.00031°.

Average dependability of a measurement (A. D.) = 0.00015.

[a] Smith: Calibration of 0.5° on a Pfeuffer calorimetric thermometer. Series II, complete (1926). [b] Observed and corrected times are here proportionally adjusted to make 100 seconds correspond to the mean 0.01° interval for this range, taken as standard.

thermal leakage modulus on the assumption of its proportionality to the fluctuation of the bath; for, though this proportionality has been shown to hold for small bath heads when these are constant,[19] it must be affected in opposite senses by the lag of the bath thermometer and that of the insulating air gap when the bath temperature fluctuates, and perhaps asymmetrically for its rise and fall. These lags, furthermore, make the calculation of corrections for imperfect adiabaticity inapplicable to calorimetric temperatures simultaneous with those of the bath from which they were derived; they must, therefore, be determined, if such corrections are to be correctly applied, to successive readings of a changing temperature. For these reasons it is highly desirable, if not imperative, that

TABLE IV

CORRECTIONS FOR DIVERGENCE FROM UNIFORM CONDITION[a] IN DEGREES × 10^4, OR CALORIES × 10^1

A. Total corrections for influx of heat in two hours

	Correction	Observer	I	II	III	IV	Precision[e] of the correction
1a	Drift from initial equilibrium[b]	B. and W.	+19	+11	+5	+ 3	±3.0
		S.	− 3	− 3	±0	...	±1.7
1b	Direct leakage to environment[c,f]	B. and W.	− 3.5	− 3.9	−3.3	− 4.7	±0.00
		S.	− 0.17	+ 0.28	−0.11	+ 0.30	
1c	Leakage to the bath[d]	B. and W.	+ 4.1	+ 2.1	−3.7	− 1.1	<±0.6
		S.	+11.2	+21.9	−9.0	−60.6	<±0.5
1d	Inconstancy of heating current	B. and W.	+ 0.17	Less than		0.20	±0.02
		S.	...	+ 0.15	+0.05	+ 0.17	

B. Maximal corrections for single determined 0.01° intervals

	Correction	Observer	I	II	III	IV	Precision of the correction
2a	Drift from initial equilibrium	B. and W.	+0.4	+ 0.2	+0.96	+ 0.52	±0.05
		S.	−0.06	− 0.06	±0.00	....	
2b	Direct leakage to environment	B. and W.	−0.07	− 0.08	−0.07	− 0.09	±0.00
		S.	±0.00	+ 0.01	±0.00	+ 0.01	
2c	Leakage to bath	B. and W.	+2.4	− 2.2	+1.1	+ 1.0	<±0.11
		S.	−3.0	− 1.5	−2.0	− 3.0	
2d	Inconstancy of heating current	B. and W.	+0.004	Less than		0.004	
		S.	....	± 0.00	±0.00	± 0.00	
2e	Exposure of thermometer stem[f]	B. and W.	−8.58	−11.40	−9.60	−11.70	±0.01
		S.	+0.12	+ 0.19	−0.17	−0 .14	

[a] Applicable to the calibrations recorded in Tables II and III. [b] Determined from pre-period and post-period drift under thermostatic control, see p. 3797. [c] Conduction leakage through thermometer, stirrer-rods and electrical leads. [d] The bath fluctuates within a range of 0.05° or less: values here shown are maximal. The large corrections of observer S. are due to isodiabatic control. [e] Precision is discussed on p. 3793 *ff*. [f] The smaller corrections of observer S. are due to control of the temperature of the surrounding air.

[19] Ref. 1, p. 918 *ff*.

corrections for imperfect adiabaticity be made quite negligible, and not only in operations of calibration or standardization like those here discussed, but in all measurements that involve the determinations of rates in the development or absorption of heat. The slight improvement of control which is necessary to ensure this result is easily attained by the use of a thermoelement to indicate the difference of temperature between bath and calorimeter; not in this case because of its greater sensitivity, but because of its small lag and the ease with which the bath temperature can be regulated so as to maintain a galvanometer reading close to the null point. Such installations, therefore, have now replaced that of twin mercury thermometers in all precision work in this Laboratory, with the result that corrections for imperfect adiabaticity are habitually reduced to negligible magnitude.

Finally, in this as in all protracted adiabatic measurements, the slow temperature drift that is usually detected when, under precise thermostatic control, the system should remain constant, causes the most serious uncertainties. This drift measures, of course, the aggregate effect of all disturbing influences either not yet identified or not yet brought under control: minute leakages, evaporations and condensations, adsorptions,[20] oxidations or other chemical changes, and so on. Inasmuch as it cannot be determined from accessory measurements in which its magnitude is proportionally exaggerated, but must be measured directly during preperiods and post-periods the durations of which are at best of the same order of magnitude as that of the measurement itself, it is necessary that the utmost care be exercised to make it as small as possible by meticulous observance of all the precautions which minimize leakages, adsorptions and chemical changes in the system, and that it be measured with the highest precision.[21] The data of Table IV show that the uncertainty of the total correction of this drift, which affects the definition of the whole temperature interval calibrated, may approach $\pm 0.0002°$, but that it will not sensibly affect the determination of the relative values of 0.01° intervals.

It is perhaps worth remarking, in conclusion, that the efficacy of the precautions here discussed will be conditioned by a close observance of all the other niceties of technique which characterize measurements of like

[20] Ref. 1, pp. 931 *ff*. These observations have recently been amply confirmed, and the effects measured with precision under conditions that practically eliminate the possibility that they are due to chemical change. A paper descriptive of this work is now in press.

[21] For this measurement, electrical thermometry is most efficacious; but since calorimetric mercury thermometers may, under carefully chosen conditions, be not only read to $\pm 0.0001°$ but made to indicate chosen stationary temperatures with a consistency of $\pm 0.0002°$, such measurements may be made by their means quite satisfactorily when the time which elapses between the observed isothermal periods does not exceed three or four hours—as is the case in calibrations like those here described.

sort: in particular, it will be important that the influence of external temperatures and pressures be exactly known. The air thermostat will, if properly controlled, eliminate corrections for stem exposure, but corrections for fluctuations of barometric pressure frequently cannot be avoided, and in work of this precision are likely to be significant, for changes in the registration of calorimetric mercury thermometers due to a change in external pressure of 1 millimeter of mercury usually approach 0.0002°, and with the most sensitive instruments may exceed this value.

Addendum

Those who are familiar with the techniques of the electrical calibration and precise adiabatic control of calorimeters will predict that, with the same exactitude that a calibration can be made by this method with reference to an arbitrary standard temperature interval, a complete standardization can be made with the same apparatus, with reference to that scale of equal energy increments which is defined by the electrical units. So far as can be told from a study of the estimated errors of one such standardization actually carried out, such is the fact. The experimental demonstration of this possibility, however, demands the comparison of two or more such standardizations of the same thermometer in which significantly different heat capacities and energy rates are involved, and such data are not at present available.

It will also be evident that, with mercury thermometers calibrated in the manner described, the actual heats of chemical reactions and other processes may be determined with the exceptional precision of calibration ($\pm$0.0002°) by working between fixed temperatures. After the usual isothermal period, the electric current, regulated as in calibration, is allowed to generate heat in a coil within the calorimeter. The times at which adjacent selected points on the thermometer are passed are then taken. The reaction is initiated and completed either while the current still flows, or after its interruption at another known time if the process is protracted. Finally, after its completion, the times are taken at which another previously selected group of points is passed—the current, if interrupted, having been started again at a known time. The precision with which the electrical heat can be measured will ordinarily be better than that of the experiment as a whole, so that no new systematic errors are introduced by the procedure. The advantages are: first, all readings are made with a rising meniscus and on exact scale divisions, the fractional temperatures determined by the reaction itself being calculated from the time measurement, and thus wholly without error. Second, the best portions of the thermometer capillary can be chosen for end-temperatures since the interval read may be of any range greater than that of the temperature change caused by the reaction. Third, since several different points are read as initial and

final temperatures, a number of different determinations with different accidental reading errors are obtained in one measurement, as with the slowly changing temperatures in non-adiabatic work, and yet with the advantages of adiabatic method. The maintenance of the adiabatic condition during the slow changes of end-temperatures is very easy if the calorimeter bath is also heated electrically. Finally, it will be noted that, if the heat capacity of the calorimeter has been accurately determined, this type of measurement yields the heat of reaction directly in units of energy, the thermometer acting as an indicating instrument only—or primarily.

Summary

This paper describes a procedure, dependent upon the precise maintenance of an adiabatic condition for a few hours, whereby the relative values of all the nominal 0.01° or other minute marked intervals of thermometers may be determined to ±0.0002° or less by a continuous process, that, namely, of the generation within the calorimeter of electrical heat at a constant rate, precision of reading being secured by observations of the intervals of time during which the scale intervals are traversed. The accuracy of the method is demonstrated by data on the calibration of calorimetric mercury thermometers, and on errors of measurement which are briefly discussed.

The method is presented as the essential basis of a procedure for the complete standardization of calorimetric mercury thermometers.

Its direct applicability to thermochemical measurement is briefly discussed.

NEW YORK CITY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

LIGHT SCATTERING IN UNDERCOOLED BENZOPHENONE

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Introduction

The light scattering of pure liquids has been successfully described by von Smoluchowski and Einstein.[1] They have calculated from the fundamental postulate of the Boltzmann entropy-probability principle the fluctuations in density of a liquid at a given temperature, and applied to these the Clausius–Mosotti–Lorentz law which relates index of refraction n to density ρ

$$\frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho} = \text{const.} \qquad (1)$$

An expression emerges which gives quantitatively the relation between

[1] Von Smoluchowski, *Ann. Physik*, **25**, 205 (1908); Einstein, *ibid.*, **33**, 1275 (1910).

the intensity of light incident, I_0, and that scattered, I_s. This may be written

$$\frac{I_s}{I_0} = kT\beta_T(n^2 - 1)^2(n^2 + 2)^2 \left[\frac{V\pi^2(1 + \cos^2\vartheta)}{18D^2\lambda^4}\right] \qquad (2)$$

where T is the absolute temperature, β_T the isothermal compressibility, k the Boltzmann constant, V the volume of liquid subjected to radiation of wave length λ, and D the distance at which the intensity I_s is measured. The angle ϑ is that between the direction of the incident light and the scattered beam.

The experimental confirmation of Equation 2, with which the names of Cabannes and Raman are chiefly associated, has been highly gratifying. A more elaborate expression of the same type has been developed which includes a factor depending on molecular anisotropy, and describes the depolarization of the scattered light. Theoretical and experimental treatment has been extended to liquid solutions near their critical mixing point, to the phenomenon of critical opalescence, and to anisotropic liquids. Hitherto, however, no experiments appear to have been made with undercooled liquids. This is probably due to the difficulty with which they may be maintained for long periods of time far below their solidification temperatures.

Recently it has been shown that, with certain liquids, prolonged undercooling is possible provided that the walls of the containing vessel, and any other adsorbents which may be present, have been wholly freed from crystals by heating the crystalline adsorbate above its melting point, which may be far above the melting point of the unbound substance.[2] As a result it is possible to prepare undercooled liquids which are practically permanent even far below their temperatures of solidification. One of these, benzophenone, is suitable for light scattering measurements since it melts at a convenient temperature, and may be distilled at 200° *in vacuo* without decomposition. The latter qualification is of course essential for light scattering measurements, since dust-free liquids may be obtained only by distillation.

Most of the measurements on scattered light, which have been reported to date, are based on comparison of intensities by eye. A photographic method has been used in this work because it permits the use of a spectrograph, records extremely small intensities of monochromatic light, and makes subjective error out of the question. A photographic method permits two types of measurement of light scattering. The first of these measures the absorption coefficient, h, which is defined by the expression

$$I_x = I_0\, e^{-hx}$$

where I_x represents the intensity of light transmitted through a thickness x of liquid. The absorption coefficient is, therefore, compound, consisting

[2] Richards, THIS JOURNAL, 54, 479 (1932).

at any particular wave length of the sum of scattering and selective absorption losses. It is only where selective absorption is absent that deductions may be drawn from Equation 2, for when the index of refraction is very large the Clausius–Mosotti–Lorentz expression is without meaning, and the so-called "resonance scattering" appears. The absorption coefficient recommends itself highly for scattering studies on grounds of elegance: by integrating Equation 2 for all values of ϑ, the total energy of scattered light may accurately be related to the energy of the incident light and to the physical constants of the liquid. Unfortunately, however, the amount of light scattered is so small that an excessively long path is necessary and significant results were not obtained by this method. The second method of measuring the intensity of scattered light is to photograph it laterally while the liquid is intensely illuminated. Here, also, selective absorption must be absent for Equation 2 to be applicable. Since relating the intensity of the incident to the scattered beam is an exercise in photometry of considerable difficulty, and since, moreover, the quantities V, D and ϑ of Equation 2 are difficult to define experimentally, it is customary to limit an investigation of this type to the relative intensities of light scattered by two different liquids, or by the same liquid under different conditions. Since this communication deals only with the temperature dependence of monochromatic light of constant incident intensity scattered from a given liquid, Equation 2 will be used in the abbreviated form

$$I_s = T\beta_T(n^2 - 1)^2(n^2 + 2)^2A \qquad (3)$$

where A is a constant. This equation is shown in the experimental section to represent the behavior of carbon tetrachloride between 20 and 55°, but to fail conspicuously in the case of undercooled benzophenone using the same apparatus and method. A test of the photographic process is also provided, in which it is found to give results of satisfactory reproducibility, but not always of rigorously quantitative significance.

Measurements

Preparation of Materials, and Source of Illumination.—The two liquids were prepared in a dust-free condition by the method of Martin,[3] distillation without ebullition *in vacuo*. The carbon tetrachloride was of a guaranteed reagent grade and the benzophenone of the quality listed commercially as C. P., before distillation. The liquids were distilled into cylindrical tubes 30 cm. long and of 2.3 cm. internal diameter, which were provided on each end with sealed optical windows. A side-arm carrying a bulb was affixed to each tube to allow for thermal expansion when the cylindrical tube was completely filled. The tube enclosing the carbon tetrachloride was washed many times with dust-free distillate before finally being filled and sealed off. Since benzophenone became too viscous at room temperature to be an effective washing agent, the tube which was to contain it was first washed by water distilled *in vacuo*. It was then sealed off from the original container of water, and connected by means of a magnetic valve to the flask containing benzophenone. After evacuation the magnetic break was

[3] Martin, *J. Phys. Chem.*, **24**, 478 (1920).

opened, and the benzophenone distilled with as little ebullition as possible. Since it was found impossible wholly to prevent ebullition, an elaborate series of large bulbs was arranged above the vaporizing liquid benzophenone to prevent mechanical carrying of the undistilled liquid into the receiving vessel. The resulting distillate was satisfactory in appearance, being of crystal transparency and of a very pale greenish hue. Its melting point was 48.1°, 0.4° above that of the original C. P. sample. It has remained for ten months at 20–25° without crystallization.

The dust-free samples of carbon tetrachloride and benzophenone so prepared were used both for the extinction and for the scattering measurements.

Considerable attention was devoted to securing a constant source of illumination. Voltages constant over long periods of time were not available. It was necessary, therefore, to choose the source which was as nearly as possible independent of voltage. The General Electric Type S-1 bulb, which is a combination of a tungsten filament and mercury arc, was finally selected as most satisfactory for the purpose. The slight variations in line voltage which could not be prevented had at no time as much as one-half of one per cent. effect on the intensity of the mercury lines from the arc, on which conclusions are based. During long exposures these fluctuations canceled, and may be considered entirely absent. After the first few hours of running the deterioration of the lamp, even on long exposures, was negligible.

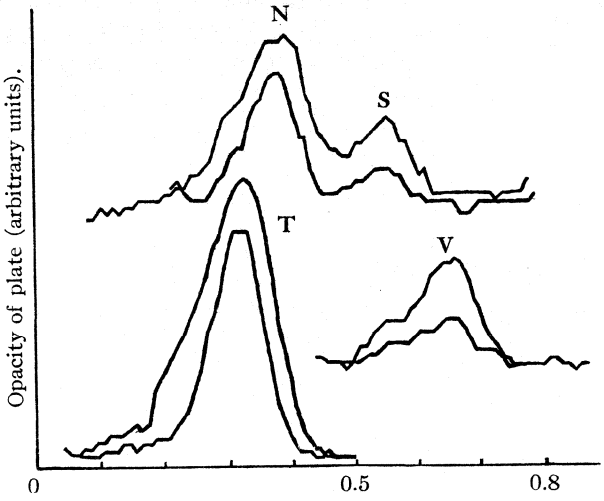
The spectroscope was of glass. It was of small aperture and about 25 cm. focus. It distributed the visible region over about 2.5 cm. of plate.

Absorption Measurements.—A few photographs were taken of the intensity of parallel light of various wave lengths transmitted through a 20.0 cm. layer of benzophenone at 20 and 70°. In the experimental arrangement the cylindrical tube described above was supported by two water-tight rubber washers, which pressed tightly against the optically flat ends of the tube, and was immersed in a thermostated cylinder containing an optically opaque solution of crystal violet in glycerin. Thus all light scattered by the liquid in the tube was absorbed by the surrounding medium. The transmitted light entered and emerged from the tube by means of small holes cut in the rubber washers, and was defined by diaphragms at suitable positions outside the tube. Exposures of varying duration through benzophenone and through Pyrex windows were taken on the same plate in order to secure adequate calibration of the plate. The photographs showed that benzophenone began to absorb strongly in the violet at about 4200 Å. at all temperatures between 20 and 70°. Photometric analysis of the plates showed slightly greater absorption at the lower temperature, indicating a stronger scattering by undercooled than by stable liquid benzophenone, but also made clear that much longer paths must be used if results of unquestionable significance are to be obtained.

Scattering Measurements.—The apparatus used for the scattering measurements was based on that devised by Wood for photographing Raman spectra,[4] but was modified in several respects to suit the work in hand. A brass box 20 cm. square by 30 cm. deep was provided with a thin plate glass window on one side, and pierced as close to the window as possible by two holes large enough to receive stoppers which held the scattering tube. Thus the cylindrical scattering tube was held within 0.5 cm. of the window, with about 4 cm. of each end projecting out of the box. One of these ends was painted black except for a 2-mm. diaphragm in the center of the sealed-on glass. The other was immersed in an optically absorbing solution of crystal violet in glycerin, chosen because its index of refraction is nearly that of Pyrex glass. In this way the aperture of the tube was decreased and a black background for the photographs provided. A cylindrical reflector was then placed around the 19-cm. illuminated portion of the tube. The box was finally filled with distilled water which had been boiled to remove air and main-

[4] Wood, *Phil. Mag.*, **6**, 729 (1928).

tained at constant temperature by thermostated water circulated through a long copper coil. The lamp, behind which was also an efficient reflector, was of course necessarily outside the box, being about 10 cm. removed from the axis of the scattering tube. The slit of the spectrograph was placed about 15 cm. from the diaphragm opening of the tube, and scrupulously directed down the tube's axis. The resolution of scattered light secured by this arrangement may be seen from the photometric records, Figs. 1 and 2.



N, 3650 Å.; S, 3655 Å.; T, 4047 Å.; V, 5461 Å.

Fig. 1.—Tracings of photometric records showing the light of various wave lengths scattered laterally by carbon tetrachloride at 18 and at 54°. The scattering is always less intense at the lower temperature in accordance with the Einstein–Smoluchowski theory. Logarithmic integration of these curves gave the photographic densities recorded in Table I for Plate 2.

Exposures of density suitable for photometering were obtained with carbon tetrachloride in four hours. Exposures which gave approximately equal density with benzophenone required only twenty minutes, so that if, as is customary, the light scattered laterally by ether at 20° is taken as unity, and that scattered by carbon tetrachloride at the same temperature as 1.1, the scattering factor of benzophenone is about 12. Because of the failure of the reciprocity law with photographic plates, this number must be regarded as only approximate.

In order to indicate as clearly as possible the relative intensities of scattering at two different temperatures only two strips were put on each plate, each having identical exposure times and intensities of illumination. The apparatus was wholly untouched between the two exposures except for an external adjustment of the temperature regulating mechanism and, of course, a slight movement of the plate-holder in the spectrograph. Exposures were taken on plates in alternate order as Plate 1, 20°, and then 56°, Plate 2, 56° and then 20°, etc., in order to guard against errors due to deterioration of the light source. No indications of such deterioration were found, however. The plates were developed at constant temperature by a standard procedure.

Typical photometric records of the results are given in Figs. 1 and 2, representing carbon tetrachloride and benzophenone, respectively. The greater photographic density for carbon tetrachloride at the higher temperature in accordance with Equation 2 is at once apparent to the eye. It is also apparent that no corresponding difference is obtained with benzophenone. The benzophenone photographs analyzed in Fig. 2 were those showing least divergence between the higher and lower temperatures. In all others which were photometered the difference was greater, and in the opposite direction to that predicted by the Einstein–Smoluchowski theory.

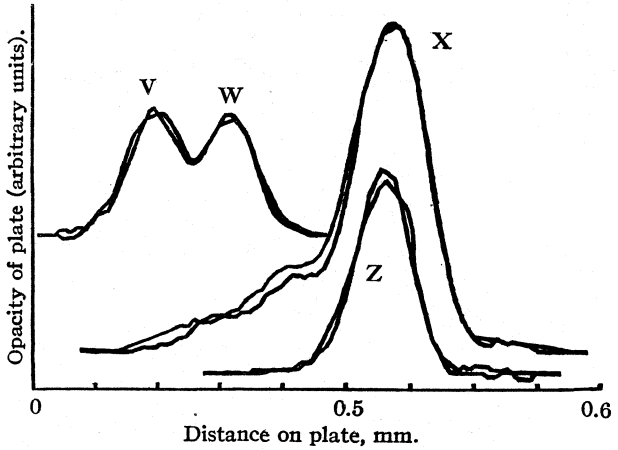


Fig. 2.—Tracings of photometric records showing the light of various wave lengths scattered laterally by benzophenone at 19 and 53°. The intensity of the two is identical within experimental error, in contradiction to the Einstein–Smoluchowski theory. Logarithmic integration of these curves gave the photographic densities recorded in Table II for Plate 3.

These records were obtained by focusing a straight-filament 4-volt lamp on the emulsion of the plate through a 10x microscopic objective, and moving the plate between this image and a Weston photronic cell. The cell, which was covered with a wide slit to eliminate scattered light and connected directly to a critically damped Leeds and Northrup Type HS galvanometer, functioned admirably throughout, showing no deterioration on prolonged illumination, and no zero drift. A microscopic comparator of conventional design served to give the necessary measurement of length on the plate.

The interpretation of the photometric records was based on well-known photographic practice. The photographic densities were obtained by logarithmic integration of opacity curves of the type given in Figs. 1 and 2. Since the densities to be interpreted were neither very small nor very great, the approximation

$$d = I^p t^p \tag{4}$$

where d is density, I intensity, t time of exposure and p an empirical exponent between unity and 0.8, was taken to be applicable, the validity of this approximation having been tested roughly over the range of densities considered. Since on each plate the exposure times are equal, it is obvious that at temperatures T_1 and T_2 Equations (3) and (4) may be combined to give

$$\frac{d_1}{d_2} = \frac{I_{s_1}}{I_{s_2}} = \frac{T_1\beta_{T_1}(n_1^2 - 1)^2(n_1^2 + 2)^2}{T_2\beta_{T_2}(n_2^2 - 1)^2(n_2^2 + 2)^2} \tag{5}$$

provided monochromatic light of constant incident intensity is used to excite the scattering.

A comparison of the intensity of scattering observed and calculated from Equation 5 is given for carbon tetrachloride in Table I, together with other pertinent data. The compressibilities of carbon tetrachloride are taken from Tyrer, and the refractive index at 20° from Landolt-Börnstein. The refractive index at other temperatures has been calculated from Equation 1, with the help of densities obtained from the "International Critical Tables." The dispersion of carbon tetrachloride has been neglected, since it introduces a factor far below experimental error. The agreement of the observed increase of scattering with that calculated is qualitatively satisfactory, but quantitatively leaves much to be desired. Lack of accuracy in the photographic method is more likely to be responsible for this than failure of the theory.

TABLE I

COMPARISON OF LIGHT SCATTERED BY CARBON TETRACHLORIDE AT TWO DIFFERENT TEMPERATURES

Refractive index for 4860 Å. at 56°, 1.444; at 20°, 1.468. Isothermal compressibility atm.$^{-1}$ at 56°, 1.40×10^{-4}; at 20°, 1.05×10^{-4}.

	Exposure time, hours	Wave length, Å.	Photographic density in arbitrary units at 56°	Photographic density in arbitrary units at 20°	Observed $\frac{I_{56} - I_{20}}{I_{20}} \times 100$	Calculated $\frac{I_{56} - I_{20}}{I_{20}} \times 100$
Plate 1	4	4358	192	131	+47	+28
	4	4046	139	108	+29	+28
Plate 2	4	4358	202	139	+45	+28
	4	4046	174	124	+40	+28

The refractive index of benzophenone has been determined at 53.5° by Auwers and Eisenlohr[5] but its density and compressibility at various temperatures in an undercooled condition are unknown. The density was readily determined by sealing a known weight of the pure solid in a calibrated tube, heating to 150° to ensure the destruction of adsorbed crystalline nuclei, and measuring the volume, with suitable corrections for the expansion of the glass, at various temperatures. The linear relationship, where T is now in °C.

$$\rho_T = 1.132(1 - 0.00098T)$$

[5] Auwers and Eisenlohr, *J. prakt. Chem.*, **84**, 37 (1910).

represents the density of supercooled benzophenone between 10 and 60° to better than 1%, and hence suffices for the purposes of this communication. The isothermal compressibility is not so readily accessible, and attempts to measure it by direct methods failed owing to the persistent inoculation of the undercooled liquid by nuclei from the air. It is evident, therefore, that any such measurement must be undertaken in a sealed all-glass vessel, which alone permits adequate sterilization of the liquid. An investigation of this character is outside the scope of the present communication, and the compressibility must, therefore, be estimated by an approximate relationship. It is reasonable to suppose that a large part of the increased compressibility of the liquid at higher temperatures is due to its increased specific volume. In other words, the fact that the molecules are more widely spaced at higher temperatures should make it easier to compress them. If this is the case an approximation of the type

$$\text{const.} \times \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{\beta_T}\left(\frac{\partial \beta_T}{\partial T}\right)_P$$

where v is the specific volume, might hold for all liquids. The constant is, in fact, surprisingly good considering the extreme simplicity of the assumption. For carbon tetrachloride it is 64, for carbon bisulfide 81, for benzene 63, for toluene 66 and for ethyl alcohol 73 as calculated from the data given by Freyer, Hubbard and Andrews.[6] Water alone of the liquids compared in this way formed an important exception. The constant has been taken as 70 for benzophenone for the calculation of the percentage increase in scattering to be expected at higher temperatures according to simple fluctuation theory. Table II presents a complete analysis of two plates from densitometric records. Table III gives only the opacities of the points of maximum density of these two, and of two more plates taken under similar conditions. A comparison of corresponding points of maximum opacity with carbon tetrachloride may be made by means of Fig. 1.

It is considered that the measurements summarized in Table II establish unequivocally the irregular temperature dependence of light scattered by

TABLE II

COMPARISON OF INTENSITIES OF LIGHT SCATTERED BY BENZOPHENONE AT DIFFERENT TEMPERATURES

Refractive index for 4860 Å. at 53°, 1.616; at 49°, 1.619; at 19°, 1.639; at 17°, 1.641. β_T/β_{19} atm.$^{-1}$ at 53°, 1.214; at 49°, 1.181; at 19°, 1.00; at 17°, 0.989.

	Exposure time, hours	Wave length, Å.	Photographic density at 53°	49°	19°	17°	% increase obs.	% increase calcd.
Plate 3	2	4358	567	...	563	...	+ 1	+12
	2	4046	217	...	224	...	− 3	+12
	2	5770 and 5791	260	...	269	...	− 3	+12
Plate 6	0.5	4358	...	237	...	293	−24	+12
	0.5	4046	...	106	...	131	−25	+12

[6] Freyer, Hubbard and Andrews, THIS JOURNAL, 51, 759 (1929).

TABLE III

MAXIMUM OPACITIES IN ARBITRARY UNITS (FULL LIGHT = 0, TOTAL DARKNESS = 3.00) READ FROM PHOTOGRAPHS OF MERCURY LINES SCATTERED BY BENZOPHENONE AT VARIOUS TEMPERATURES

Exposure	T, °C.	4358 Å.	4046 Å.	5770 Å.	5791 Å.
Plate 3, 2 hours	53	2.05	1.69	1.50	1.47
	19	2.04	1.67	1.50	1.48
Plate 4, 1 hour	51	2.00	1.69	1.49	1.45
	17	2.02	1.70	1.50	1.47
Plate 5, 1 hour	54	2.00	1.56	1.35	1.33
	17	1.99	1.58	1.36	1.35
Plate 6, 0.5 hour	49	1.86	1.46	1.29	1.28
	17	1.91	1.50	1.31	1.30

undercooled benzophenone. Failure of Equation 4 may easily account for the discrepancy between measured and calculated values noted in Table I, but it cannot, at moderate light intensities, cause the reversal of the sign of the effect observed. Again, uncertainty of the compressibility coefficient as calculated from Equation 6 can cause the reversal of the sign only if the compressibility itself increases with decreasing temperature, a situation almost without precedent. The compressibility alone causes temperature variation of Equation 3, since the changes in T and n^2 almost exactly balance each other. The cause for the notable difference in temperature effect observed between Plates 3 and 6 follows as a natural consequence of the argument advanced in the next section.

Discussion

In the previous section measurements are reported which show that light scattering in undercooled benzophenone increases with decreasing temperature. Since the theory of density fluctuations in a homogeneous liquid predicts the opposite effect, it evidently cannot be applied in this case, and some constitutional difference must be assumed between undercooled benzophenone and a normal liquid. The formation of molecular aggregates, of structure between that of the crystalline state and that of the loose complexes met with in "associated" liquids above their melting temperatures, suggests itself as a reasonable explanation. These, if they are of lower energy content than the undercooled liquid, will be favored at lower temperatures. If a density change accompanies their formation, they will scatter light according to the expression developed by Lord Rayleigh[7] for colloidal particles, which may be written

$$\frac{I_s}{I_0} = \frac{9\pi^2 N v^2}{\lambda^4 D^2}\left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2}\right)^2 (1 + \cos^2\vartheta) \qquad (6)$$

Nv^2 here represents the product of the number and the squared volume of the scattering particles, and n_1 and n_0 refer to disperse phase and dispersion

[7] Lord Rayleigh, *Phil. Mag.*, **47**, 375 (1899).

medium, respectively. Evidently, then, the increased light scattering which has been observed can be explained on the basis of aggregate formation only if it can be shown that the quantity Nv^2 will be increased with decreasing temperature. For this purpose it will be convenient to assign definite bounds to the volume of the aggregates, however difficult this might be to measure experimentally.

It must be emphasized at the start that the properties of undercooled benzophenone are for all practical purposes independent of time. Light scattering at 20° is equally intense whatever the previous thermal history of the undercooled liquid. The properties of the aggregates present are, therefore, undergoing reversible changes with temperature, and at a given temperature must reach a stationary condition which is subject only to thermal fluctuations. For this reason it is permissible to describe them by methods applicable only to the equilibrium state, although the undercooled liquid is of course metastable to the crystalline condition.

The free energy change accompanying the formation of a gram molecular weight of aggregates of radius r from the metastable liquid at a temperature T will be called ΔF_r. The corresponding molar heat content and entropy changes will then be ΔH_r and ΔS_r. Since

$$\Delta F_r = \Delta H_r - T\Delta S_r$$

and

$$\Delta F_r = -RT \ln \frac{p_r}{p_l}$$

where p_r and p_l are the vapor pressures of aggregate and liquid respectively, it follows that, if the aggregate is in equilibrium with the undercooled liquid at $r = r_0$

$$\frac{p_{r_0}}{p_l} = e^{\Delta S_{r_0}/R}\, e^{-\Delta H_{r_0}/RT} = 1$$

and consequently that

$$\frac{\Delta S_{r_0}}{R} - \frac{\Delta H_{r_0}}{RT} = 0 \qquad (7)$$

The question evidently turns, therefore, on the variation of ΔH_r and ΔS_r with r and T. ΔH_r is compound, being partly work done against the surface energy and partly that gained by liberation of what may be called the latent heat of association. If we call N_r the number of aggregates of radius r which are formed by a gram molecular weight of undercooled liquid, the heat change accompanying the substitution of an aggregate for an equal mass of undercooled liquid in the interior of the latter will be

$$\frac{\Delta H_r}{N_r} = (4\pi r^2 \sigma_r - \Delta e_r)$$

where σ_r is considered the total surface energy, and Δe_r is the energy liberated due to the orientation of the molecules in the interior of the aggregate. Since neither of these quantities will be very sensitive to tem-

perature, their variation in this respect may be neglected, and the variation of $4\pi r^2\sigma_r - \Delta e_r$ with r alone considered. In general, since Δe_r increases with r^3 and $4\pi r^2\sigma_r$ with r^2, their difference will change in sign with increasing values of r, and unless σ_{r_0} is very large, ΔH_{r_0} will be negative, that is, the heat content of the aggregate will be less than that of an equal mass of undercooled liquid, for all radii not very close to molecular magnitudes.

The dependence of ΔS_r on r must now be considered. If two aggregates of radius, respectively, r_0 and r_1 such that $r_1 > r_0$ are considered, we may gain some idea of this dependence if we neglect surface energy and consider that $\Delta H_{r_0} = \Delta H_{r_1}$. In this case Boltzmann's principle may be applied, the probabilities for the existence of the two states being given by

$$\frac{P_{r_0}}{P_{r_1}} = e^{(\Delta S_{r_0} - \Delta S_{r_1})/k}$$

and it is seen that the larger radius is the less probable if, as can hardly be questioned, a loss of entropy accompanies the association of the metastable liquid. This is in agreement with what is to be expected from general considerations. Since the aggregates are of lower energy content than the metastable liquid, it is reasonable to suppose that only liquid molecules of energy lower than the average may lead to their formation. Thus a large radius becomes more probable at lower temperatures, and the value of r for which Equation 7 is satisfied increases as the average thermal energy of the system is reduced. The increased power to scatter light follows as a natural consequence.

Concerning the state of aggregation of the associated complexes, it may only be said that it must differ in some important respect from the stable crystalline lattice, for if the condition $\Delta F_{r_0} = 0$, $p_{r_0} = p_1$ is applied to a crystalline nucleus, the corresponding radius will be great enough to cause crystallization if increased by an infinitesimal amount. Thermal fluctuations would ensure this increase, and a stationary state like that described above is therefore out of the question. In so far as the scattering centers undergo reversible changes with temperature it must be concluded that the anomalous light scattering in an undercooled liquid has no direct bearing on its crystallization at low temperatures. It is perhaps most reasonable to suppose that the arrangement of molecules in the aggregates resembles that in the amorphous layers periodically adsorbed on crystals which are growing into their melts.

The rate of formation of crystal nuclei in the liquid is a problem with which this communication has no concern, since no time dependence of the intensity of light scattered has been observed. As undercooled benzophenone crystallizes readily at about $-60°$, it is necessary to suppose crystal nuclei present at this temperature, and no reason is apparent for doubting their existence at any other temperature below the melting point.

At a temperature near that where spontaneous crystallization becomes likely, they may well play a preponderant role in scattering by the liquid. Such a case is familiar with a glass which has become milky by partial devitrification at a uniform temperature. The time dependence of this type of scattering in a liquid of low viscosity would be an interesting study, and one likely to yield information of value concerning the kinetics of the crystallization process. Since the number of crystallites in undercooled benzophenone is inappreciable at 20°, a far lower temperature is evidently necessary to obtain results of clear significance in this respect.

A quantitative description of the temperature dependence of light scattering in undercooled liquids by means of fluctuation theory is difficult because no intimate knowledge of the nature of the aggregation taking place is at present available. In general it is by no means certain that all metastable liquids will show an increase in scattering similar to that of benzophenone below their melting temperatures. Glasses, for example, and extremely viscous liquids like glycerin, may be expected to undergo changes in molecular aggregation so slowly that the reasoning used above has no practical application. Similar behavior to that of benzophenone is rather to be expected from those liquids which show anomalous dispersion of the dielectric constant immediately above their crystallization temperatures.

We wish gratefully to acknowledge the criticism of Dr. Henry Eyring concerning the conclusions reached in this communication, and the loan of the photometric equipment by the Loomis Laboratory in Tuxedo, N. Y.

Summary

It has been demonstrated by a photographic method that the light scattered by undercooled benzophenone is greater at 20° than at 55°. This result is not to be expected from the Einstein–Smoluchowski theory of fluctuations in a homogeneous medium. The hypothesis is advanced that molecular aggregates are present in the undercooled liquid which increase in number and magnitude as the temperature is lowered. It is pointed out that this is energetically possible without crystallization of the liquid, provided that the aggregates are not crystalline in character.

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[CONTRIBUTION FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY OF THE UNIVERSITY OF CALIFORNIA]

DISTRIBUTION RATIOS AND ASSOCIATION OF CARBOXYLIC ACIDS*

BY ALBERT E. SMITH AND JOHN W. NORTON

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Probably the best methods for quantitative analysis of mixtures of fatty acids are based on distribution ratios.[1] Distribution also offers a possible method for separating these acids from each other. In certain cases, however, the distribution ratio of a given acid varies greatly with concentration; a theory of this is given below, after listing the experimental results. An analogous theory explaining relative physical properties of certain substituted benzene derivatives has been given elsewhere.[2]

Experimental

Since different solvents will obviously give different results, it is evidently important to investigate solvents of various types. Solvent pairs studied were first 2,2,4-trimethylpentane ("*i*-octane") and methanol; second, 2,2,4-trimethylpentane and methyl cyanide (acetonitrile). A paper from this Laboratory on distribution ratios between certain other solvent pairs (each pair including water) is now in press.[3] Methyl cyanide (acetonitrile) and *i*-octane were very pure samples prepared in this Laboratory, to be described in a later paper. Properties of the *i*-octane did not agree with Edgar's[4] but checked exactly with later results of Edgar and Calingaert;[5] 25 cc. of *i*-octane and one drop of 0.1 *N* sodium hydroxide gave a pink color with phenolphthalein; with the methyl cyanide the second drop of the sodium hydroxide gave pink. Like these solvents, the methanol was also distilled in a 6.09-meter fractionating column previously described.[6] The methanol (measured in equilibrium with *i*-octane at 0°) contained 0.48 milliequivalent of acid per liter. Since the co-existing *i*-octane layer con-

* Aided by grants from the Committee for Research in Problems of Sex of the National Research Council, and from the Rockefeller Foundation. These funds have been generously augmented by the Board of Research and the College of Agriculture of the University of California.

[1] (a) W. U. Behrens, *Z. anal. Chem.*, **69**, 97 (1926); (b) C. H. Werkman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 302 (1930); (c) O. L. Osburn and C. H. Werkman, *ibid.*, **3**, 264 (1931); (d) C. H. Werkman and O. L. Osburn, *ibid.*, **3**, 387 (1931).

[2] N. V. Sidgwick and Elinor K. Ewbank, *J. Chem. Soc. London*, **119**, 979 (1921); N. V. Sidgwick and W. M. Aldous, *ibid.*, **119**, 1001 (1921); N. V. Sidgwick and H. E. Rubie, *ibid.*, **119**, 1013 (1921).

[3] R. C. Archibald, THIS JOURNAL, **54**, 3178 (1932).

[4] G. Edgar, *Ind. Eng. Chem.*, **19**, 145 (1927).

[5] G. Edgar and G. Calingaert, THIS JOURNAL, **51**, 1540 (1929).

[6] Evans, Cornish, Lepkovsky, Archibald and Feskov, *Ind. Eng. Chem., Anal. Ed.*, **2**, 339 (1930).

tained no appreciable acid, the acid was probably formic; this was corrected for by subtraction. The formic, acetic and butyric acids were commercial C. P. products (formic being Eastman "99½ to 100%" which may contain some water). Caprylic, lauric and palmitic acids were very pure samples prepared in this Laboratory (to be described in another publication). The oleic acid and the 50% oleic–50% linoleic acid were less pure, but gave correct iodine values and titration values. All titrations in determining distribution ratio were with 25-cc. samples, using also phenolphthalein and 0.1 *N* sodium hydroxide. Both layers were titrated. With all but methyl cyanide layers difficulty was found owing to emulsification during titration; this was avoided by making up the 0.1 *N* sodium hydroxide in absolute ethyl alcohol instead of in water.[7] Values in Tables I and II are means of duplicate titrations. Equilibrium between the layers at 0° was obtained by shaking flasks by hand, these flasks being immersed in ice and water; tests showed that the liquid in the flasks reached 0°. Checks between duplicate samples indicated sufficiency of this procedure for our purposes. The dicarboxylic acids stood for about a week in the solvent mixture at room temperature with occasional shaking. This mixture was filtered and cooled to 0° with shaking. A certain amount of solid acid appeared to separate at the interface, but this was avoided in pipetting out samples. However, the solubilities for dicarboxylic acids in Table II are

TABLE I

DISTRIBUTION RATIOS BETWEEN 2,2,4-TRIMETHYLPENTANE AND METHANOL AT 0°

Concentrations in millimoles per liter

Acid	Hydroc. layer	Methanol layer	Ratio	Av. ratio
Formic	5.05	163.3	0.0309	0.0280
Formic	12.71	508.4	.0250	
Acetic	6.75	144.21	.0468	.0457
Acetic	11.29	252.93	.0446	
Butyric (*n*)	6.91	81.20	.0840	.0878
Butyric (*n*)	18.98	206.33	.0916	
Caprylic (*n*)	6.86	38.01	.180	.190
Caprylic (*n*)	21.20	105.75	.201	
Lauric (*n*)	5.25	15.80	.332	.352
Lauric (*n*)	7.20	20.89	.345	
Lauric (*n*)	21.53	56.98	.378	
Palmitic (*n*)	9.91	16.03	.618	.649
Palmitic (*n*)	29.56	44.18	.669	
Oleic	9.26	15.12	.613	.629
Oleic	18.66	29.76	.627	
Oleic	26.79	41.41	.647	
50% Oleic }	7.84	14.21	.552	.5545
50% Linoleic }	20.02	35.91	.557	
Linoleic ("Vitamin F") calculated from above data				.487

[7] See O. Folin and A. H. Wentworth, *J. Biol. Chem.*, **7**, 421 (1910), who used sodium ethylate in absolute alcohol for similar purposes.

TABLE II

DISTRIBUTION BETWEEN 2,2,4-TRIMETHYLPENTANE AND METHYL CYANIDE AT 0°

Concentrations in millimoles per liter

Acid	Hydroc. layer (c_1)	Cyanide layer (c_2)	c_1/c_2	$\sqrt{c_1}/c_2$
Lauric	15.42	9.34	1.651	0.420
Lauric	45.51	16.57	2.75	.407
Lauric	86.36	22.80	3.79	.408
Oleic	12.73	4.04	3.15	.882
Oleic	65.23	8.21	7.94	.984
Maleic	None (not satd.)	22.9		
Fumaric	None (satd.)	9.1		
o-Phthalic	None (satd.)	17.7		
m-Phthalic	None (satd.)	4.4		
p-Phthalic	None (satd.)	2.5		

probably of value only in the absence of better data. The values of Tables I and II for oleic and linoleic acids (and in fact all data of this paper) were determined because of their relation to the purification of vitamin F,[8] which has been claimed to be linoleic acid.[9] For plotting, the simple averages of Table I were used although the values show definite and regular change with concentration. From average values of Table I for oleic and oleic + linoleic acids, one calculates the distribution ratio of linoleic acid between *i*-octane and methanol at 0° as 0.487.

Comparison with Results of Others.—The figure shows the results of the authors for *i*-octane and methanol with "saturated" acids. In the figure are also plotted distribution ratios for acids in isopropyl ether and water at 25°,[1b,c,d] using weighted means from the three papers cited and neglecting their earlier value for butyric acid. An obvious typographical error by Osburn and Werkman is the interchanging of what they call "partition constants" for the two different proportions of ether and water. The distribution ratios chosen (for a mean concentration of both layers of about 0.05 *M*) are: formic 0.145, acetic 0.184, propionic 0.810, butyric 2.90. Values at 25° for ethyl ether and water are estimated for 0.001 *M* acid in the aqueous layer[1a,10] (as the ratio changes somewhat with concentration) as: formic 0.30, acetic 0.44, propionic 1.34, butyric 4.6, valeric 17.5, caproic 75. For glycolic and lactic acids in ethyl ether and water at 25°[11] one may select round values: glycolic 0.03, lactic 0.08. The α-hydroxy acids apparently give a curve parallel to that for the unsubstituted acids. Values for acetone and glycerol[12] are insensitive to concentration changes;

[8] H. M. Evans and G. O. Burr, *J. Biol. Chem.*, **74**, lxxii (1927); *Proc. Soc. Exptl. Biol. Med.*, **25**, 41, 390 (1928).

[9] G. O. Burr and M. M. Burr, *J. Biol. Chem.*, **82**, 345 (1929); **86**, 587 (1930).

[10] H. W. Smith, *J. Phys. Chem.*, **25**, 619 (1922).

[11] J. Pinnow, *Z. anal. Chem.*, **54**, 321 (1915); *Z. Untersuch. Nahrungs. Genussm.* **37**, 49 (1919).

[12] H. W. Smith, *J. Phys. Chem.*, **25**, 721 (1921).

one may select for 25°: formic 1.37, acetic 1.78, propionic 3.5, butyric 12.7. From the figure it is evident that for separation of fatty acids from each other, *i*-octane and methanol give by far the poorest separation of the solvent pairs shown.

Distribution Ratio of Stearic Acid between Ethyl Ether and Water; Analysis of Higher Fatty Acid Mixtures.—By extrapolating the curve for ethyl ether and water (assuming a straight line in the figure), one finds for

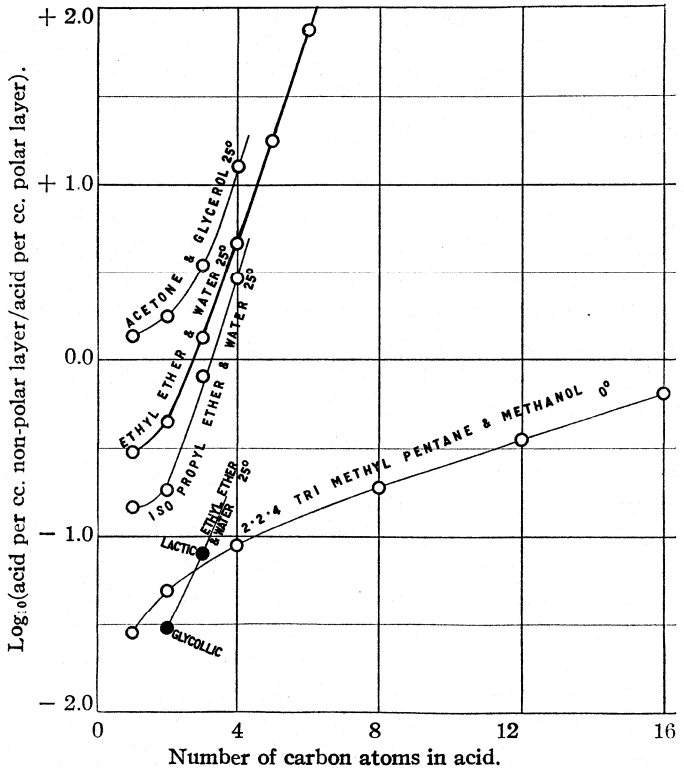

Fig. 1.—Distribution ratios between solvents of normal monocarboxylic fatty acids ($C_nH_{2n}O_2$). These ratios change somewhat with concentration of acid (see text of article). A curve is also shown for α-hydroxy acids.

stearic acid ($C_{18}H_{36}O_2$) a distribution ratio of about 10^9 at 25°; no direct measurement is available. Since the dissociation constants of paraffin fatty acids[13] are around 1.5×10^{-5} it would seem that the analytical method of Behrens[1a] could be extended to higher fatty acids by keeping the aqueous layer at a definite, fairly high alkalinity during the partition process.

[13] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923, 5th ed., p. 1127.

Owing to emulsification a centrifuge might be necessary. It should be possible to modify this method to cover dicarboxylic acids.

Self-Association of Monocarboxylic Acids.—Reference to Table I shows that with *i*-octane and methanol, the distribution ratio changes but slightly with concentration, indicating the acids to have single molecules in both layers. However, Table II shows that the *square root* of the acid concentration in the *i*-octane layer is proportional to the acid concentration in the methyl cyanide; this indicates that here the acid is "self-associated" as double molecules in this *i*-octane layer. By "self-association" is meant combination of carboxyl groups with each other in pairs; this self-association appears to be a strong tendency of the carboxyl group, but may be prevented by the presence of sufficient other molecules which also tend to associate with the carboxyl group. This second type of association (which thus differs from "self-association") *prevents* double acid molecules forming.

Thus self-association evidently is very slight in the methanol or methyl cyanide layers. *i*-Octane is a very non-polar solvent and has little tendency to prevent self-association of the acid, but in Table I a considerable amount of methanol must be dissolved in the co-existing *i*-octane layer. The experiments were at 0°, and one has the "critical solution temperatures" for *i*-octane with methanol at 42.5°. An experiment like Table I at, say, −50°, would undoubtedly show self-association in the *i*-octane layer, due to low solubility of methanol in *i*-octane at that temperature. Similarly, the critical solution temperature of *i*-octane and methyl cyanide is 81°; by conducting the experiments of Table II at, say, +50°, enough methyl cyanide would probably dissolve in the *i*-octane to prevent the self-association of the acid.

Again, when benzoic acid or an aliphatic fatty acid is distributed between water and petroleum ether, the acid is associated as double molecules in the petroleum ether layer.[14]

With water and ethyl ether as the two solvents,[13a] the ordinary "distribution ratio" is reasonably constant (except for a slight trend due partly to ionization in the water layer), indicating no great association in the ether layer. With chloroform and water distribution of these acids,[15] a fair amount of self-association of acid in chloroform layer is found. This all agrees with solubilities of fatty acids in ethyl ether, chloroform and petroleum ether; the solubilities (more particularly with acids having a high ratio of total carboxyl to total carbon) decrease rapidly if solvents are tested, respectively, in the order named. Hence in ethyl ether the affinity of the carboxyl group is satisfied by solvent molecules, the same being true

[14] J. Grossfeld and F. Battay, *Z. Unters. Lebensm.*, **62**, 99 (1931); J. Grossfeld and A. Miermeister, *Z. anal. Chem.*, **85**, 321 (1932).

[15] For complete data see A. Seidell, "Solubilities," D. Van Nostrand Co., New York, Vol. I, 1919, and Vol. II, 1928.

in water, methyl cyanide, methyl alcohol, etc., but only partially so in chloroform, benzene or toluene, and not at all in pure petroleum ether.

Self-Association of Polycarboxylic Acids.—"Self-association" of polycarboxylic acids evidently differs from self-association of monocarboxylic acids, since the latter form only double molecules, while there is hardly any limit to the length of chain possible with the polycarboxylic acid (or with its esters). No definite proof of existence of these chains is presented, but numerous disconnected facts are easily explained by this theory.

Thus, in petroleum ether dicarboxylic acids might form chains of great length, but the dicarboxylic acids tried (Table IV) were almost insoluble in the *i*-octane, even in the presence of the methyl cyanide. This property of low solubility in petroleum ether may be used to separate the dicarboxylic acids from the monocarboxylic of Japan wax.[16] Apparently the chain formation is so effective that the acid crystallizes out of the hydrocarbon. However, the "japanic acids" from the Japan wax, *i. e.*, $C_{20}H_{40}(COOH)_2$ and $C_{21}H_{42}(COOH)_2$ are somewhat soluble in warm petroleum ether and a distribution experiment would probably show a very high power of the acid concentration in the water layer (or in the methyl cyanide layer, whichever is used) proportional to the acid concentration in the petroleum ether layer. The "peculiar coherence and tenacity" of Japan wax fatty acids, found by Tsujimoto[16] to depend on the presence of about 5% of dibasic "japanic acids" is seen to be a mechanical demonstration of affinity between carboxyl groups. Tsujimoto found the same tenacity caused by japanic acid esters of glycerin, which esters he believes cause the "peculiar tenacity" of Japan wax itself. The well-known tenacity of cellulose esters is a further example of "self-association" between ester linkages; tenacity may apparently be produced by esters of either polyhydroxy alcohols or of polycarboxylic acids. Self-association of cellulose esters explains the fact that "the greater the solvent power of a liquid, the lower the viscosity of its solutions," referring to solutions of cellulose ester in pure or mixed solvents.[17] Again, the viscosity of 5 to 25% cellulose nitrate solutions in a given solvent varies as the fourth to fifth power of the cellulose nitrate concentration, according to data of Bogin and Simms;[18] self-association would be expected to increase rapidly with concentration. Their empirical formula is incorrect, however, since, according to them, at a given weight percentage of cellulose ester the viscosity is proportional to the viscosity of the pure solvent mixture. This would give lowest viscosities to cellulose ester solutions with high hydrocarbon content whereas they actually have the highest viscosities.

Evidence of chains is also found in relative melting points of isomers. Comparisons with maleic and fumaric acids (Table III) indicate that the

[16] M. Tsujimoto, *Bull. Chem. Soc. Japan*, **6**, 325, 337 (1931).

[17] T. H. Durrans, "Solvents," D. Van Nostrand Co., New York, 1931, p. 22–29.

[18] C. D. Bogin and C. W. Simms, *Ind. Eng. Chem.*, **20**, 192 (1928).

former acid has its carboxyl groups close together and hence conjugated within the molecule. The series *o-m-p* phthalic acids (Table III) shows the same astonishing gradation in properties here again, *with esters as well as free acids*. Similar melting point series are found with picolinic, nicotinic and isonicotinic acids, with *o-m-p* phthalic dinitrile, etc.[19]

TABLE III

PROPERTIES OF DIBASIC ACIDS[a]

Acid	*o*-Phthalic	*m*-Phthalic	*p*-Phthalic	Maleic	Fumaric
M. p., acid, °C.	191	347	Sublimes	130.5	287
M. p., dimethyl ester, °C.	Liquid	68	140	Liquid	102
M. p.,diethyl ester, °C.	Liquid	11.5	44	Liquid	0.6
G. acid soluble in 100 g. cold water	0.65(13°)	0.013(25°)	0.0015	78.8(25°)	0.70(25°)

[a] Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin (1918 to 1932).

To illustrate the application of the above ideas to other than carboxyl compounds, consider the polymerization of 1,2-divinylacetylene (C_6H_6). This reaction takes place slowly in the pure substance, even in absence of air and light, but the polymerization is greatly retarded by dissolving the 1,2-divinylacetylene in "aromatic solvents."[20] Evidently self-association of the 1,2-divinylacetylene would be largely inhibited by the benzene, and one might reasonably assume self-association to occur preliminary to the irreversible polymerization. One would accordingly predict that the rate of polymerization of the 1,2-divinylacetylene would be many times as fast (perhaps thousands) when highly diluted with a saturated hydrocarbon, as when diluted to the same extent with benzene.

Comparison of Ethyl Ether and Chloroform as Solvents.—"Self-association" of carboxyl groups will be relatively slight, not necessarily in "polar" solvents, but rather in liquids which are good solvents for the carboxyl group. Thus, ethyl ether is a relatively "non-polar" solvent.[21] Potentially, however, ether is a base and chloroform an acid. One may regard high solubilities of acids in ether, and of bases in chloroform, as incipient salt formation (see Table IV).

One is accordingly not surprised to find the base quinine self-associated as double molecules in the ether layer if distributed between ethyl ether and water.[22]

[19] For further discussion of effect of association chains on melting point, see N. V. Sidgwick and others, Ref. 2.

[20] O. M. Hayden, *Ind. Eng. Chem.*, **24**, 563 (1932).

[21] J. H. Hildebrand, THIS JOURNAL, **38**, 1452 (1916); **39**, 2297 (1917); **41**, 1067 (1919); also "Solubility," Chemical Catalog Co., New York, 1924.

[22] W. E. Treadwell, *Helv. Chim. Acta*, **6**, 744 (1923).

TABLE IV

SOLUBILITIES IN CHLOROFORM AND IN ETHYL ETHER[15]

Substance	Soly. per 100 g. of $CHCl_3$, g.	Soly. per 100 g. ether, g.
Atropine $C_{17}H_{23}NO_3$	64.10 (25°)	6.02 (25°)
Quinidine $C_{20}H_{24}N_2O_2?H_2O$	100 (20°)	0.78 (20°)
Fumaric acid $C_4H_4O_4$	0.02 (25°)	0.72 (25°)
Maleic acid $C_4H_4O_4$	0.011 (25°)	8.19 (25°)

Distribution of Mixtures of Fatty Acids in Solvents Allowing Self-Association.—Assume a distribution of mixed monocarboxylic acids between petroleum ether and water. One might reasonably assume all pairs of carboxyl groups to have equal chances of self-association. It accordingly follows that for each acid present its concentration ratio between the two solvents is the same as if that acid were distributed alone with its concentration in the petroleum ether layer, the same as the total acid concentration in the petroleum ether layer of the given mixture. Thus with three mixed acids 0.1 *M*, 0.3 *M* and 0.4 *M*, respectively, in the petroleum ether, each acid has the same distribution ratio as if it were the only acid present, at 0.8 *M*, in the petroleum ether layer. No data are available to test this; some correction would be needed for ionization in the water layer.

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Summary

It is indicated that carboxyl groups have considerable tendency to associate with each other in pairs; this tendency is not destroyed by esterification. This "self-association" may be inhibited by presence of enough of either a somewhat polar or somewhat basic solvent, examples being given. Two carboxyls *close together* in the same molecule self-associate with each other rather than with carboxyls from other molecules. The tenacity of Japan wax and of cellulose esters is explained by these theories. Measurements are given of distribution of fatty acids between *i*-octane and methyl cyanide, and between *i*-octane and methanol; results are compared with those from other solvent pairs. A method is suggested for analyzing mixtures of higher fatty acids. The quantitative influence of fatty acids on each other is discussed for solvents allowing self-association.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

AN ELECTROCHEMICAL INVESTIGATION OF SOLID CADMIUM–GOLD ALLOYS

BY ARNE ÖLANDER[1]

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For an electrode potential to be of theoretical interest one must know what it means; it is the surface layer that determines the potential, and without a knowledge of the condition of this the potentials are of little value. There seems, then, to be an especially serious risk in measuring the potential of an alloy whose one component is as volatile as cadmium at the temperatures which are to be considered here, but the reproducibility of the present results and their dependence on the gross composition of the electrodes leave no doubt that the latter has also been very near the composition of the surface. Thus the conclusion must be drawn that the diffusion in these alloys is quite considerable—with exceptions that will be dealt with later.

Figure 1 shows the phase diagram of the cadmium–gold alloys as given by the investigations of Vogel,[2] Saldau[3] and Durrant,[4] with the adjustments and additions caused by the present measurements. A comparison with Durrant's very careful work shows no differences in the existence limits of the various phases, and also transition temperatures work out very much the same; this must be considered as a proof that the surface composition of the electrodes has been the same as that found by analysis of the whole piece of metal.

The phase diagram closely resembles those of the homologous alloys CuZn, CuCd, AgZn, AgCd and AuZn. Saldau has found that the ϵ-, β- and α'-alloys possess a high electrical conductivity, which indicates that the atoms have an ordered distribution, whereas the α-alloys have a much smaller conductivity. Below 135° there is an α''-modification, which also has a high conductivity.

The alloys were made from 0.9999 gold from Shreve and Co., San Francisco, and C. P. cadmium from Powers, Weightman and Rosengarten, Philadelphia. The metals were melted together in evacuated silica glass tubes, which were sealed to prevent losses. The buttons weighed about 3–4 g. They were remelted in hydrogen and with the aid of this gas forced into 1-mm. capillary silica tubes. When this was done with silver–gold alloys,[5] the capillary tubes had to be made in spiral form, because on

[1] Rockefeller Foundation Fellow.

[2] Vogel, *Z. anorg. Chem.*, **48**, 337 (1906).

[3] Saldau, *Intern. Z. Met.*, **7**, 3 (1914); *J. Russ. Phys.-Chem. Soc.*, **46**, 994 (1914); **55**, 275 (1924).

[4] Durrant, *J. Inst. Met.*, **41**, 139 (1929).

[5] Ölander, THIS JOURNAL, **53**, 3577 (1931).

cooling the thermal contraction tore off the wires if they were cast in a straight tube. This precaution was unnecessary here—it would, moreover, not have been possible afterward to straighten the wire—but great care had to be taken when cracking the silica off the brittle α'-, γ- and ϵ-alloys so that they did not break into small pieces. Before the silica was cracked the alloys were annealed for one to three days in hydrogen, the α-alloys at 550°, the β-alloys at 450° and the γ- and ϵ-alloys at 400°.

The alloys with less than 15 atomic per cent. of cadmium were malleable, the other α-alloys soft and brittle, like rotten wood. The β-alloys with less than 50% cadmium were elastic, this property having a sharply marked maximum at 47.5%. A 1-mm. wire of this alloy was so elastic that it almost reminded of rubber. The alloys with more than 50% cadmium were hard and brittle, over 60% very brittle.

The color of the alloys was: α, all yellow; β, reddish-white up to 50%, the rest bluish-white.

For the measurement of the electrode potentials the cells were set up in the same iron furnace that was used for the investigation of the silver–gold alloys.[5] A 40-cm. Pyrex tube with a diameter of 25 mm. was placed in the furnace, about 25 cm. projecting outside. It contained at the bottom 6–7 ml. of electrolyte and in Runs 1–9 and 14–18 below this about 3.5 ml. of molten cadmium, which was the standard electrode. The upper end of the tube was closed with a cork, which carried six Pyrex tubes and was made air tight with sealing wax. One of these tubes terminated just inside the cork and admitted a very slow current of hydrogen. This gas was taken from a tank, led over hot copper, and dried with phosphorus pentoxide. Another tube, which reached down into the molten cadmium, was closed at its lower end with a short tungsten wire sealed through it, thus making a connection with the cadmium electrode. The tungsten was soldered with German silver to a silver wire, which outside the apparatus was continued by copper wires. The other four tubes—or in the case of no liquid electrode, the other five tubes ended 2 cm. above the surface of the electrolyte. They held the other electrodes, which dipped about 7 mm. down into the liquid. These were 5–10 cm. long and also welded to silver wires.

In order to prevent any air from entering through these tubes capillary "swan necks" were attached to their upper ends with short rubber tubings. The silver leads were run through the rubber.

The electrolyte used was in Runs 1–10 the eutectic mixture of lithium and potassium chlorides (melting at 359°), in Runs 11–18 that of lithium and rubidium chlorides (melting at 312°), and in Runs 19–20 the lowest melting mixture of sodium and potassium acetate (melting at 233°). To each of these a small amount of cadmium chloride or acetate was added.

Runs 19 and 20 could not be made in a hydrogen atmosphere because

this reduced the cadmium acetate; but they were made in nitrogen. This gas was taken from a tank and allowed to pass over hot copper to absorb the oxygen.

An addition of alkali, as used by N. W. Taylor,[6] was not found to be of any advantage and was omitted. The cell, however, was allowed to remain overnight in order to be thoroughly dried, before the alloy electrodes were put in position.

The electrolyte had no tendency to creep on the metallic surface as in the previous investigation.[5] Hence it was possible to keep the junction alloy–silver wire inside the furnace. The correction due to thermopotentials was therefore very small. It was determined after the main run. The cork with the electrodes was taken out, the electrolyte, cadmium and tungsten sealing removed, and the cork replaced in its former position after the electrodes had been soldered together at their lower ends. It was only in a few cases, when very long electrodes had been used, that this correction exceeded 0.2 millivolt. All potentials given in this paper are corrected values.

The temperature was measured with a chromel–alumel thermocouple, which was placed outside the Pyrex tube beneath the end of the electrodes. It was checked between runs at the melting point of zinc (419.5°). The potentials were measured with a Leeds and Northrup type K potentiometer. In the main runs the null-point instrument was a Dolezalek electrometer; the readings were made to 0.1 millivolt. The thermopotential correction runs and the thermocouple readings were made with the aid of a galvanometer, the readings being made to 0.01 millivolt. The accuracy of the temperature readings might be estimated at $\pm 1°$.

No such drifting of the potentials occurred as when silver chloride was used as an electrolyte.

The composition of the alloys was determined by analysis. About 0.25 g. of the immersed end of the electrode was broken off and dissolved in aqua regia. The solution was evaporated to dryness, hydrochloric acid added and evaporated, and the chlorides dissolved in water. Then sodium hydroxide was added and the gold reduced with hydrogen peroxide, the excess being destroyed by boiling. Now the solution was acidified and the gold taken on a filter. However, the gold is not completely precipitated by the peroxide, so the filtrate always had to be reduced once more. The second filtrate, however, was free from gold. The gold was ignited and weighed; the cadmium was taken as 100% minus the gold.

The alloys are characterized by their mole fraction of cadmium.

The alloys with a large cadmium content showed a slow drift in their composition (and potential) during the run, and of these another sample was analyzed to ascertain the composition at the beginning of the experi-

[6] Taylor, THIS JOURNAL, 45, 2865 (1923).

ment. In cases where two compositions are given, the potentials at the beginning and the end of the run have been attributed to the composition at the beginning and end, respectively.

This relatively rapid drifting of the composition shows that the diffusion within the metal must be quite considerable.

The α-alloys, which have higher melting points, show a much smaller diffusion. In fact, it was not possible to measure electrodes of this composition against an electrode of liquid cadmium; the surface was at once whitened by the volatile metal and gave potentials which showed the outer part to be of $\alpha + \beta$ or even β-composition. The α-alloys were then measured against standard electrodes of $\alpha + \beta$-alloys, whose cadmium gas pressure is only one one hundred fiftieth that of pure cadmium. This exchange made it possible to measure alloys down to 20% of cadmium. The alloy with the gross composition 0.158, however, has evidently had a surface composition of about 0.20. The same held good about an electrode of composition 0.11, which, moreover, behaved rather irregularly (not given in the tables). In the table the potential of $\alpha + \beta$ against pure cadmium has been added to the potential measured.

In Runs 19 and 20, where the standard electrode was solid cadmium, the temperature was so low that no drifting of the composition occurred.

In the following table are given: the time in hours from the setting up of the cell, the absolute temperature and the potential of the cell measured, corrected for thermopotential. In the heading of the table are given the compositions of the electrodes, in one case both before and after the run. The standard electrode has been liquid cadmium. Below the table are given interpolation formulas for the potentials and the mean deviation of the readings, together with the temperature of transition points.

RUN 17

t	T	0.640–0.637	0.664	0.676	0.698
2.3	740	39.7	(37.0)	35.3	35.5
2.6	743	39.7	37.2	35.0	35.2
2.9	733	40.2	37.9	36.7	36.7
3.6	731	40.1	37.9	36.8	37.1
4.0	718	41.0	38.8	38.4	38.7
4.4	717	40.8	38.9	38.6	39.0
4.9	704	41.5	40.5	40.1	40.4
5.3	702	41.7	40.9	40.6	40.6
5.9	683	42.9	43.0	42.8	42.9
6.3	681	43.3	43.2	43.0	43.1
6.9	665	45.1	45.0	44.9	44.8
7.3	661	45.3	45.4	45.2	45.4
7.8	650	46.6	46.3	46.5	46.4
8.3	641	47.0	46.8	46.8	46.7
8.6	635	47.3	47.2	47.2	47.1
9.5	630	47.6	47.3	47.5	47.5

RUN 17 (*Concluded*)

	T	0.640–0.637	0.664	0.676	0.698
9.9	619	48.2	48.1	48.2	48.2
10.3	612	48.7	48.5	48.9	48.8
10.6	611	48.8	48.5	48.9	48.7
10.9	625	47.8	47.6	47.8	47.7
11.3	635	47.0	46.9	47.0	46.9
11.5	644	46.6	46.5	46.6	46.5
11.8	647	46.3	46.3	46.4	46.2
12.5	680	43.3	43.1	43.1	43.3
13.0	702	41.9	41.0	40.8	40.7
13.4	714	(41.7)	39.6	39.1	39.1

0.640:	$41.8-0.050(T-700) \pm 0.1$	$T > 688$
(0.639):	$41.1-0.110(T-700) \pm 0.1$	$659 < T < 688$
0.637:	$42.9-0.066(T-700) \pm 0.1$	$T < 659$
0.664:	$40.1-0.07\ (T-700) \pm 0.1$	$T > 725$
	$41.1-0.113(T-700) \pm 0.1$	$657 < T < 725$
	$43.2-0.060(T-700) \pm 0.1$	$T < 657$
0.676:	$42.1-0.168(T-700) \pm 0.1$	$T > 728$
	$40.7-0.118(T-700) \pm 0.1$	$660 < T < 728$
	$42.6-0.070(T-700) \pm 0.1$	$T < 660$
0.698:	$42.1-0.163(T-700) \pm 0.1$	$T > 728$
	$40.8-0.116(T-700) \pm 0.1$	$662 < T < 728$
	$42.5-0.071(T-700) \pm 0.1$	$T < 662$

Similar tables for the other runs are summarized in Tables I–III. Table I shows the temperature interval covered in each run, the number of

TABLE I

Run	Temp., °K.	Number of readings	Electrodes
1	665–748	28	0.401, 0.475
2	670–761	29	.441
3	657–753	20	.467, .478, .493
4	656–740	28	.540, .544, .555
5	655–748	23	.510, .516
6	643–743	28	.606–(.624)–(.628)–.624, .633–(.635)–.627
7	682–869	10	.418, .440
8	661–749	14	.505
9	666–753	14	.409
10	647–780	10	.203, .275
11	632–740	11	.284, .299, .326
12	627–756	15	.158, .253
13	642–750	15	.227, .241, .266, .271
14	614–747	26	.599, .619, .643
15	612–696	16	.714–.712, .733–.728, .741–.739, .758–
16	635–750	19	.471, .473, .482
17	611–743	26	.640–.637, .664, .676, .698
18	615–675	15	.696, .763, .755
19	520–579	19	.563, .577, .668, .669
20	519–566	14	.846, .893, .977, .987

accepted readings for each electrode and the composition of the alloy electrodes, in some cases both before and after the run. Values in parentheses have only been estimated from the value of $E_{700°}$, and have been valid during part of the run.

Mostly the first readings were irregular and have been discarded. Especially the electrodes with large gold content usually did not come to equilibrium until the second day of the experiment. Thus some runs lasted sixty hours. Sometimes hysteresis occurred when passing over a transition point. It has been judged from a graphical plot when a reading should not be used. It is seen that the potentials of these alloys are much better defined than those of silver–gold. The α-alloys often showed hysteresis with respect to changes in temperature and were rather irregular when passing over the α–α' transition. On the whole many α-electrodes had to be discarded because of their irregular behavior. Also with other compositions many electrodes have been discarded, but when care was taken that electrodes with very different compositions were not used in the same run, they were not so liable to drift.

The results are given in Tables II and III. The first column refers to Table I, the second and third describe the alloy electrode, and the fourth gives the potential in millivolts at 700°K. or (for Runs 19 and 20) 500°K.

TABLE II

POTENTIAL OF THE CELL $Cd_{liquid}/K(Rb)Cl, LiCl, CdCl_2/(Cd, Au)_{solid}$

Run	Cd	Phase	$E_{700°}$	$dE:dT$	$\pm\delta$	T	$-\Delta\bar{F}_{700°}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
18	0.763	ϵ	6.0	+0.017	0		277	−270	+0.78
15	.758	ϵ	8.1	+ .009	1		374	+ 80	+ .42
18	.755	ϵ	9.0	+ .005	2		415	250	+ .23
15	.741	ϵ	26.4	− .136	2		1218	5610	−6.27
15	.739	ϵ	27.9	− .126	2		1287	5350	−5.81
15	.733	ϵ	31.5	− .125	1		1453	5490	−5.77
15	.728	ϵ	32.3	− .120	1		1490	5370	−5.54
15	.714	ϵ	37.2	− .113	2		1716	5360	−5.21
15	.712	ϵ	38.5	− .110	1		1776	5320	−5.07
17	.698	$\gamma + \epsilon$	42.5	− .071	1	<662			
18	.696	$\gamma + \epsilon$	42.4	− .064	1	<659			
17	.676	$\gamma + \epsilon$	42.6	− .070	1	<660			
17	.664	$\gamma + \epsilon$	43.2	− .060	1	<657			
14	.643	$\gamma + \epsilon$	43.4	− .060	1	<655			
17	.637	$\gamma + \epsilon$	42.9	− .066	1	<659			
			42.8	− .065		<659	1974	4070	−3.00
17	.698	$\delta' + \epsilon$	40.8	− .116	1				
17	.676	$\delta' + \epsilon$	40.7	− .118	1				
17	.664	$\delta' + \epsilon$	41.1	− .113	1				
14	.643	$\delta' + \epsilon$	41.0	− .113	1				
17	(.639)	$\delta' + \epsilon$	41.1	− .110	1				
			40.9	− .114		659–728	1887	5570	−5.26

TABLE II (*Continued*)

Run	Cd	Phase	$E_{700°}$	$dE:dT$	$\pm\delta$	T	$-\Delta\bar{F}_{700°}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
17	0.698	$\delta+\epsilon$	42.1	−0.163	1	>728			
17	.676	$\delta+\epsilon$	42.1	− .168	1	>728			
			42.1	− .166		>728	1942	7300	−7.66
17	.664	δ ?	40.1	− .07	1	>725	1850	4090	−3.2
17	.640	δ'	41.8	− .050	1	>688	1928	3550	−2.31
6	(.635)	δ'	43.6	− .035	2		2011	3140	−1.61
6	.633	δ'	44.2	− .035	4		2039	3170	−1.61
6	(.628)	δ'	46.8	− .032	1		2159	3200	−1.48
6	.627	δ'	47.7	− .030	1		2200	3170	−1.38
6	(.624)	δ'	48.5	− .030	1		2237	3200	−1.38
6	.624	δ'	48.6	− .030	2		2242	3210	−1.38
14	.619	$\beta+\gamma$	44.8	− .096	1	<654			
14	.599	$\beta+\gamma$	44.8	− .095	1	<653			
			44.8	− .096		<654	2066	5170	−4.43
14	.619	$\beta+\delta'$	49.0	− .005	3	>654			
6	.606	$\beta+\delta'$	49.3	− .004	4				
14	.599	$\beta+\delta'$	49.1	− .004	2	>653			
			49.1	− .004		>654	2265	2390	−0.18
4	.555	β	51.8	− .003	1		2389	2490	− .14
4	.544	β	55.6	− .001	2		2565	2600	− .05
4	.540	β	54.9	− .002	2		2532	2600	− .09
5	.516	β	71.2	+ .021	2		3284	3960	+ .97
5	.510	β	82.8	+ .021	3		3819	4500	+ .97
8	.505	β	88.0	.000	3		4059	4060	.00
3	.493	β	128.3	− .110	4		5918	9470	−5.07
16	.482	β	131.0	− .127	3		6043	10150	−5.86
3	.478	β	133.1	− .113	4		6047	9690	−5.21
1	.475	β	133.1	− .115	3		6047	9760	−5.30
16	.473	β	137.3	− .127	2		6333	10440	−5.86
16	.471	β	137.0	− .121	3		6319	10230	−5.58
3	.467	β	143.1	− .118	3		6601	10410	−5.44
2	.441	β	151.0	− .106	3		6965	10390	−4.89
7	.440	β	150.1	− .099	1		6924	10120	−4.57
7	.418	$\alpha+\beta$	153.1	− .063	2				
9	.409	$\alpha+\beta$	153.0	− .064	2				
1	.401	$\alpha+\beta$	153.3	− .067	2				
			153.1	− .065			7062	9160	−3.00
11	.326	α	162.7	− .013	2		7505	7930	−0.60
11	.299	α	177.5	− .009	2		8187	8480	− .42
11	.284	α	185.9	− .002	3		8575	8640	− .09
10	.275	α	191.0	− .004	1	>660	8810	8940	− .18
13	.271	α	193.7	− .004	4	>695	8935	9060	− .18
13	.266	α	194.5	+ .010	2	>696	8972	9060	+ .46
12	.253	α	201.7	+ .018	3	>687	9304	8720	+ .83
13	.241	α	209.7	+ .007	1		9673	9450	+ .32

TABLE II (*Concluded*)

Run	Cd	Phase	$E_{700°}$	$dE:dT$	$\pm\delta$	T	$-\Delta\bar{F}_{700°}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
13	0.227	α	211.2	+0.031	1		9742	8740	+ 1.43
10	.203	α	225.3	+ .028	3	>685	10392	9490	+ 1.29
12	(.158	α	229.4	+ .040	1	>676	10581	9290	+ 1.85)
13	.266	α'	194.8	+ .112	4	<696	8985	5370	+ 5.17
12	.253	α'	207.6	+ .468	3	<687	9576	−5540	+21.59
10	.203	α'	220	− .29	13	<685	10150	19520	−13.38
12	(.158	α'	222.2	− .258	3	<676	10249	18580	−11.90)

TABLE III

POTENTIAL OF THE CELL $Cd_{solid}/(K, Na, Cd)OCO.CH_3/(Cd, Au)_{solid}$

Run	Cd	Phase	$E_{500°}$	$dE:dT$	$\pm\delta$	T	$-\Delta\bar{F}_{500°}$	$-\Delta\bar{H}$	$+\Delta\bar{S}$
20	0.987	η	0.3	0.000	0		14	14	0.00
20	.977		.5	.000	0		23	23	.00
20	.893	$\epsilon+\eta$	.5	+ .006	0				
20	.846		.5	+ .006	0		23	−120	+ .28
19	.669	$\gamma'+\epsilon'$	47.9	+ .007	1	<537			
19	.668		47.9	+ .007	1	<547			
			47.9	+ .007		<542	2209	2050	+ .32
19	.669	$\gamma'+\epsilon$	47.5	+ .018	1	>537			
19	.668		47.1	+ .024	1	>547			
			47.3	+ .021		>542	2182	1700	+ .97
19	.577	$\beta'+\gamma'$	63.5	− .066	1	<538			
19	.563		63.4	− .068	1	<542			
			64.4	− .067		<540	2924	4470	−3.09
19	.577	$\beta+\gamma'$	64.4	− .090	1	>538			
19	.563		64.4	− .092	1	>542			
			64.4	− .091		>540	2971	5070	−4.20

For the sake of uniformity this has been done also when the existence range of a certain modification does not include this temperature. The fifth column gives the temperature coefficient, the sixth the mean deviation $\pm\delta$, in 0.1 mv., of the readings from the linear function given by the table and the seventh transition temperatures. The three last columns give the partial molal free energy, heat content and entropy of cadmium in the alloy minus the same quantities of pure cadmium (respectively, liquid and solid). $-\Delta\bar{F}$ and $\Delta\bar{S}$ are found from E and $dE:dT$ by multiplication with 46,126 cal./int. volt.

In order to compare the measurements made with liquid with those carried out with a solid standard electrode, we must know the heat of fusion of cadmium. The values published vary considerably, but the most recent[7]

[7] Umino, *Science Reps. Tokyo Imp. Univ.*, **15**, 597 (1926).

is 12.90 cal./g. or 1450 cal./atom. The molar entropy of fusion is then 2.44 E. U., and thus the temperature coefficient of a cell would be 2.44: 46126 volt/degree = 0.053 mv./degree greater in the case of a solid cadmium electrode than a liquid one. The heat capacities of solid and liquid cadmium are given rather different values by different authors; if their difference were taken into consideration the value given above would be some microvolts/degree smaller. This has, however, been neglected, as the influence does not exceed the uncertainty of the heat of melting.

The potential of $\beta + \gamma'$ against solid cadmium can be written $55.9 - 0.091(T-594)$ mv. and the potential of $\beta + \gamma$ against liquid metal $55.0 - 0.096(T-594)$ mv. If the latter were measured against solid cadmium, it would thus show the potential $55.0 - 0.043(T-594)$ mv., 594°K. being the melting point of cadmium. This shows that there is a transition point in this alloy and (assuming there is only one) it lies at 613°K.

For $\gamma' + \epsilon$ and $\gamma + \epsilon$ the potentials of the table can be written $49.3 + 0.021(T - 594)$ and $49.7 - 0.065(T - 594)$, and the potential of the latter against solid cadmium will then be $49.7 - 0.012(T-594)$. Here the transition is found to be at 606°K.

This transition of the γ-phase has not been previously observed.

The transition of the $\beta + \gamma'$-phase at 540°K. and $\gamma' + \epsilon$ at 542°K., however, cannot be another transition of the γ'-phase, but must be due to transitions in both β- and ϵ-phases, which happen to be at nearly the same temperature. For in $\gamma' + \epsilon$ the partial molal entropy of cadmium is greater above the transition and in $\beta + \gamma'$ smaller, contrary to the case at 606–613°K. If the transition were in the γ'-phase, this would mean that the total entropy of this phase is greater below the transition than above, which is easily seen by integration (see Lewis and Randall, "Thermodynamics," p. 38, about the connection between total and partial quantities). But this cannot be true, and we must draw the conclusion that there is one transition[8] in the β and another in the ϵ-phase. Then the latter should also be seen in the $\epsilon + \eta$ range, but it can be shown that the change in partial molal entropy in this range is so small that it cannot be detected. By integrating the difference in partial molal entropy above and below the transition point = 0.65 E. U. over the $\gamma' + \epsilon$-range, *i. e.*, from 37 to 27% gold, we find the transition entropy at the latter composition $0.65 \times 10/37 = 0.18$ E. U. This is probably not far from the transition entropy at the other side of the ϵ-range, *i. e.*, 24% gold. The $\epsilon + \eta$-range extends to 3% gold, and hence the difference in partial molal entropy below and above the transition of these alloys is $0.18 \times 3/21 = 0.025$ E. U., corresponding to a difference in temperature coefficient of only 0.5 microvolt/degree. The present measurements are not accurate enough to show this effect.

[8] This has been verified by an x-ray investigation. See Ölander, *Zeitschrift für Kristallographie*, (A) **83**, 145 (1932).

If the ϵ'-ϵ transition entropy 0.18 E. U. be multiplied with the transition temperature 542°K., we get the transition heat, 100 cal.

The thermal effects for the other transitions observed are

For $\beta' - \beta$ at 47% gold	$\Delta S = 1.11 \times 8/39.5$	$= 0.23$ E. U. and	$\Delta H = 120$ cal.
For $\gamma' - \gamma$ at 38%	$2.21 \times 7/45$	$= 0.34$ E. U. and	210 cal.
at 36%	$1.52 \times 7/29$	$= 0.37$ E. U. and	220 cal.

Thus the two integrations give the same result 220 cal.

For $\gamma - \delta'$ at 37%	$4.25 \times 5/42$	$= 0.51$ E. U. and	330 cal.
at 36.5%	$2.26 \times 6.5/30$	$= 0.49$ E. U. and	320 cal.

also a good agreement, 330 cal.

For $\delta' - \delta$ at 33.5%	$2.40 \times 3.5/30$	$= 0.28$ E. U. and	200 cal.

All these data refer to one gram atom of alloy.

The $\epsilon' + \eta$-alloys have such a large temperature coefficient that the potential would be zero at 420°K. = 150°. This indicates that between this temperature and 246°, where the present measurements are ending, there should be another transition yielding a smaller temperature coefficient at lower temperatures. Since the partial molal entropy is smaller at lower temperatures, the transition must lie on the cadmium side of the two-phase range, *i. e.*, in the cadmium phase. No transition of cadmium seems, however, to be reported in this temperature range.

During the thermopotential correction runs it was found that this quantity yields a good means for determining the transition points.

It is possible that there is another transition in the ϵ-phase at 485°. The sharp curves in the boundaries by Durrant suggest this and on his published cooling curves there seems to be a very small arrest at this temperature.

The activity coefficient of cadmium in the 0.987 and 0.977 alloys is 0.999 and 1.000, in both cases equal to unity within the experimental errors.

Figure 2 gives the potentials of the alloy electrodes against liquid cadmium at 700°K. The intersections of the curved one-phase lines and the straight two-phase lines give the existence limits of the various phases at this temperature. The slope of the β-curve at higher cadmium contents is rather small and the composition of the intersection point is not so certain. In accordance with Durrant it has been taken as 57.8% cadmium, although a smaller value would not be impossible. However, it is only with the limit 58.0% at 654° that the entropy of the transition γ-δ' would obtain the same value when the difference of partial molal entropy is integrated over the $\beta + \gamma,\delta'$ range as when integrated over $\gamma,\delta' + \epsilon$.

At this temperature (700°K.) the α-phase exists up to 34.4% cadmium, β between 43.3 and 57.8%, δ' between 62.3 and 64.0% and ϵ from 69.9 to about 76%. Owing to the possibility that the composition might not be exactly the same at the surface as in the interior of the electrode, the deci-

mals are, of course, uncertain. Still, the agreement with Durrant's work (thermal analysis) is good.

Similar curves may be plotted at other temperatures, and it is in this way that the boundaries in the phase diagram, Fig. 1, have been obtained.

The eutectic point $\alpha + \beta$, which Saldau[3] gives at 43% and 612° seems to lie at a slightly smaller cadmium content, in order to come to the left of the boundary of the β-phase.

Figure 3 gives the temperature coefficient. The ordinates to the left are valid if the standard electrode is liquid metal, whereas those to the right are to be used for solid cadmium, the difference between the two scales being 0.053 millivolt/degree. On the different branches of the curve is shown to which phase they belong.

A striking feature of this diagram is the pronounced leaps of the values for α', β and ϵ when the composition passes over 25, 50 and 75%. This phenomenon deserves to be dealt with at some length.

If two kinds of atoms are mixed and form a perfect solution, the entropy of formation of the mixture is $\Delta S = -R(x \log x + (1 - x)\log(1 - x))$, when the quantities mixed are x and $1 - x$ gram atoms. If this value is plotted, the tangent at any point of the curve cuts the axes $x = 0$ and $x = 1$ at the values $\Delta\bar{S}_2 = -R \log(1 - x)$ and $\Delta\bar{S}_1 = -R \log x$ (see Lewis and Randall, *loc. cit.*). This is, however, only the case if the two kinds of atoms are randomly distributed over all points in the crystal lattice.

Let us assume that there were an absolutely ordered distribution at 50%, but at no other composition. That means half of the places are reserved for one kind of atoms, and the others for the other kind. Between 0 and 50% the mixing will then only refer to half the places, and the entropy will be $-R(x \log 2x + (1/2 - x)\log(1-2x))$. The same holds good between 50 and 100%, except that the formula will be $-R((1 - x)\log(1 - x) + (x - 1/2)\log(2x - 1))$. In a plot the entropy forms two small arcs similar to the big arc in the first case. The intercepts of the tangent in this case will also give the values of the partial molal entropies, but these quantities have now a discontinuity at 50%, where they change their values from $+\infty$ to $-\infty$. The value of $\Delta\bar{S}_1$ is from 0–50% $-R(\log 2x - 1/2 \log(1 - 2x))$ and from 50–100% $-1/2R \log(2x - 1)$.

But this cannot occur above the absolute zero; the partial molal entropies will remain finite. For when it is possible to substitute one atom in the lattice for one of the other kind, when the composition is not 50%, one must expect that when the mixture is exactly that, there must still be a small number of atoms substituting one another, or be misplaced—of course the same number of each kind. These misplaced atoms act as impurities and increase the entropy, so there is no sharp cusp at 50% in the plotted curve of entropy, but the cusp is rounded off, as in Fig. 4. Then the partial molal entropies will not pass to infinity at 50%, but the two

branches will bend together and join, and the curve looks like the branch at 50% in Fig. 3.

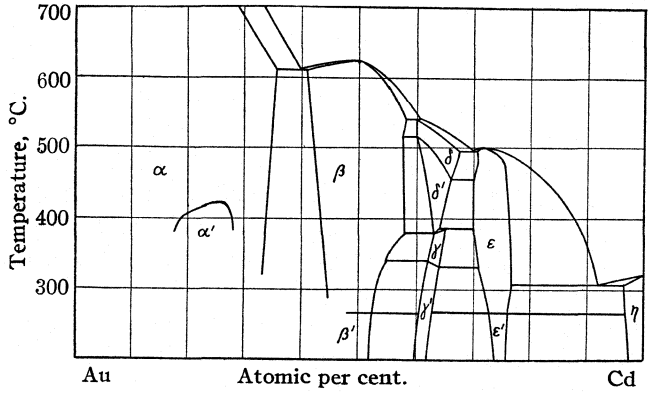

Fig. 1.—Phase diagram of the gold-cadmium system.

In those cases we meet with in practice the lattice will exist only in a limited composition range around 50%, as in the system cadmium–gold. But this does not alter the conditions fundamentally; we must expect that around 50% the mixing term of entropy behaves in the way now described.

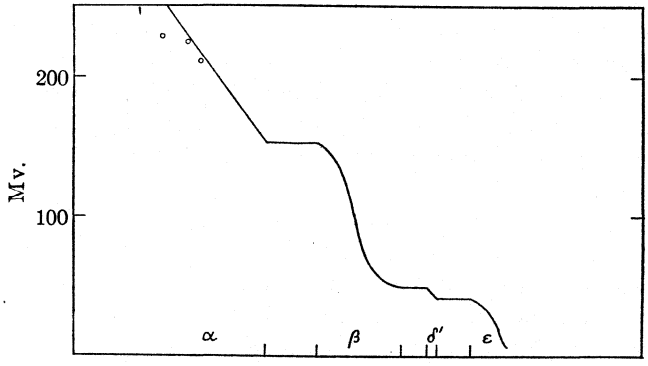

Fig. 2.—Potential of the cell Cd/KCl, LiCl, $CdCl_2$/(Cd, Au) at 700°K.

To this term is added another, because it is not a perfect solution, being the excess of the formation entropy at the temperature of the experiment over the formation entropy of the same alloy at absolute zero, or $\int_0^T \frac{\Delta c_p}{T} dT$. If this value in the first approximation is a linear function of the composition in some limited range, the corresponding term in the partial molal entropy will in this range be a constant.

If the mixing term of the partial molal entropy in the neighborhood of 50% be plotted after the formulas given and the two branches moved to

join the curve in Fig. 3 experimentally found around 50% in the best way possible, they will fall as shown by the dotted curves. Below 48 and above 52% cadmium each branch deviates from the experimental curve only by 0.004 mv./deg. or 0.18 E. U., a quantity of the same magnitude as the experimental errors. The null-point of the mixing term curve will fall at −0.057 mv./deg. if the standard state of cadmium is liquid, and on −0.004 mv./deg. if it is solid, or in entropy units −2.63 and −0.18, which thus is the approximately constant second term in the partial molal entropy of alloy formation.

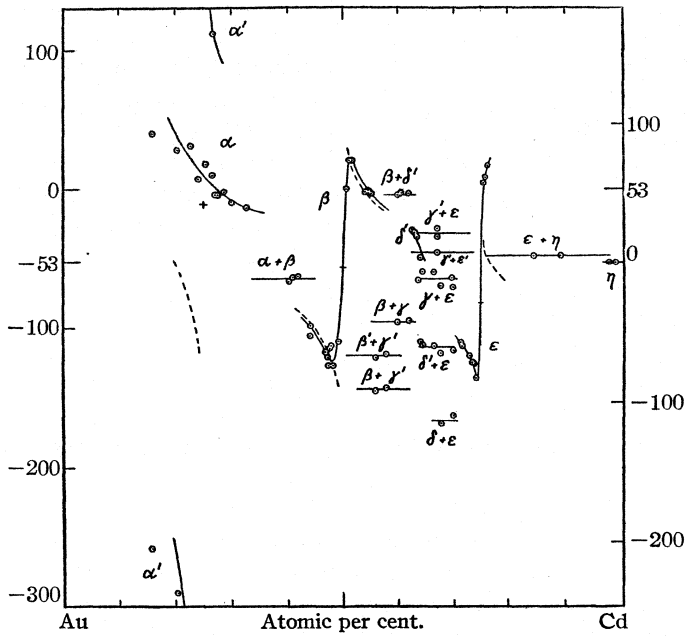

Fig. 3.—Temperature coefficient of the cell Cd/electrolyte/(Cd, Au) in microvolts/degree. Ordinates to the left for liquid cadmium, to the right for solid cadmium. *Cf.* the phase diagram.

From the fact that the deviation of the experimental curve from the theoretical does not begin until 48 and 52% we shall draw the conclusion that the misplaced atoms must be few as compared with the excess of either kind at the compositions quoted, *i. e.*, much less than 4%.

The mixing term of the total entropy may be calculated for $x = 0.48$ from the formula given, *viz.* $-R(x \log 2x + (1/2 - x)\log(1 - 2x))$; it is 0.167 E. U. The value for 0.52 is of course the same. From the experimental values of the mixing term of the partial molal entropy (*i. e.*, the observed quantities +2.63 E. U.) between 48 and 52% we can find the total quantity by a process of integration, starting from 0.167 E. U. at 48

and 52%. Figure 4 shows this mixing term of the total entropy, compared with the hypothetical curve that would exist if the atoms were in perfect order at 50%. The excess entropy which the experimental curve shows at 50%, and which is due to the misplaced atoms, is about 0.06 E. U.

From this value we are able to estimate the deviation from perfect order in the crystal lattice. An x-ray investigation, which is published elsewhere,[7] shows that at the temperatures in question the β-phase forms a cesium chloride lattice, *i. e.*, the gold and the cadmium atoms form two simple cubic lattices body-centering each other. The elementary cube, containing one gold and one cadmium atom, has an edge of about 3.34 Å.

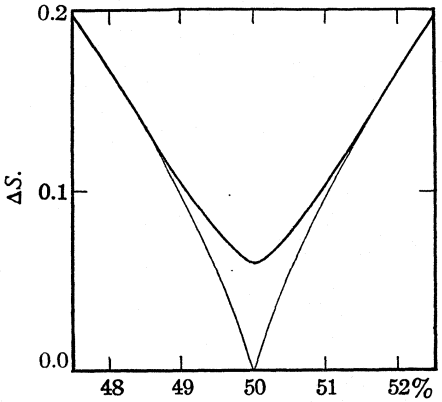

Fig. 4.—The mixing term of entropy around 50 atomic per cent.

A few of these elementary cubes AuCd contain misplaced atoms, so their formula will be AuAu or CdCd. At 50% there will be the same number of these two kinds. A much smaller number of cells will contain two misplaced atoms, CdAu. We may neglect these in the first approximation. If the fraction of cells AuAu or CdCd be x, the excess entropy of one mole AuCd will be

$$-R(x \log x + x \log x + (1 - 2x)\log(1 - 2x)) = 2 \times 0.06$$

(because 0.06 E. U. is the excess entropy for $^1/_2$AuCd). This equation has the solution $x = 0.0048$. This means that 0.5% of the atoms are misplaced in the crystal lattice at the temperatures in question, 400–450°.

At 25 and 75% cadmium, however, this simple theory does not work quantitatively. Around the composition $AuCd_3$ the partial molal entropy is expected to be $-R(\log {}^4/_3x - {}^1/_4 \log(1-{}^4/_3x))$ to the left and $-{}^1/_4R \log (4x - 3)$ to the right. The slope of the first branch is the same as that of the experimental curve between 71 and 74%, but if these are made to coincide, yielding the constant term −0.029 mv./deg. or −1.34 E. U. (solid cadmium) the right branch will fall as the dotted line, far below the experimental points.

Around Au_3Cd the two expressions will be $-R(\log 4x - {}^3/_4 \log(1 - 4x))$ and $-{}^3/_4R \log({}^4/_3x - {}^1/_3)$. The experimental material is somewhat scarce, but if the latter branch is laid through 5.17 E. U. at Cd = 0.266, giving the constant term 0.042 mv./deg. or 1.94 E. U. (solid cadmium), the left branch will fall far above the corresponding points measured. In both these cases the leap experimentally found is much bigger than that ex-

pected. Below 75% cadmium the mixing term seems to describe the conditions, but above this composition the total entropy rises faster, yielding a bigger partial entropy of cadmium. This could be caused if the change in composition were brought about not only by substitution of gold atoms by cadmium, but also by leaving vacant places in the lattice. But this can probably not explain the whole discrepancy. Another possibility is that the quantity $\int_0^T \frac{\Delta c_p}{T} dT$ previously referred to is not a linear function of the composition across 75%, but that $\frac{\partial}{\partial[\mathrm{Cd}]} \int_0^T \frac{\Delta c_p}{T} dT$ changes rapidly in the neighborhood of this composition. At present nothing can be said with certainty about this matter.

Attention may be drawn to the fact that in the α-phase, that has no maximum of its conductivity at 25%, and hence is expected to have a random atom distribution, the temperature coefficient is a monotonous function of the composition, as is to be expected.

Summary

The potential of the cell $Cd_{liquid}/K(Rb)Cl, LiCl, CdCl_2/(Cd, Au)_{solid}$ and its temperature coefficient have been measured for fifty-four compositions of the alloy electrode for temperatures above 340°.

The potential of the cell $Cd_{solid}/(K, Na, Cd).OCO.CH_3/(Cd, Au)_{solid}$ and its temperature coefficient have been measured for eight compositions of the alloy electrode between 250 and 300°.

The phase diagram of the cadmium-gold system has been completed, three new transitions having been found.

The heat effect at some transitions has been calculated.

In those cases where other indications existed that the atoms were distributed in an orderly manner in the crystal, the temperature coefficient showed a dependence on the composition that could be anticipated from statistical considerations of the entropy. At the composition AuCd it has been possible to calculate the degree of randomness in the crystal lattice. Around 450° there are 0.5% of misplaced atoms.

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THE VELOCITY AND MECHANISM OF RACEMIZATION. I. ROCHELLE SALT

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The so-called catalytic racemization in presence of caustic alkali or strong acid is a process which has received very little attention from the physico-chemical point of view. Walker[1] studied the velocity of racemization of amygdalin and found it to comply with the formula of a unimolecular reaction. Extensive measurements of the velocity of racemization of tartaric acid and mandelic acid are due to Winther.[2] He finds the reaction to be unimolecular in both cases, but his method of experiment leaves something to be desired. Realizing that the decrease in the rotation of tartaric acid or its salts might be due to the formation of either racemic or meso form or both, he thought it necessary to acidify the alkaline solution after heating and carry out a laborious analysis for the two forms. From our experience of this method we have concluded it to be hopelessly inaccurate. Indeed, Winther himself in certain cases incorporates truly enormous correction factors, which render the method undesirable. By this method of experiment too he overlooked what we consider an important factor, *viz.*, the change in the sign of rotation in strong alkali.[3] It is somewhat remarkable that the ordinary student preparation of racemic acid from *d*-tartaric acid is really a racemization from the levo side.

With regard to the mechanism of racemization, even less has been done. McKenzie and Thompson[4] attribute racemization to direct interchange of the groups attached to the asymmetric carbon atom, but they find racemization by alkali inexplicable. Rothe[5] attributes racemization to a mobile hydrogen atom, tautomerism and racemization being analogous processes. This being the state of affairs, we thought it advisable to repeat and extend the work of Winther.

When we consider the possible mechanisms in virtue of which tartaric acid becomes inactive, it seems surprising that the formula for a unimolecular reaction should ever have been complied with. As soon as *l*-tartrate forms, a back reaction of equal velocity constant sets in. The differential equation for the velocity is therefore

$$\begin{aligned} dx/dt &= k(a - x) - kx \\ &= k(a - 2x) \\ \therefore k &= 2.3/2t \log_{10} a/(a - 2x) \end{aligned}$$

[1] Walker, *J. Chem. Soc.*, **83**, 472 (1903).

[2] Winther, *Z. physik. Chem.*, **56**, 465–511 (1906).

[3] *Cf. Nature*, **129**, 281 (1932).

[4] McKenzie and Thompson, *J. Chem. Soc.*, **87**, 1004 (1905).

[5] Rothe, *Ber.*, **47**, 843 (1914).

If α_0 is original rotation, α_t is rotation after time t, then

$$\alpha_0 \propto a$$
$$\alpha_t \propto (a - 2x)$$

Hence

$$k = 2.3/2t \log_{10} \frac{\alpha_0}{\alpha_t} \qquad \text{(i)}$$

When the inactive (racemic) form begins to precipitate (as it obviously does after a certain time), the l-form will have an approximately constant concentration $= y$. Hence, after this stage

$$dx/dt = k(a - x - y)$$

If t' is time to precipitation, $x = y$. Hence

$$k = 2.30/(t - t') \log_{10} (a - 2y)/(a - (x + y))$$
$$\alpha_{t'} \propto (a - 2y)$$
$$(\alpha_0 - \alpha_t) \propto (x + 2y) \propto (x + y) \qquad \text{(if } y \text{ is small and constant)}$$
$$\therefore k = 2.30/(t - t') \log_{10} \frac{\alpha_{t'}}{\alpha_t} \qquad \text{(ii)}$$

Therefore, if the process of inactivation is simply and entirely $d \longrightarrow l$, the formula for a unimolecular reaction should be complied with, except that the constant should have half the numerical value of the ordinary formula, in the initial stage of the reaction, after which there should be a sudden decrease in the value of the constant to half its initial value, provided the same formula is used, at the point where the solution becomes saturated with the sparingly soluble racemate. Since, however, supersaturation with racemate is likely to occur, this will reduce the suddenness of the transition.

According, however, to Winther, racemate formation takes place via the meso form, a view which stereochemical considerations would seem to favor.

$$d \longrightarrow \text{meso} \begin{matrix} \nearrow d \\ \searrow l \end{matrix}$$

Hence

$$dx/dt = k_1(a - x) - {}^1/_2k_2x;$$
$$\text{let } k_3 = k_1 + {}^1/_2k_2, \text{ then}$$
$$k_3 = 1/t \log_e k_1a/(k_1(a - x) - {}^1/_2k_2x) \qquad \text{(iii)}$$

If $k_2 = 0$, this becomes the formula for a unimolecular reaction. If k_2 is real, the constant calculated in accordance with the simple formula for a unimolecular reaction will increase with time. If therefore we calculate throughout with the simple formula, we may expect the following behavior. (1) The formula yields a constant value of k, decreasing, however, more or less sharply to half the initial value at a certain stage. This corresponds to $d \longrightarrow l$ as the sole process. (2) The value of k increases steadily. This corresponds to $d \longrightarrow$ meso $\longrightarrow l$ as the sole process. (3) Processes 1 and 2 may be consecutive or simultaneous.

Experimental

Preliminary experiments with different tartrates and tartaric acid heated for varying periods of time in the neighborhood of 100° convinced us that under these circumstances the acid racemization is inappreciable. We therefore decided to confine ourselves to alkaline racemization and to choose as our active tartrate sodium potassium tartrate, since this salt is cheap and readily obtained pure. The salt used was Mallinckrodt U. S. P., and the sodium hydroxide Mallinckrodt U. S. P. sticks. Although the solutions of sodium hydroxide were not made up from metallic sodium, they were almost entirely free from carbonate, a fact which is eventually to be attributed to the extreme dryness of the climate in central Canada.

The apparatus for the velocity measurements was constructed of Pyrex glass and consisted of two concentric chambers. The inner chamber was furnished at the top with a ground-in Pyrex condenser and at the bottom with a capillary neck and stopcock. The outer jacket had side inlets like a condenser, but flush with the bottom and top to prevent dead space. The side arms were connected by pressure tubing to a circulating pump and boiler. The pump was driven on the axis of an electromotor, which was run well below its maximum speed. The water in the boiler was kept vigorously boiling and the whole apparatus was heavily lagged with cotton wool and asbestos. In this way it was possible to keep the temperature constant at 96.2° within 0.1°. The temperature was read through a telescope focused on a small Anschütz thermometer suspended in the inner chamber, a small window being left in the lagging for this purpose. To conduct an experiment 0.1 mole of Rochelle salt (0.1 $NaKC_4H_4O_6 \cdot 4H_2O$ = 28.22 g.) was dissolved in the appropriate sodium hydroxide solution and made up to 100 cc. In the meantime the motor was started and, when the temperature had risen to its constant value of 96.2°, the inner chamber was filled with solution up to a mark on the constricted neck. The time of commencement was taken as the time at which the thermometer rose to 96.2° after introduction of the solution. After the lapse of one hour, in the first case, the solution was run into a buret tube packed at the bottom with glass wool, and immediately cooled under the tap, the time of completion of the run being taken as the mean of the time of cooling. After determination of the rotation of the solution, it was returned to the apparatus, any slight loss due to evaporation being made up by addition of water; with a ground-in condenser this loss was extremely small. All apparatus was washed out with solution so that there was no loss in volume due to adhering to the sides of the apparatus. The rotations were read in a Hilger 3-field polarimeter, using a 2-dcm. tube. An accuracy in reading of 0.01° was always obtained, although the stronger solutions required filtration through asbestos to obtain the necessary brightness.

The hydroxyl-ion concentrations of all solutions were determined after dissolving the (hydrated) Rochelle salt. Considerable difficulty was experienced in finding a suitable electrode for the strongly alkaline solutions containing Rochelle salt; the hydrogen electrode gives wavering and uncertain values in strongly alkaline solutions of Rochelle salt. Eventually, the manganese hydroxide electrode was found to give good comparative values between caustic soda solutions and solutions of Rochelle salt in caustic soda. A method based on the saponification of ethyl acetate also gave fair results in the less alkaline solutions, but failed at higher concentrations, owing to the increasing insolubility of the ethyl acetate. All methods, however, without exception, indicated that the hydroxyl-ion concentration in the solutions containing Rochelle salt was distinctly lower than that in the corresponding sodium hydroxide solution alone. We consider this good qualitative evidence of the formation of a complex between the Rochelle salt

and hydroxyl ions. Table I contains a selection of the results to indicate the magnitude of the differences observed.

TABLE I

HYDROXYL-ION CONCENTRATIONS

Strength of NaOH, *N*	(OH) of NaOH, *N*	(OH) of solution, *N*
1.07	0.775	0.110
1.907	1.350	0.368
2.93	1.965	1.3
3.66	2.54	1.5
5.16	3.075	1.8
6.97	3.059	2.02
9.36	2.807	1.88

Velocity Constants.—The method of determining these was to plot the observed rotations against time, draw a smooth curve through the points and calculate the constants for each hour. For the purpose of comparison with Winther's figures, we have used his formula $k = 100/t \log_{10} (\alpha_0/\alpha_t)$.

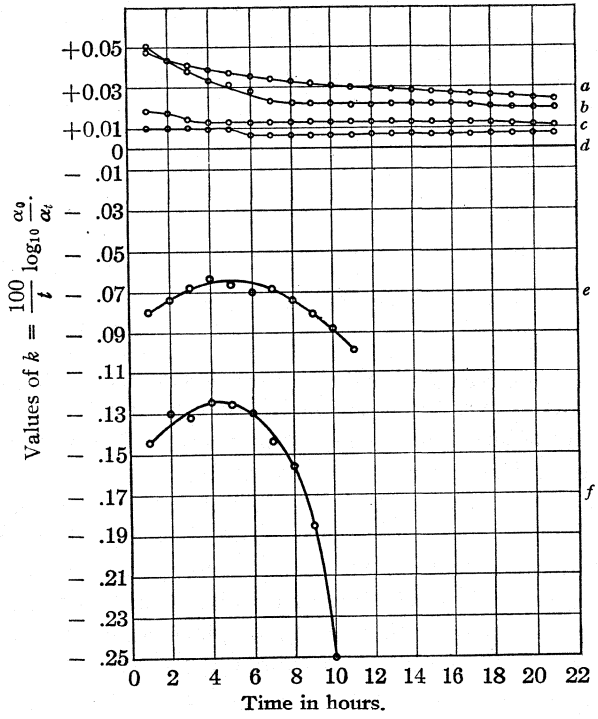

Fig. 1.—(*a*), 6.97 *N* NaOH; (*b*), 5.16 *N* NaOH; (*c*), 3.66 *N* NaOH; (*d*), 1.907 *N* NaOH; (*e*), 9.36 *N* NaOH; (*f*), 13.8 *N* NaOH.

The results are embodied in Fig. 1, where the values of k are plotted against time; the constants for the levorotatory solutions (see below) are given

negative values and this accounts for the inversion of the curves pertaining to 9.36 *N* and 13.8 *N* NaOH.

Specific Rotations of Rochelle Salt in Sodium Hydroxide.—As we used sodium hydroxide solutions of increasing strength we observed that the initial rotation dropped more and more, that is, that the specific rotation became less and less. We thought it advisable therefore to carry out a complete series of measurements of the rotation of (cold) solutions of Rochelle salt in sodium hydroxide; the solutions were always molar with respect to Rochelle salt. Unfortunately, our polarimeter was not fitted with a monochromator, so we were obliged to use a series of light filters. The filters were Wallace color filters and had the following transmissions.

	Filter number				
	2	3	4	5	6
Transmissions, Å.	7608–6100	7608–5800	7608–5400	7608–5300	7608–5000

For analytical purposes, filter 3 was used throughout. The results are given in Table II.

TABLE II

SPECIFIC ROTATIONS OF MOLAR ROCHELLE SALT (ANHYDROUS) IN SODIUM HYDROXIDE OF VARYING CONCENTRATION

Strength of NaOH, *N*	Specific rotation at 22.2°			Filter nos.	
	2	3	4	5	6
0.0 (water)	25.2	26.8	28.1	28.5	28.5
1.10	23.3	25.2	26.3	26.8	27.1
1.907	21.7	22.9	24.0	24.4	24.5
2.72	19.7	20.8	21.7	22.1	22.1
5.16	13.1	13.7	14.4	14.8	14.9
6.97	6.68	6.99	7.2	7.4	7.5
9.36	−0.43	−0.91	−1.12	−1.22	−1.26
14.18	−10.9	−12.0	−12.7	−12.7	−12.8

The 14.18 *N* sodium hydroxide solution of Rochelle salt preserved its rotation unchanged over the week-end. There is therefore no question of progressive racemization at room temperature. The two levorotatory solutions were acidified, when potassium hydrogen tartrate precipitated. This was redissolved in water and the rotation taken; the rotation of the acidified mother liquor was also taken. Both were dextrorotatory. From the observed dextro rotations the corresponding amount of *d*-Rochelle salt was calculated. This was always much less than the original, in other words, considerable racemization had taken place simply as a consequence of dissolving the Rochelle salt in cold sodium hydroxide. In the case of the 9.36 *N* solution, the cold racemization amounted to 16% and of the 14.18 *N* to 83%.

Discussion

The form of the *k*-curves for solutions of sodium hydroxide concentration ranging from 1.097 *N* to 6.97 *N*, considered in the light of the theoretical considerations previously laid down, leads to the conclusion that in these

strengths of alkali, the process is direct formation of racemate, accompanied by slight meso formation. When the curves are drawn on a larger scale, a slight upward trend of the constants is observable, after the fall to half value, corresponding to the process, dextro ⟶ meso ⟶ levo. It is possible that in the above concentrations of alkali, the process is that given.

It has already been remarked that in alkali concentrations greater than 9 *N*, the solution is levorotatory, and the *k*-curves for these cases are distinct from the others. It seems reasonable to attribute this phenomenon to the formation of a levorotatory complex between the Rochelle salt and the sodium hydroxide, or rather hydroxyl ions. The measurements of hydroxyl concentration bear this out. The experiments on acidification of the levorotatory solutions show that the instantaneous formation of the complex has already accomplished a large part of the racemization. As an instance of the puzzling nature of the phenomena here, it may be observed that whereas the 9.36 *N* solution had become completely inert in ten hours, the 13.8 *N* solution was still distinctly levorotatory after twelve hours of heating.

If we assume that an equilibrium is established in cold solution between levorotatory complex and dextrorotatory Rochelle salt, and that racemization takes place via the complex, we can still introduce an appearance of reason into these intricate results, as follows. The process whose velocity is measured on heating is a slow change of levorotatory complex into inactive complex, the decrease in concentration of levo complex being made up by transformation of residual dextro into levo complex. Alternatively, the change of levo complex into inactive tartrate can be brought about instantaneously by acidification. All this may seem far fetched, but the following experimental facts have to be met.

1. There is definite experimental evidence of the formation of a complex.
2. "Acid racemization" (instantaneous and in the cold) is more nearly complete in 13.8 *N* sodium hydroxide.
3. "Heat racemization" is more rapid in 9.36 *N* sodium hydroxide than in 13.8 *N*.

Evidence of the sufficiency of our experimental technique is afforded by a study of the racemization of mandelic acid, which we have just completed. Here, both acid and alkaline racemization yield true constants by the unimolecular formula, and there is no evidence of complex formation, or change of sign of rotation. The drift of the constants is peculiar to Rochelle salt, *i. e.*, presumably, to tartrates.

The assumption of complexes in optically active solutions is by no means new, but, so far as the authors are aware, no definite experimental evidence for their existence has yet been brought forward. As our hypothesis, though not our facts, depends on the demonstration of the existence of such a complex, we decided to carry out a phase rule study of the system sodium

hydroxide–Rochelle salt–water. This was done, using Schreinemaker's method. The method cannot, of course, yield definite information where one of the components undergoes decomposition, that is, when it ceases to be a component at all, but the form of the curves should indicate whether or not complex formation takes place. The solubility determinations were carried out in a thermostat at 25°, using a technique described elsewhere.[6]

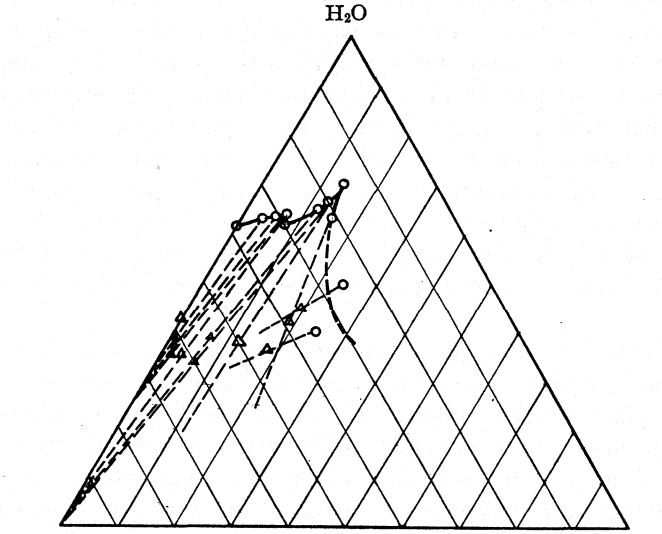

Fig. 2.

We were unable to carry the observation beyond 8 *N* sodium hydroxide, because at this concentration the solid phase becomes a glutinous mass impossible to filter. The solubility curve shows three distinct portions, the first of which corresponds to Rochelle salt hydrated, the second to anhy-

TABLE III

SOLUTIONS IN EQUILIBRIUM SOLID PHASE

	Liquid phase			Solid phase		
Expt.	Rochelle salt, %	NaOH, %	H_2O, %	Rochelle salt, %	NaOH, %	H_2O, %
1	39.0	..	61.0	58	..	42
2	33.3	3.7	63.0	61	1.7	37.3
3	31.0	5.8	63.2	61.8	1.7	36.5
4	29.0	7.3	63.75	62.5	2.6	34.9
5	29.5	7.6	62.9	61.7	3.9	34.4
6	20.2	13.5	66.3	60.0	6.8	33.2
7	22.6	12.2	65.2	54.7	7.2	38.1
8	16.1	13.85	70.05	50.0	12.5	37.5
9	21.6	15.3	63.1	39.6	19.0	41.4
10	35.2	24.8	40.0	45.3	18.9	36.8
11	25.7	23.9	50.4	36.9	19.4	43.7

[6] Campbell and Yanick, *Trans. Faraday Soc.*, in press.

drous Rochelle salt, and the third we tentatively suggest corresponds to solid complex. At all events, the tie-lines show no indication of running to the sodium hydroxide corner. For the reason previously given, it cannot be expected that the tie-lines should intersect in a point. The appearance of the solid phase at this stage is remarkable. It swells in bulk so as to occupy almost the total volume and resembles a stiff gel. The numerical results are contained in Table III.

The triangular diagram is interesting and has therefore been reproduced.

It is hoped shortly to communicate similar work which has been done on camphoric acid and substituted tartaric acid. Work is now proceeding on the acid and alkaline racemization of mandelic acid.

Summary

The process of inactivation of Rochelle salt when heated with sodium hydroxide has been investigated mathematically. Measurements of the velocity of inactivation have been made in a special apparatus. The drift of the constants is interpreted in the light of the equations deduced. The interpretation is rendered difficult by the fact that a levorotatory complex is formed, but the matter is discussed at length. Experimental evidence for the existence of the complex, depending on (1) sign of rotation, (2) hydroxyl-ion concentration and (3) a phase rule study of the system Rochelle salt–H_2O–NaOH, is also adduced.

WINNIPEG, CANADA

[CONTRIBUTION FROM THE RYERSON PHYSICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE ATOMIC ARRANGEMENT IN GLASS

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1. Introduction

It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses. Glasses are described as supercooled liquids or as solids. The former term is justifiable from the point of view of physical chemistry, the latter from the theory of elasticity. It seems rather futile, however, to try to decide which of the two descriptions is the proper one to use, when we are ignorant about the characteristic properties of the atomic arrangement.

It has been said that the x-ray diffraction patterns obtained from glasses indicate that glasses consist of crystalline material.[1] It is claimed, for example, that the main features of the diffraction pattern of vitreous silica can be accounted for on the following basis: (1) vitreous silica consists of cristobalite crystallites; (2) the average linear dimension of the crystallites

[1] J. T. Randall, H. P. Rooksby and B. S. Cooper, *Z. Krist.*, **75**, 196 (1930).

is of the order of 15 Å.; (3) the lattice constants of the crystallites are 6.6% greater than those of large cristobalite crystals. These assumptions lead, however, to discrepancy between observed and calculated density. The diffraction patterns obtained from heat-treated specimens of vitreous silica cannot be satisfactorily accounted for, and above all the characteristic thermal properties can hardly be said to be in accordance with the assumptions. A generalization of this "crystallite hypothesis" to glasses of the general type would lead to even more serious difficulties. For these reasons it seems necessary to rule out the possibility that glasses are built up of crystalline material.

2. The Atomic Arrangement in Glass

Over large ranges of temperature the mechanical properties of glasses are directly comparable with those of crystals. As a matter of fact there is experimental evidence which indicates that the strength of glass may excel that of the corresponding crystalline form. It seems necessary therefore to assume that the atoms in glass are linked together by forces essentially the same as in crystals and that the atoms are oscillating about definite equilibrium positions. As in crystals, the atoms in glasses must form extended three dimensional networks. From the results of the x-ray diffraction experiments it follows, however, that this network is not periodic and symmetrical as in crystals. Yet it is not entirely random due to the fact that the internuclear distances do not sink below a given minimum value. All interatomic distances are for this reason not equally probable and x-ray diffraction patterns of the type observed will be a direct consequence.

If we make use of crystal structure terminology, we may say that the network in glass is characterized by an infinitely large unit cell containing an infinite number of atoms. Because of the lack of periodicity no two atoms are structurally equivalent, while in a crystal lattice like that of sodium chloride all the sodium atoms are equivalent and all the chlorine atoms (disregarding surface conditions arising in a lattice of finite extension).

The presence or absence of periodicity and symmetry in the network distinguishes a crystal from a glass.

The characteristic properties of glasses seem to be in accordance with our ideas of the atomic arrangement.

The isotropic character of glass is, of course, a natural consequence of the absence of symmetry in the network. The atomic arrangement will be statistically the same in all directions, unless external fields of sufficient intensity are present.

Since all atoms in glass are structurally unequivalent, the energy required to detach an atom from the network will be different for each individual atom. With increasing temperature we would therefore expect

to get an increasing number of detached atoms, so that the breakdown of the network would be a continuous rather than an abrupt phenomenon. Migration of the detached atoms at a given temperature naturally would occur too. In a crystal lattice on the other hand the atoms are structurally equivalent. As soon as the thermal energy reaches a definite value, all the equivalent atoms will be simultaneously detached; the crystal network breaks down abruptly. With the migration of the detached atoms in a glass network it is impossible to say at which temperature a given glass passes from the solid to the liquid state.

It is a well-known fact that the chemical composition of a glass in general cannot be expressed by a simple formula, or rather a glass is not a chemical compound in the ordinary sense of the word. Crystals on the other hand are compounds. This principal difference between crystal and glass again follows from the presence of periodicity in the network of the former and from the absence of periodicity in the latter. Each unit cell in a crystal necessarily must contain an integral number of stoichiometric molecules since all unit cells are alike. It follows that the chemical composition can be expressed by a simple formula. (It is to be remembered that certain modifications have to be introduced as a consequence of the phenomenon of isomorphous replacements.) In glass the unit cell is infinitely large and consequently there will be no restrictions with regard to the relative numbers of chemically different atoms (except, of course, that the valences must be balanced).

The transparency of glasses is explained by the existence of extended networks in just the same manner as the transparency of crystals is accounted for.

From simple considerations of this kind one gets the impression that our picture of the atomic arrangement in glass is a very promising one. So far our discussions have been of a very general type; in the following sections, however, we will go into more detailed considerations.

3. The Vitreous Oxides.—In the following only oxide glasses will be discussed, except for a few references to fluoride glasses. At first we will consider the very simplest type of oxide glasses, namely, those formed by individual oxides, like SiO_2 and B_2O_3.

Of all the possible oxides only a very few are able to form glass. While for example SiO_2 and B_2O_3 very readily may be prepared in the form of glass, all attempts to make a TiO_2 or an Al_2O_3 glass have been in vain. An explanation of the glass-forming ability of the oxides has not yet been given. V. M. Goldschmidt[2] has tried to correlate the ability to form glass with the value of the radius ratio R_A/R_O for oxides A_mO_n. His results are very interesting. He finds that the radius ratio for all the oxides which have

[2] Goldschmidt, "Geochemische Verteilungsgesetze der Elemente VIII," Vid. Akad. Skr. Oslo, No. 8, 137, 1926.

been prepared in the vitreous form is around 0.2–0.4. This range of the radius ratio in general corresponds to a tetrahedral arrangement of oxygen atoms around atom A, and Goldschmidt therefore believes that tetrahedral configurations are necessary for the formation of glass. However, we cannot reason the other way and say that any oxide with a radius ratio of about 0.3 can form a glass. The value of the radius ratio for BeO for example is very nearly the same as for SiO_2. Still BeO has never been prepared in the vitreous form.

The conditions for the formation of a glass apparently are more complicated.

We have stated that the atomic arrangement in glass is characterized by an extended three-dimensional network which lacks symmetry and periodicity. The interatomic forces we concluded had to be essentially the same as in crystals. In the glass network no two atoms could be structurally equivalent. For these reasons it may be concluded that the energy of a glass will tend to run higher than that of the corresponding crystal. The same result is borne out by the fact that glasses show a more or less pronounced tendency to devitrify. Glasses which do not devitrify very rapidly will have an energy only slightly greater than that of the crystal. The ultimate condition for the formation of a glass we may consequently express as follows: the substance can form extended three-dimensional networks lacking periodicity with an energy content comparable with that of the corresponding crystal network.

In the crystalline forms of the oxides it is invariably found that the oxygen atoms form polyhedra of one kind or another around atoms A, just as if we could treat the oxygen atoms as anions and the atoms A as cations. Whether the atoms are truly ionized or not is of little consequence as long as we can use the ionic interpretation as a convenient means of description. Because we have postulated that the interatomic forces in crystal and glass are essentially the same, it follows that also in glass networks we should have polyhedra of oxygen atoms around the atoms A. We can in this manner conveniently describe the whole crystal or glass as a network of such oxygen polyhedra. The three-dimensional linking is effected by the sharing of corners between different polyhedra. The energy of the network will in the first place depend upon the nature of the oxygen polyhedra, in the second place upon the way in which the polyhedra are linked together. From our experience with crystal lattices we have learned that there may be several ways of linking polyhedra of a given type together so as to give approximately the same energy. TiO_2 for example can occur in three different modifications, as rutile, anatase and brookite. In all the three crystals Ti is surrounded by octahedra of oxygen atoms and only the linking together of the octahedra is different. An analogous example is the polymorphous SiO_2.

If the energy of a glass is to be comparable with that of the crystal, we must require that oxygen polyhedra in glass and crystal are essentially the same. In vitreous SiO_2 we must for example expect to find tetrahedra of oxygen atoms around silicon. If silicon were surrounded by three or by five or any other number of oxygen atoms, the potential energy would be much greater.

The linking together of the oxygen polyhedra in crystal lattices is done in such a manner that no two atoms are brought into close contact. From the point of view of ions this, of course, is obvious. If the atoms are ionized we would expect a cation to be surrounded by as many anions as possible and *vice versa*. The upper limit for the number of anions which could surround a given cation would be determined by the requirement that the anions should not be brought into contact with each other. Ions carrying charges of the same sign will tend to be as far apart as possible. We have to apply just the same principles on the network in glass. Our object is to find under which conditions we can form a network of polyhedra satisfying these requirements.

The network in vitreous silica according to our argument is built up of oxygen tetrahedra which surround the silicon atoms. The oxygen tetrahedra share corners with each other in such a manner that an oxygen atom is linked to two silicon atoms. In the crystalline forms of silica the relative orientation of two tetrahedra with a common corner will be the same throughout the entire lattice. That is not the case in vitreous silica, where the relative orientation may vary within rather wide limits. In low quartz for example the angle between the bonds from an oxygen atom to the two neighboring silicon atoms is the same for all oxygen atoms. In vitreous silica on the other hand we must expect that this bond angle varies from oxygen to oxygen atom as we pass through the network.

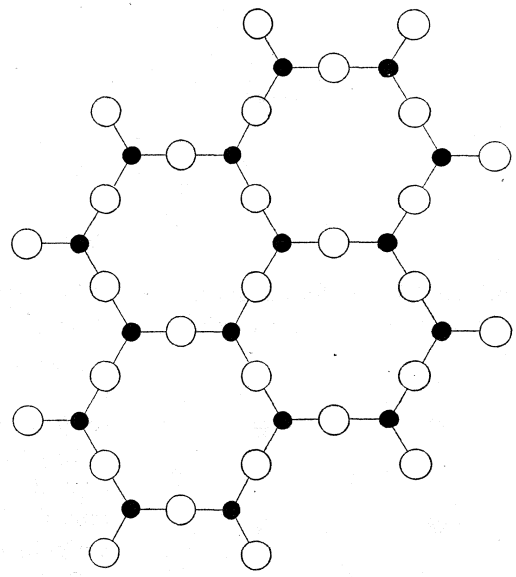

Fig. 1a.

It is somewhat difficult to illustrate the principle in drawings because of the three-dimensional arrangement. I have therefore tried to make use of two-dimensional analogies in Figs. 1a and 1b. Figure 1a shows the lattice of a

two-dimensional crystal of composition A_2O_3, while Fig. 1b represents the glass network of the same compound. It is probably obvious from the draw-

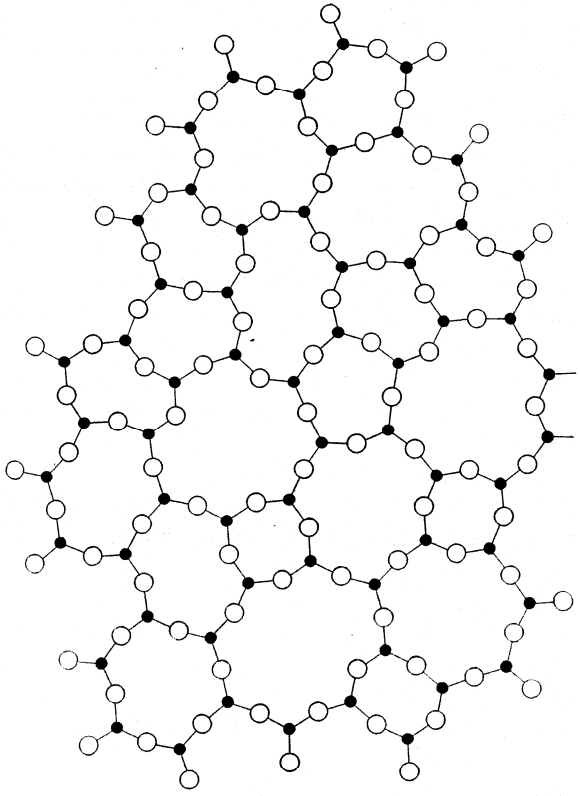

Fig. 1b.

ings that the potential energy cannot be very different in the two cases. In Fig. 2 is shown the two-dimensional lattice of a crystal AO in which three oxygen atoms surround atom A and *vice versa*. In this case it is impossible to form a two-dimensional glass with an energy content comparable to that of the crystal. The requirement of a small potential energy will necessarily lead to a periodic network. Analogous results we will obtain if we extend our considerations to three dimensions. It is as a matter of fact possible from simple considerations to give a series of requirements which must be satisfied if the ox-

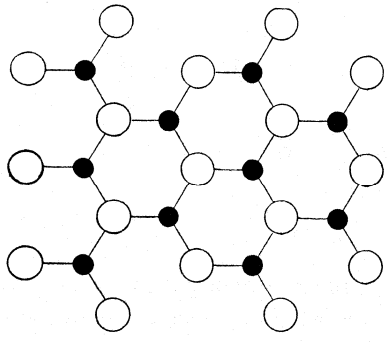

Fig. 2.

ide is to form a glass with energy comparable to that of the crystalline form. These simple rules are: (1) an oxygen atom is linked to not more than two atoms A; (2) the number of oxygen atoms surrounding atoms A must be small; (3) the oxygen polyhedra share corners with each other, not edges or faces.

If we further require the network to be three-dimensional, (4) at least three corners in each oxygen polyhedron must be shared.

Oxides X_2O or XO do not satisfy these requirements under any conditions. Under certain conditions other oxides, however, will fit our rules. We find readily the requirements (1), (3) and (4) are satisfied by oxides: A_2O_3 if the oxygen atoms form triangles around each atom A; AO_2 and A_2O_5 if the oxygen atoms form tetrahedra around each atom A; AO_3, A_2O_7, AO_4 if the oxygen atoms form octahedra around each atom A; AO_4 if the oxygen atoms form cubes around each atom A.

Whether all of these oxides satisfy the requirement expressed in Rule 2 cannot easily be decided. However, as no oxide AO_3, A_2O_7 or AO_4 to my knowledge has been prepared in the vitreous state, we may take that as an indication that only oxygen triangles and tetrahedra agree with Rule 2.

From crystal structure data we have quite extensive information about the oxygen polyhedra which are formed around the different cations.

Of trivalent cations only the following have been found within oxygen triangles in crystal lattices: B^{+3}, As^{+3}, Sb^{+3}. There is no available information about P^{+3}; but I do not think that there can be much doubt that the coördination number is three for this ion also. One important fact is worth mentioning. Whereas boron is lying in the plane of the three surrounding oxygen atoms, arsenic, antimony and probably also phosphorus are displaced out of the plane. The configuration around the latter ions is as a matter of fact a hybrid between a triangular and octahedral configuration. In As_4O_6 and Sb_4O_6 there are six oxygen atoms around As or Sb, three of the oxygen atoms being closer to the cation than the rest. In As_4O_6 the two distances are 2.01 Å. and 2.78 Å.; in Sb_4O_6 the two distances are more nearly equal, namely, 2.22 Å. and 2.61 Å. The approximation to the coördination number three is thus closer for As^{+3} than for Sb^{+3}, and we must expect that for P^{+3} the approximation is still closer than for As^{+3}.

In the series P_2O_3, As_2O_3, Sb_2O_3 the ability to form glass therefore will decrease in the order given. B_2O_3, however, should form glass with greater ease than any other oxide.

No other sesquioxide than the four given can be expected in the vitreous form.

Of the quadrivalent cations only Si^{+4} and Ge^{+4} are surrounded by oxygen tetrahedra in crystal lattices. SiO_2 and GeO_2 consequently may occur in

the vitreous state. The ability to form glass will be less than for B_2O_3 because of the greater coördination number.

The pentavalent cations P^{+5} and As^{+5} are always surrounded by oxygen tetrahedra, probably also V^{+5}. It is possible that also Sb^{+5}, Cb^{+5} and Ta^{+5} may occur with coördination number four with respect to oxygen. The available crystal structure data are, however, too few to allow definite conclusions.

Summarizing our results we conclude that B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, P_2O_3, As_2O_3, Sb_2O_3, V_2O_5, Sb_2O_5, Cb_2O_5, Ta_2O_5 may occur in vitreous forms. From lack of the necessary crystal structure data we may have included in the list some oxides which do not belong there.

References to the literature show that B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, and As_2O_3 have actually been prepared in the vitreous state. Indications that also V_2O_5 and Sb_2O_3 can form glass are found, while we have not been able to procure any data for P_2O_3.

We feel that this surprising agreement cannot be due to mere coincidence, but rather that it must be ascribed to the fact that our reasoning is closely connected with fundamental principles of the atomic arrangement in glass.

It is a simple task to extend our results also to fluorides. We find that BeF_2 is the only fluoride which can be expected to form glass, again in complete agreement with observations.

4. Oxide Glasses in General.—From our discussion of the vitreous oxides we have seen that the formation of vitreous networks of low potential energy could take place only under certain conditions. We found that we could build up a vitreous network of oxygen tetrahedra or of oxygen triangles, while oxygen octahedra or oxygen cubes would lead to a periodic network. We found further that the presence of oxygen tetrahedra or of oxygen triangles is not the only condition. In order to prevent the regular lining up of the polyhedra when building the network we had to require that the polyhedra have only corners in common and that oxygen atoms do not belong to more than two polyhedra. For the vitreous oxides these rules led to very simple conclusions, since in a given oxide we have only one kind of oxygen polyhedra present.

In oxide glasses of the general type the circumstances are much more complicated. The rules we found for the individual oxides therefore must be somewhat modified. These modifications are fairly obvious from the discussions in the preceding chapter.

An oxide glass may be formed (1) if the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or by oxygen triangles; (2) if these tetrahedra or triangles share only corners with each other and; (3) if some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations.

In reality this means that the glass must contain appreciable amounts

of the cations which can form vitreous oxides or of other cations which are able to replace any of the former isomorphously. These glass-forming cations are: B^{+3}, Si^{+4}, P^{+3}, P^{+5}, As^{+3}, As^{+5}, Ge^{+4} and possibly also V^{+5}, Sb^{+5}, Cb^{+5}, Ta^{+5} and in addition Al^{+3} which is capable of replacing Si^{+4} isomorphously. It is worth mentioning that Al_2O_3 alone cannot form glass.

These results are in excellent agreement with observations. We know of no oxide glass which does not contain appreciable quantities of one or another of the cations listed. These cations are responsible for the glass-forming ability, and they compose together with oxygen atoms what we may conveniently call the vitreous framework of the glass.

The chemical composition of a glass we can express by a gross "chemical formula" of the form A_mB_nO. In this formula m and n are in general not integers, but represent merely the number of atoms A and B per oxygen atom. By atoms B we will understand the glass-forming cations listed above, while all other cations in the glass are grouped together as atoms A. Cations B may be surrounded by oxygen tetrahedra or by oxygen triangles; accordingly we may for convenience use the terms tetrahedral or triangular glasses.

It may be expected quite generally that the glasses would have the most advantageous properties (*e. g.*, from the point of view of devitrification difficulties and with respect to strength) if the tetrahedral or triangular network had three-dimensional extension. For a tetrahedral glass this will mean that at least three corners in each tetrahedron are shared with other tetrahedra, or rather that the value of n in the gross formula will lie between 0.33 and 0.50. For a triangular glass n analogously will be 0.67.

We have calculated the gross chemical formula for practically all the glasses whose chemical compositions are given in "International Critical Tables." For nearly all of these glasses n lies around 0.40; in a few cases n is slightly greater than 0.50, namely, if the B_2O_3 content is high. That this agreement is due to coincidence is hard to believe.

When we build up the three-dimensional framework of oxygen atoms and atoms B, the valences will in general not be balanced, so that we must introduce additional cations. Because the oxygen polyhedra in this framework are tetrahedra or triangles, holes necessarily must exist in the network. These holes will be bounded by oxygen atoms, so that they are excellently suited as positions for the cations A. Furthermore, since the framework itself is without periodicity and symmetry, the holes must be statistically distributed and there will be no restriction on behalf of symmetry as to which and how many of these holes are to be filled by cations A. In agreement with previous results this shows that the chemical composition cannot be expressed by a rational chemical formula. Continuing our argument, we can make some statements as to the nature of atoms A. We will simply require that the introduction of the cations A

into the framework does not cause great increase of the potential energy. The fact that the cations A go into the holes is in agreement with this requirement. We must not be deceived by our reasoning and think that the framework is first formed and that then the holes are filled. Naturally the holes are being filled as the framework is being formed, so that the dimensions of the holes are determined by the size of the cations occupying them. When the cations A are put into the network, repulsive potentials will arise between cations A and B. These repulsive potentials according to our requirement must be small. The holes are to a great extent bounded by edges of the oxygen triangles or tetrahedra or by tetrahedral faces, and furthermore the cations B carry charges 3, 4 or 5. In order to make the repulsion between cations A and B small, the charge on cation A must be small and the distance between the cations large. We increase the distance if we enlarge the holes. But as we have stated earlier that the dimensions of the holes are determined by the size of cations A, it follows that cations A must be large. Consequently: *Cations A must be large and carry a small charge.* Small and highly charged cations like Ti^{+4}, Mg^{+2} will on the other hand tend to produce devitrification. The cations A which are present in typical oxide glasses agree with our result: they are chiefly Na^+, K^+, Ca^{+2}, Ba^{+2}, Pb^{+2}.

Our fundamental ideas of the atomic arrangement in glasses thus have led to an explanation of the more prominent features of the chemical composition of oxide glasses.

Some conclusions regarding the relation between different properties and the chemical composition also may be drawn.

The rigidity which glasses possess over large ranges of temperature must be attributed to the fact that no appreciable migration of the atoms occurs at relatively low temperatures. The cations A, especially if they are alkali ions, will be bound less tightly to the surrounding oxygen atoms than the cations B. As the temperature rises we must therefore expect to get an increasing number of migrating atoms A, without any appreciable breakdown of the vitreous framework proper. Univalent cations will, of course, migrate with greater ease through the framework than the divalent cations, and again smaller cations will migrate more easily than large cations with the same charge. Thus Na^+ migrates more easily than K^+, both these ions more readily than say Ca^{+2}. The electric conductivity of a glass for these reasons must be chiefly electrolytic, the charge being carried by cations and for the most important part by the alkali ions. Owing to the increasing number of detached atoms with increasing temperature, the conductivity will also increase with the temperature. These conclusions seem to be substantiated by actual observations. Glasses rich in alkali invariably are relatively good conductors. Pyrex glass containing negligible amounts of cations A has a very low conductivity.

At higher temperatures breakdown of the vitreous framework proper will begin, and large parts of the framework may start migrating. As a matter of fact we must expect that even in the melt oxygen atoms and atoms B to a very great extent are linked together so as to form rather large groups, the degree of polymerization being, of course, a function of the temperature. In melts where there are highly associated groups like that the viscosity will be high.

It must be remembered that the conditions which we have given for the glass formation are not the only ones. Whether a substance will form a glass or not naturally will depend also on the conditions under which the melt is cooled down. We have stated therefore that certain substances *may* form glass, namely, when the melt is cooled under conditions favorable for glass formation.

Summary

It is shown that the following picture of the atomic arrangement is in complete agreement with the characteristic properties of glasses. The atoms in glass are linked together by forces essentially the same as in crystals. Over large ranges of temperature the atoms are oscillating about definite equilibrium positions. As in crystals extended three-dimensional networks are formed. The principal difference between a crystal network and a glass network is the presence of symmetry and periodicity in the former and the absence of periodicity and symmetry in the latter.

A glass network with an energy content comparable to that of the corresponding crystal can be formed only under certain conditions. These conditions are deduced for oxide glasses. It is found that the following oxides may be expected to occur in vitreous forms: B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, P_2O_3, As_2O_3, Sb_2O_3, V_2O_5, Sb_2O_5, Cb_2O_5, Ta_2O_5. Analogously it is deduced that BeF_2 is the only fluoride which can be prepared as glass. In a similar manner it is found that an oxide glass of the general type must contain appreciable amounts of one or more of the following types of cations: B^{+3}, Si^{+4}, Ge^{+4}, P^{+5}, As^{+5}, As^{+3}, P^{+3}, Sb^{+3}, V^{+5}, Sb^{+5}, Cb^{+5}, Ta^{+5}, Al^{+3}. The gross chemical composition of a glass can be expressed by a formula A_mB_nO, where B represents the cations listed above and where A represents all other cations present. m and n give the number of cations A and B per oxygen atom. It is concluded that a glass will have the most advantageous properties if n has a value of about 0.5. Cations A must carry a small charge and have a large radius.

These restrictions concerning the chemical composition are in complete agreement with empirical facts.

Some conclusions with respect to other properties of oxide glasses are given.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 323]

THE CHLORINE-SENSITIZED PHOTO-OXIDATION OF TETRACHLOROETHYLENE IN CARBON TETRACHLORIDE SOLUTION

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In 1821, Michael Faraday[1] found that a solution of chlorine in tetrachloroethylene yielded hexachloroethane when exposed to sunlight. This reaction should offer perhaps the simplest possible case for kinetic study of photochemical chlorination of a double bond; there is no opportunity for complication arising from simultaneous substitution, and there is little likelihood of the formation of more than one chlorination product; moreover, at room temperature dark reaction apparently does not occur. On the other hand, it has been found[2] that tetrachloroethylene and oxygen alone give on prolonged exposure to sunlight, trichloroacetyl chloride and phosgene. We have undertaken a study of the kinetics of the chlorination in carbon tetrachloride solution using light absorbed only by the chlorine; we have found: (1) that this photochlorination, in common with many others, is strongly inhibited by dissolved oxygen; and (2) that in the presence of sufficient oxygen, oxidation of the tetrachloroethylene occurs to the practical exclusion of the chlorination although chlorine remains the light absorber. The present paper is concerned mainly with the products and kinetics of this photochemical oxidation sensitized by chlorine.

Apparatus

The Reaction Vessel.—Most of the illuminations were carried out with the solution in the vessel shown in Fig. 1. This vessel consisted of two flat-windowed Pyrex cells so joined together that the solution could be transferred from one to the other by inverting the vessel; the solution was placed in the thin cell A for illumination and in the thick cell B for photometric analysis. The cell A, which was of 5 mm. internal thickness and about 35 mm. diameter, was made thin in order that light absorption in it be low and all parts of the solution under nearly the same intensity of illumination. The cell B, which was of 3.30 cm. internal thickness and of slightly smaller volume than A, gave a longer optical path through the solution. The light absorption measured with the solution in B was used to compute the chlorine concentration and to compute the smaller absorption occurring in the cell A. The vessel was filled through a ground-glass stopper C which was protected with a water-tight cap D, since the vessel was placed in a water thermostat for illumination.

The Light Thermostat.—This was a tank of water provided with a window, stirrer and heater; temperatures were kept constant to one-half degree or better. The reaction vessel was mounted in a position accurately reproducible from one experiment to another, and about 1 cm. from the window.

[1] M. Faraday, *Ann. chim. phys.*, [2] **18**, 55 (1821).

[2] M. A. Besson, *Compt. rend.*, **121**, 125 (1895).

In experiments in which the mercury radiation λ4358 was used, the intensity of the radiation was measured by means of a thermopile and galvanometer. This thermopile was mounted in a waterproof brass case with a glass window and was so arranged that after removing the reaction cell, the thermopile could be placed in a reproducible position approximating that occupied by the cell during illumination.

The Sources of Illumination.—For most experiments of a preliminary or of a qualitative nature, the source of illumination was a 500-watt projection lamp. The infra-red was removed by a water-cooled filter consisting of a 1-cm. layer of 6% copper sulfate solution. The light was approximately collimated by a 16-diopter lens of aperture about *f* 1.5. An ammeter and variable resistance were placed in series with the lamp to assist in securing reproducible intensities. This source was the one used in experiments with "white light" described below.

A series of experiments was made using the mercury line λ4358; this was obtained from an upright type quartz arc placed just outside the thermostat (in a reproducible position) about 6 cm. from the reaction vessel and used without collimating lenses. The radiation was passed through the copper sulfate filter mentioned above and then through the Corning glasses Noviol A and blue-purple ultra. Spectrographic examination of the transmitted radiation showed it to be entirely free from strong mercury lines other than λ4358. Similar filters were used in the photometer.

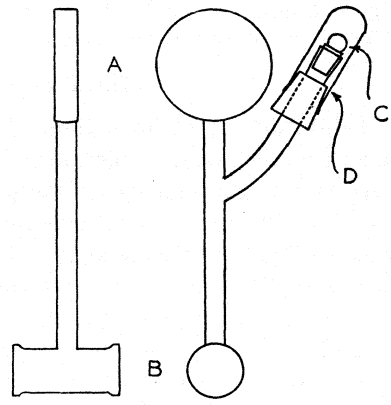

Fig. 1.—Cell employed for illuminating the solution and for measuring its light transmission.

The Photometer.—In order to determine chlorine concentrations without removing samples for analysis, and in order to compute the low absorption in the thin cell in the experiments with λ4358, its absorption in the thick cell (B) was determined with the aid of a photometer. This apparatus employed simultaneously two thermopiles and two galvanometers and a divided light beam in one branch of which the absorption cell was placed. Beer's law was used, the molal absorption coefficient of chlorine being taken as 2.26.[3]

Materials

Carbon Tetrachloride.—The carbon tetrachloride was obtained from a C. P. sulfur-free product. This was given prolonged illumination with chlorine dioxide and chlorine; it was then refluxed, washed with sodium hydroxide solution, with water, dried over C. P. calcium chloride, and finally distilled in an all-glass apparatus. The product was found to give only negligible quantities of acid when its chlorine solution was subjected to more prolonged illumination than those used in the measurements. Two separate samples of carbon tetrachloride were used.

Tetrachloroethylene.—The tetrachloroethylene was obtained from Eastman's C. P. product. It was found that when a carbon tetrachloride solution of chlorine was mixed with an excess of the original tetrachloroethylene in the dark, a small fraction of the chlorine disappeared immediately but no more disappeared on standing; this indicated a small amount of easily chlorinated impurity in the tetrachloroethylene. It was accordingly further treated by passing chlorine into it and illuminating it. It was

[3] Dickinson and Jeffreys, THIS JOURNAL, **52**, 4288 (1930).

washed with sodium hydroxide solution, and then with water, dried with calcium chloride, and fractionally distilled. The fraction coming over at 118.0–118.1° at 740 mm. was retained. (It constituted most of the sample.) The product (of which two different preparations were used) yielded a little acid on shaking with water but the amount was small enough to ignore in all experiments except at very high tetrachloroethylene concentrations; in these a small blank correction was applied.

Chlorine.—The chlorine was taken from a commercial tank. It was passed successively through glass-connected wash bottles containing potassium permanganate solution, dilute sulfuric acid, concentrated sulfuric acid, glass wool and finally desichlor. The effluent gas was passed directly into carbon tetrachloride in a glass-stoppered bottle. The chlorine solutions so prepared were found to be completely acid-free.

The Products of the Reaction

Inhibition of Chlorination.—The effect of oxygen in preventing the disappearance of free chlorine is shown by the following pair of experiments carried out with solutions initially 1.6 molal in tetrachloroethylene and 0.075 molal in chlorine. In one experiment, the reaction vessel (Fig. 1) was filled with oxygen and then enough solution introduced to fill cell A. The solution was illuminated in A for twenty minutes; the illumination was occasionally interrupted and the solution run back and forth between cells A and B to keep the solution supplied with oxygen. The chlorine concentration showed no detectable decrease in this time. A second sample was illuminated in the same way except that the cell was initially filled with nitrogen and was not disturbed during the illumination. At the end of five minutes most of the chlorine had disappeared; its molality was now 0.012. The non-disappearance of chlorine in solutions containing oxygen was verified in many experiments.

Formation of Hydrolyzable Product.—That oxygen not only inhibited the chlorination but also produced an oxidation was evident from the phosgene-like odor from the illuminated solution. It was shown more convincingly by the fact that when the illuminated solution was shaken with water and the free chlorine removed with iodide and thiosulfate, the water was found to be acid. The photochemical formation of oxidation products hydrolyzable to acid is the feature of which we have made use in following the reaction quantitatively.

Analysis for Acid.—In order to determine the number of equivalents of acid obtainable by hydrolysis of the illuminated solution, it was poured into a weighed, glass-stoppered flask containing water, and shaken for five minutes. Then potassium iodide was added and the color just discharged with thiosulfate. The acid was then determined by adding potassium iodate and titrating the iodine with thiosulfate. Special experiments were made to show that sufficient time was allowed for the hydrolysis.

Dark Reaction.—Several solutions similar to those used for illumination were allowed to stand in the dark for periods exceeding the times required for the light experiments; one solution was as high as 3.2 molal in

tetrachloroethylene, and another was kept at 36°. In no case was either chlorination or oxidation found.

Equivalents of Acid per Formula Weight of Tetrachloroethylene.—A series of experiments was made starting in each case with a solution of the same composition, *viz.*, 0.0113 volume molal in tetrachloroethylene and 0.07 in chlorine. A supply of oxygen was maintained in the solution in the manner described above. (The oxygen present in the vessel was several times the amount needed to oxidize all the tetrachloroethylene to phosgene.) The samples were exposed for various times to the white light source under identical conditions of illumination, and were then hydrolyzed and titrated for acid. The results of this series are shown in curve A of Fig. 2 in which

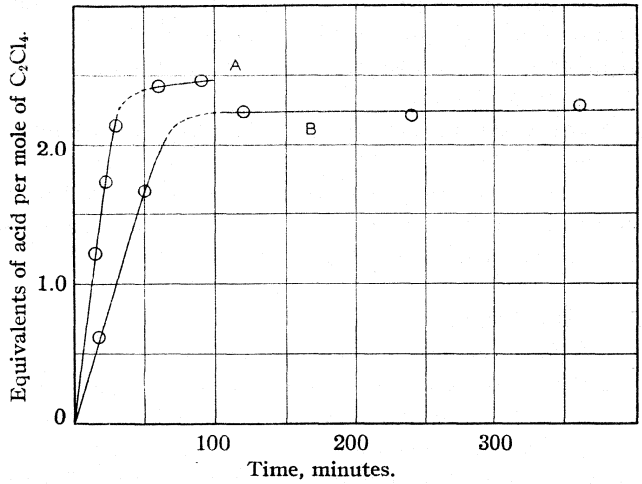

Fig. 2.—Amount of oxidation produced in various times of illumination.

the equivalents of acid found per formula weight of tetrachloroethylene taken are plotted as ordinates against the times of exposure in minutes as abscissas. It may be seen that in the early part of the reaction the amount of acid-producing material formed is nearly linear with the time; this suggests that the rate of oxidation is not strongly dependent on the tetrachloroethylene concentration. With continued illumination the formation of acid-producing material ceases abruptly and before the tetrachloroethylene is at all completely oxidized to phosgene; for complete oxidation to phosgene would give four equivalents of acid per formula weight of tetrachloroethylene in accordance with the equations

$$C_2Cl_4 + O_2 = 2COCl_2$$
$$2(COCl_2 + H_2O = CO_2 + 2HCl)$$

Oxidation to trichloroacetyl chloride would, however, give two equivalents of acid per formula weight of tetrachloroethylene

$$C_2Cl_4 + {}^1/_2O_2 = CCl_3COCl$$
$$CCl_3COCl + H_2O = CCl_3COOH + HCl$$

Since, in this series, the original solution was prepared volumetrically and the concentration of tetrachloroethylene was not known to better than a few per cent., two more experiments were made with solutions carefully prepared by weighing. These gave, after sixty minutes of the same exposure as before, the values 2.22 and 2.28 for the equivalents of acid per formula weight of tetrachloroethylene.

In another series of measurements a solution 0.0113 molal in tetrachloroethylene and 0.05 molal in chlorine was exposed in a larger cell (not shown) under slightly different conditions of illumination. The cell was provided with an oxygen reservoir into which the solution was occasionally run. Successive samples of solution were withdrawn and titrated. The illumination was continued for six hours although the initial reaction was apparently over in a little over one hour.

The results are shown in B of Fig. 2. The experiment makes it clear that the products of the oxidation of tetrachloroethylene undergo little if any further oxidation even on prolonged illumination. On the assumption that the oxidation is to trichloroacetyl chloride and phosgene, the average value of 2.25 equivalents of acid obtained per formula weight of tetrachloroethylene leads to the conclusion that 87.5% of the tetrachloroethylene oxidized goes to trichloroacetyl chloride.

Isolation of Trichloroacetic Acid.—In order to determine whether trichloroacetic acid could be isolated from the products of hydrolysis, an illuminated solution was shaken with water and both liquids were evaporated together at 40°. Drying in a desiccator yielded a hygroscopic solid. Two separate samples gave melting points of 55 and 56°, respectively; that of trichloroacetic acid is 57°. Furthermore the solid gave a strongly acid solution and an isocyanide odor when heated with potassium hydroxide and aniline.

Ratio of Acid to Chloride.—An independent estimate of the fraction of the oxidation leading to trichloroacetyl chloride was obtained from a determination of the ratio of equivalents of acid to equivalents of chloride in the hydrolysis products; this ratio would evidently be 2 were the oxidation completely to trichloroacetyl chloride and 1 were it completely to phosgene. We have accordingly, in certain experiments, supplemented the titration for acid with an electrometric titration for chloride on a separate sample. The procedure was as follows: twenty cc. of carbon tetrachloride solution was illuminated in white light (oxygen being present) until a suitable amount of reaction was judged to have occurred. The solution was then shaken with 10 cc. of water in a small separatory funnel and the carbon tetrachloride layer rejected. Separate distribution experiments showed that the aqueous layer should retain all of the trichloroacetic acid and hy-

drochloric acid but only a portion of the free chlorine. The aqueous layer was diluted to 30 cc. Ten cc. of this solution was titrated for free chlorine and then for acid using potassium iodide and potassium iodate and 0.01 *N* thiosulfate. To another 10-cc. sample was added 1 cc. of 0.1 *N* sodium sulfite to convert the free chlorine to chloride. The total chloride in this sample was then determined by electrometric titration with 0.01 *N* silver nitrate solution. The chloride in the original hydrolysis products was then obtained by subtracting from this total chloride the number of equivalents of free chlorine found in the first titration.

The results of these experiments are shown in Table I. The composition of the original carbon tetrachloride solution is shown in the first two columns; the results of the titrations are shown in the next two columns, and the ratio of acid to chloride in the hydrolysis products in the fifth column. In agreement with expectations, the value of this ratio is much greater than 1 but less than 2 in all cases. If x be the fraction of the reacting tetrachloroethylene which gives trichloroacetyl chloride and $(1-x)$ the fraction which forms phosgene, then per formula weight of tetrachloroethylene oxidized the hydrolysis products contain $2x + 4(1-x)$ equivalents of acid and $x + 4(1-x)$ equivalents of chloride; the ratio of acid to chloride is then $(4-2x)/(4-3x)$. With this relation, values of x were calculated from the observed acid to chloride ratio; these are given in the last column of Table I. The average value 0.86 agrees with that previously obtained (0.875) in indicating that the oxidation is mainly to trichloroacetyl chloride.

TABLE I

RATIO OF ACID TO CHLORIDE IN HYDROLYZED PRODUCTS

C_2Cl_4, mole/liter	Cl_2, mole/liter	Equiv. acid in 10-cc. sample	Equiv. chloride in 10-cc. sample	Ratio of acid to chloride	Fraction of oxidation to CCl_3COCl; x
0.097	0.07	12.69×10^{-5}	8.57×10^{-5}	1.48	0.79
.097	.07	11.18	6.84	1.63	.87
.097	.07	2.64	1.80	1.47	.78
.097	.07	4.27	2.57	1.66	.89
.485	.05	9.57	5.73	1.67	.89
.97	.05	7.43	4.04	1.84	.95
.97	.05	23.64	15.19	1.56	.84
				Mean	.86

The Kinetics of the Reaction

A considerable number of experiments on the effect of various factors on the reaction rate was made using white light since such experiments could be carried out with comparatively short exposures. Another series of experiments was then made using monochromatic radiation (λ 4358). In view of the facts that the latter experiments were more precise and unambiguous than those with white light, and that the experiments with white light

led to no conclusions at variance with those obtained with λ4358, we are giving in detail only the results of the latter experiments. They were all carried out by illuminating various solutions in cell A of Fig. 1, using the photometer to determine the absorption and chlorine concentration, and hydrolyzing the final solution and titrating the products for acid as described above. The results are given in Table II.

In column 5 is given the intensity of radiation in arbitrary units (cm. of galvanometer scale deflection). Since the thermopile as used was at the thermostat temperature, and since its sensitivity was found by separate experiment to decrease with rising temperature 0.24% per degree, the tabulated intensities for temperatures other than 20° have been reduced to the deflections which would have been obtained with the thermopile at 20°. In column 6 is given the fraction of radiation absorbed in the thin cell A as computed from measurements in cell B. These absorption measurements were all made at about 20°. However, we have found in a separate experiment that the absorption of a carbon tetrachloride solution 0.05 *M* in chlorine did not differ appreciably (*i. e.*, by more than 1%) at 7 and 30°; it is safe to take the values in column 6 as those actually prevailing in the experiments at other temperatures. In column 8 is given the amount of acid found by titration; and in column 9 the yield, *i. e.*, the amount of reaction per unit time per arbitrary unit of radiation absorbed. These data permit the following conclusions concerning the effect of various factors on the rate of oxidation.

TABLE II

RESULTS OF ILLUMINATING SOLUTIONS WITH λ4358

1	2	3	4	5	6	7	8	9
Expt.	C_2Cl_4, mole/liter	Cl_2, mole/liter	Temp., °C.	Intensity cm. defl. of galv., d	Fraction of rad. absorbed, a	Exposure time, min., t	Equiv. acid per g. of soln., q	Yield, $\frac{q}{adt}$
1	0.0220	0.0619	20	2.11	0.149	60	0.876×10^{-5}	0.0465×10^{-5}
2	.0420	.0318	20	2.16	.081	120	1.022	.0489
3	.0420	.0658	20	2.23	.159	60	1.062	.0500
4	.0420	.0726	20	1.97	.172	60	1.059	.0520
5[a]	.0420	.0987	20	2.74	.226	30	0.977	.0527
6	.0420	.1147	19	0.567	.258	90	0.700	.0531
7	.0420	.1260	20	2.65	.283	30	1.164	.0517
8	.462	.0614	20	2.13	.150	60	1.558	.0813
9	.881	.0460	20	2.37	.113	60	1.593	.0994
10	1.615	.0629	20	2.52	.151	50	2.260	.1181
11	2.425	.0348	20	2.16	.086	60	1.950	.1758
12	3.235	.0213	20	2.33	.053	60	2.310	.3120
13	0.0420	.0476	3	1.09	.117	120	0.564	.0369
14	.0420	.0755	3	1.52	.178	90	0.905	.0372
15	.462	.0458	3	1.74	.112	90	1.033	.0589
16	.0420	.1026	36	2.00	.235	40	1.248	.0664
17	.462	.0582	36	2.18	.140	45	1.539	.1121

[a] Solution saturated with air instead of oxygen.

Oxygen Concentration.—That the concentration of oxygen, when not too low, has little effect on the rate of oxidation is suggested by the coherence of the results shown in Fig. 2 since there was no attempt to maintain constancy of oxygen concentration in those experiments. It is shown more directly by the equality in yield (column 9) in experiments 4, 5 and 7, which differ mainly in that air instead of oxygen was used to saturate the solution in experiment 5. Similar results have been obtained with white light. From the solubility of oxygen in carbon tetrachloride given in the "International Critical Tables," the concentration of oxygen in solutions saturated with air is calculated to be 0.002 molal.

Light Intensity.—The rate of oxidation is proportional to the first power of the intensity of the incident light. This is best shown by a comparison of experiments 6 and 7, which involve a nearly 5-fold intensity range but are otherwise similar. With white light, 4-fold changes in intensity have been made using calibrated screens with similar results.

Chlorine Concentration.—Experiments 2, 3, 4 and 7 differ mainly in chlorine concentration, which is here varied four-fold. The rates per unit absorption probably do not differ by more than the error of the experiments. For a thin layer of solution, then, the rate of oxidation is proportional to the chlorine concentration, *i. e.*, the chlorine concentration affects the rate only by affecting the amount of absorption.

Tetrachloroethylene Concentration.—In experiments 1 to 10 inclusive, the concentration of tetrachloroethylene is increased 73-fold while the rate per unit absorption increases only 2.5-fold. At very high concentrations, the rate begins to increase much more rapidly. The results of the first ten experiments may be very satisfactorily represented by an empirical expression of the form

$$\text{Rate} = kI_{\text{abs.}}\,[1 + b(C_2Cl_4)^{1/2}]$$

but at very high tetrachloroethylene concentrations this expression leads to lower values than those observed.

Temperature.—Most of the experiments were made at 20°, but measurements have been made at 3° and at 36° at two different tetrachloroethylene concentrations. The yields under various conditions are summarized in Table III. In the third and fifth columns are given the ten-

TABLE III

EFFECT OF TEMPERATURE ON THE RATE OF OXIDATION

Temp., °C.	Yield at $(C_2Cl_4) = 0.0420$	$\frac{k_{T+10}}{k_T}$	Yield at $(C_2Cl_4) = 0.462$	$\frac{k_{T+10}}{k_T}$
3	0.0370×10^{-5}		0.0589×10^{-5}	
		1.21		1.21
20	.0514		.0813	
		1.17		1.22
36	.0664		.1121	

degree multiplications of the yield. In the range studied, *i. e.*, from 0.04 to 0.5 molal in tetrachloroethylene, the temperature coefficient shows no evident dependence on the yield. Since the absorption coefficient of the chlorine solutions is substantially independent of the temperature, these ten-degree multiplications may be regarded as applying either to the specific rate constants or to the quantum yields.

Quantum Yields

In view of the character of the dependence of the reaction rates on the tetrachloroethylene concentration and on the temperature, an extremely precise determination of quantum yield would appear to be without present interest; a fair estimate of the quantum yields can be had from the experiments already described.

The intensity of radiation at the front surface of the reaction cell corresponding to a deflection, d, in the experiments of Table II was found by locating the mercury arc and thermopile in the positions they occupied in those experiments, and comparing the deflection obtained with that obtained when a second calibrated thermopile was placed at the position normally occupied by the reaction cell. It was thus found that the intensity at the reaction cell was $56 \times 10^2\ d$ ergs per sq. cm. per sec. If now A be the illuminated area of liquid (the entire liquid in the cell was illuminated) and a the fractional absorption, then since the number of einsteins per erg of radiation of wave length 4358 Å is 3.66×10^{-13}, the number of einsteins absorbed by the liquid in t minutes is $3.66 \times 10^{-13} \times 56 \times 10^2 \times adA \times 60t$. If q be the equivalents of acid produced per gram of solution, ρ the density of the solution (1.59 g./cc.), and l the thickness of the solution in the cell, the equivalents of acid per Al cc. of solution is $q\rho Al$. The quantum yield expressed in equivalents of acid per einstein absorbed is then $64 \times 10^5 \times q/adt$; *i. e.*, the quantum yields so expressed may be obtained by multiplication of the numbers in column 9 of Table II by 64×10^5. The values obtained in this way range from 2.4 in experiments 13 and 14 to 20 in experiment 12. The above calculation assumes that the illumination was (1) parallel and (2) spatially uniform; these conditions, particularly the first, were only approximately satisfied.

Two measurements of quantum yield largely independent of the above were made by illuminating the solution in cell B of Fig. 1, using a uniform collimated beam defined by a circular diaphragm with an opening only 1.00 cm. in diameter so that the entire beam was intercepted by the solution. The intensity was measured by a thermopile giving a deflection of 1 cm. for an intensity of 1.340 ergs per sq. mm. per sec. The results are given in Table IV.

The intensity given in column 3 has been corrected for reflection losses and represents the intensity of the radiation entering the solution. The

TABLE IV

QUANTUM YIELD DETERMINATIONS AT 20°—λ = 4358 Å.

C_2Cl_4, mole/ liter	Cl_2, mole/ liter	Intensity ergs/ sq. cm./sec.	Fraction absorbed	Time, min.	Total equivs. acid	Equivs. acid per einstein
0.0420	0.0761	2340	0.729	232	1.34×10^{-5}	1.95
.0420	.0779	1570	.737	301	1.36	2.25

yields of Table IV are only about 66% of those calculable from Table II, but are more reliable. For a solution having (C_2Cl_4) = 0.0420, our best estimate (good to 20%) of the quantum yield is 2.5 equivalents of acid per einstein. Assuming 87% of the oxidized tetrachloroethylene to form trichloroacetyl chloride, this corresponds to 1.1 mole of tetrachloroethylene oxidized per einstein absorbed at 20°. The values of the yields in Table II should be good to within a few per cent. relative to each other. If they are all multiplied by a constant factor so as to give the yield 1.1 mole of tetrachloroethylene per einstein at (C_2Cl_4) = 0.0420 and at 20°, the absolute yields shown in Fig. 3 are obtained.

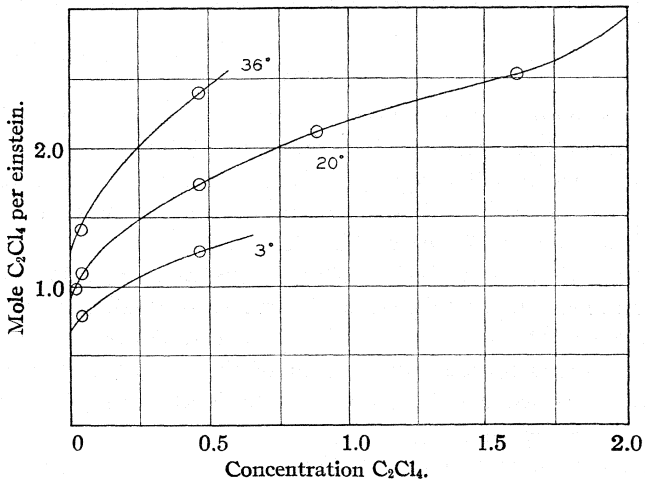

Fig. 3.—Moles of tetrachloroethylene oxidized per einstein of radiation λ4358 absorbed.

Discussion

As far as the present reaction has been studied, it is found to exhibit considerable similarity to the chlorine sensitized formation of carbon dioxide from gaseous carbon monoxide and oxygen. It is well known that carbon monoxide and chlorine unite under illumination and form phosgene;[4] when, however, oxygen is present the chlorination of carbon monoxide ceases, and oxidation to carbon dioxide occurs instead. The

[4] This reaction has been extensively studied by M. Bodenstein and his collaborators.

rate of formation of carbon dioxide is given by the expression $d(CO_2)/dt = k I_{abs.}(CO)^{1/2}$ when the pressures are low and when vessels with large surface are used.[5] The kinetics of the tetrachloroethylene oxidation in solution and the carbon monoxide oxidation at low pressures agree with respect to the effect of intensity, chlorine concentration and oxygen concentration and further agree to the extent of involving no strong dependence on the concentration of tetrachloroethylene or carbon monoxide.

A mechanism has been given to account for the rate of carbon dioxide formation. An essential feature of this mechanism is the achievement of first order dependence on the light intensity through wall recombination of the chlorine atoms. It is difficult to suppose that wall recombination is of importance in the case of a solution reaction. Accordingly, in spite of the formal resemblance of the tetrachloroethylene reaction to some aspects of the carbon monoxide reaction, we are unable to make direct use of the mechanism proposed for the latter.

We shall defer attempts to develop a mechanism for the oxidation of tetrachloroethylene until further experiments on the chlorination have been completed.

Summary

The photochemical chlorination of tetrachloroethylene in carbon tetrachloride solution has been found to be strongly inhibited by oxygen.

In the presence of both oxygen and chlorine, photosensitized oxidation to trichloroacetyl chloride and to phosgene occurs; most of the oxidation ($\sim 87\%$) leads to trichloroacetyl chloride.

With radiation of wave length 4358 Å. the rate of oxidation in a uniformly illuminated layer is found, in the ranges studied, to be proportional to the first power of the intensity of the incident radiation, the first power of the chlorine concentration, independent of the oxygen concentration and only moderately dependent on the tetrachloroethylene concentration except when this is very high.

Rates have been measured at 3, 20 and 36°; the ten-degree multiplication of the yield has been found to be 1.20.

Quantum yields for the oxidation have been determined.

PASADENA, CALIFORNIA

[5] H. J. Schumacher and G. Stieger, *Z. physik. Chem.*, [B] **13**, 169 (1931).

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

THE HOMOGENEOUS THERMAL POLYMERIZATION OF 1,3-BUTADIENE

BY WILLIAM E. VAUGHAN[1]

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Association reactions of the type A + B ⟶ C have received a very considerable amount of study and have been treated extensively both experimentally and theoretically.[2] Born and Franck[3] have concluded that in the case of atoms such a process as the direct addition would be extremely unlikely, due to the energy present in the two reacting particles, which must be dissipated for stabilization of the product; this could occur on a triple collision or at the walls. Polanyi and Wigner[4] have discussed the mechanism as a reversal of the optical Auger process or the mechanism of unimolecular decomposition; this leads to results in a formal way similar to those of Born and Franck. The work on the recombination of bromine atoms[5] and of hydrogen atoms[6] gives experimental confirmation of the theory in that the rate is within agreement with that calculated from the frequency of triple collisions.

A generalization of this criterion of association reactions to the combination of more complicated molecules has been proposed and it has been thought by some that bimolecular associations as such could not occur. This idea certainly is subject to scrutiny, since there is an urgent *a priori* reason to admit the necessity of the reverse of unimolecular reactions.

The kinetics of homogeneous thermal polymerization reactions have received relatively little attention. Indeed practically the only data available are those of Pease on acetylene,[7] and on ethylene.[8] The former of these studies was carried on in a dynamic system and it was shown that between 400 and 600° the process was homogeneous and bimolecular, and somewhat suppressed by the presence of glass packing, indicating a chain mechanism. The latter demonstrated that butylene was the primary prod-

[1] National Research Fellow in Chemistry.

[2] See Kistiakowsky, *Chem. Rev.*, **10**, 91 (1932), for a summary of the work on atomic association reactions.

[3] Born and Franck, *Z. Physik*, **31**, 411 (1925); also Polanyi, *ibid.*, **1**, 337 (1921); Herzfeld, *ibid.*, **8**, 132 (1922).

[4] Polanyi and Wigner, *ibid.*, **33**, 429 (1925).

[5] Jung and Jort, *Z. physik. Chem.*, **3B**, 83 (1929); Jung, *ibid.*, **3B**, 97 (1929).

[6] Smallwood, THIS JOURNAL, **51**, 1985 (1929); Senftleben and Riechemeyer, *Ann. Physik*, **6**, 105 (1930); Steiner and Wicke, *Z. physik. Chem.*, Bodenstein Festbd., 817 (1931).

[7] Pease, THIS JOURNAL, **51**, 3470 (1929).

[8] Pease, (a) *ibid.*, **52**, 1158 (1930); (b) **53**, 613 (1931).

uct and that again the reaction was roughly bimolecular; further experiments at pressures as high as 10 atmospheres over a temperature range of 350 to 500° in a static system confirmed the bimolecular rate and gave as the energy of activation of the reaction 35,000 cal. At 425° the reaction rate constant as calculated from the formula $Ze^{-E/RT}$ is some 2000 times the experimental value. This was interpreted as showing that only one collision of suitably activated molecules in 2000 has satisfied the energy and quantum conditions. A mechanism was proposed: a quasimolecule is produced by combination of two ethylene molecules; this may be destroyed or stabilized by another collision, provided it does not dissociate spontaneously; it is suggested that the destruction process is 2000 times as probable as the stabilization, and these steps lead to a mechanism which is of second order at high pressure and third order at low. Kassel[9] has treated this subject theoretically and concludes that in as far as conservation requirements and quantum restrictions are involved, the formation of complex molecules by a bimolecular association process should be possible at a relatively large fraction of all collisions, a conviction not shared by others.[10] Kassel also submits a modification of the earlier mechanism, in which he qualitatively apportions the efficiency factor between the two processes of the formation of the unstable complex upon collision and of the stabilization by impact with another molecule of ethylene. Pease[11] has also studied the hydrogenation of ethylene at 475 to 550° and one atmosphere pressure and finds it to be homogeneous and second order; calculations show that 10% of the collisions between hydrogen and the hydrocarbon molecules possessing sufficient energy (43,150 cal.) result in the formation of ethane.

The present set of experiments was initiated at the University of Chicago in 1930 with the intent of lessening the dearth of data in this field. In preliminary work the compound studied revealed itself very capable of thermal polymerization and as such suggested an interesting possibility. As another issue the light absorption of the vapor at one atmosphere pressure in a 20-mm. tube was determined with a Hilger E2 spectrograph; an abrupt long wave length continuous end-absorption limit at 2500 Å. was found. The effect of the total radiations of a discharge in hydrogen and of a very intense high potential spark between cadmium disks[12] was the production of decomposition of the vapor; an analysis of the data proved complex. The study of the thermal polymerization proved, however, to be extremely interesting.

[9] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., Inc., N. Y., 1932, pp. 44–47; THIS JOURNAL, **53**, 2143 (1931).

[10] See, for example, Taylor and Emeléus, *ibid.*, **53**, 562 (1931).

[11] Paper presented at the New Orleans meeting, American Chemical Society, April, 1932; THIS JOURNAL, **54**, 1876 (1932); also Ref. 8a.

[12] Wiig and Kistiakowsky, *ibid.*, **54**, 1806 (1932).

Experimental

1,3-Butadiene was prepared from the corresponding tetrabromide[13] which had been made according to the method of Muskat and Northrup.[14] The solid tetrabromide without further purification was brought by extraction with hot alcohol into the boiling flask in which was suspended by vigorous stirring an excess of finely powdered zinc; the butadiene produced by reduction distilled out through a water-cooled spiral condenser and a trap immersed in ice into a pair of traps in series chilled in a carbon dioxide–acetone mixture wherein practically complete condensation occurred. Yields were of the order of 90 to 95%. The liquid product was quite colorless. It was introduced into an evacuated storage system by slow distillation through drying tubes of phosphorus pentoxide or, as was found better, due to some adsorption of the butadiene by the phosphorus pentoxide with subsequent discoloration of the solid, through pellets of sodium hydroxide. The last third of the butadiene was discarded. The drying seemed not to influence the reaction rate as materials produced in either of these ways gave identical results. The gas in the storage bulb was freed from oxygen by repeated freezing out with liquid air and thorough evacuation to a pressure of less than 10^{-4} mm. Three separate preparations were used, with no perceptible variations in their reactivity.

The furnace consisted of extra heavy iron pipe, well insulated. The temperature, which was always high enough to keep all reactants gaseous, was determined by means of a standard chromel–alumel thermocouple in the circuit of a sufficiently accurate Leeds and Northrup potentiometer; the couple was placed in various positions within the furnace and showed only slight variations in the temperature. The heating current was manually regulated and in the course of a run of several hours' duration, the temperature did not vary more than $\pm 0.5°$. Two types of reaction vessels were employed, one of volume 80 cc., the other 320 cc.; the thermojunction was placed in the interior of the latter type. Numerous individual bulbs were used. At the termination of a run, the bulb, if to be reused, was filled with warm dichromate–sulfuric acid solution to destroy the liquid condensate which appeared upon cooling the vessel and was allowed to stand for several hours, after which it was thoroughly washed. Each cell was provided with two outlets, one of which consisted of tubing of large diameter through which thorough evacuation of the heated vessel by means of a mercury vapor diffusion pump occurred; this tube was then sealed off at the cell. The other outlet was of 2-mm. diameter capillary which communicated to the manometer system and the butadiene supply.

A quartz spiral manometer in conjunction with a mercury manometer and one of sulfuric acid served for the experiments over the pressure range from 100 to 760 mm.; for the lower pressure range from 100 to 1.5 mm. the sulfuric acid manometer and a McLeod gage in combination with an especially designed gage were used.

This latter instrument consists of a very thin disk of mica of approximately 6 cm. diameter supported by two sheet lead rings (5 cm. I. D.; 6 cm. O. D.; 1 mm. thick) from two brass plates (6 cm. diameter; 4 mm. thick), each perforated with a 1-cm. hole. The ring on the reaction system side is sealed to both brass and mica with shellac. The five parts are clamped firmly by external braces. One of the orifices in the plates communicates to the reaction system through capillary tubing joined to the brass by hard wax on the exterior of a ground joint in a brass collar. On the opposite face of the other plate is screwed a two-pronged bracket which has a sharply defined groove running across the prongs. In this depression rests the edge of a razor blade, 2 mm. × 12 mm.; to the

[13] A large quantity of quite pure butadiene tetrabromide was generously given by Dr. I. E. Muskat for this investigation, for which the author expresses his sincere appreciation.

[14] Muskat and Northrup, THIS JOURNAL, 52, 4043 (1930).

"knife edge" is cemented a mirror, 2 × 4 mm. Through the hole in the plate beneath the bracket projects a tungsten wire, 1 cm. long, sealed to the center of the mica with wax; this wire, against which the mirror rests, tilts it at an angle slightly from the vertical. A glass cylinder, 4 cm. high, is sealed to the brass disk by picein wax which is also used to render air-tight the brass–lead–mica junction. The outer ground face of the cylinder is covered with a glass plate joined to it with heavy stopcock grease. A by-pass from the reaction system to the direct-reading manometer side completes the device. The image of a single-filament lamp is thrown upon the mirror and the reflection observed on a scale, in this case a meter distant. Outside of a certain unsteadiness the entire apparatus proved to be quite satisfactory for the low pressure experiments and responded to a 0.03 mm. pressure difference at a total pressure of 2.50 mm. with a 2-mm. scale deflection. The sensitivity is dependent on the thinness of the mica and the position of the wire point against the mirror. After practice it is found relatively easy to make proper mica disks. Increase in the size of the diaphragm would enhance the sensitivity but likewise increases the likelihood of bursting or, at least, of permanent deformation; this latter point is the most serious one and necessitates care in the manipulation of the gas entry. It was found possible by means of careful regulation not to exceed a ±10-cm. deflection on the scale and yet to introduce 100 mm. of gas within the period of a minute; a gage under such treatment proved to be quite good.

Butadiene from the storage system was condensed in an auxiliary trap with carbon dioxide–acetone mixture and then allowed to vaporize; it was possible to judge the approximate amount of liquid needed for any given experiment. After thorough evacuation of the reaction vessel, the large tube was sealed and the system, with continued pumping, allowed to attain constant temperature. In the high pressure runs air was admitted to the mercury manometer to the desired value. The pumps were cut off and the stopcock separating the auxiliary trap from the reaction system was then quickly opened and vapor allowed to enter in sufficient quantity to cause coincidence of the quartz fibers; the stopcock was closed and frequent readings of the pressure and time were made. For the low pressure measurements, the only variation necessary was the simultaneous entry of both the butadiene and the air to opposite sides of the diaphragm at rates which permitted keeping the image on the scale approximately fixed.

Data and Results

A long series of preliminary runs revealed that the pressure fell off to approximately half-value, suggesting dimer formation. Thus the experimental data were treated by application of the differential form of the bimolecular reaction rate equation

$$\frac{dp_B}{dt} = k(p_B)^2$$

Table I gives the data of a typical experiment and the constants calculated therefrom. The initial pressure, p_0, was obtained in all cases by graphical extrapolation.

The increase in the value of k with time is much more strikingly shown in Fig. 1, Runs 15, 16, 17, 18. It will be noted that the curve is quite horizontal until approximately 70% conversion of monomer, at which point it begins to rise rapidly. This behavior characterizes all of the runs. It is undoubtedly due to a secondary polymerization of molecules of dimer with one another or with molecules of the monomer. That polymerization

TABLE I

80-CC. VESSEL; 326°

Time, min.	Pressure, mm.	$k \times 10^{+5}$ (mm.$^{-1}$ min.$^{-1}$)	Time, min.	Pressure, mm.	$k \times 10^{5}$
0	(632.0)		49.50	498.1	2.27
0.92	629.2	(1.54)	55.08	490.2	2.23
3.25	618.5	2.42	60.87	482.8	2.20
6.12	606.6	2.36	68.05	474.6	2.16
8.02	599.4	2.30	77.57	464.8	2.18
10.08	591.6	2.42	90.05	453.3	2.25
12.18	584.2	2.38	103.58	442.6	2.27
14.30	576.1	2.73	119.00	432.8	2.15
17.30	567.3	2.24	135.72	422.8	2.39
20.78	556.9	2.46	176.67	405.3	2.22
24.55	546.8	2.38	216.50	394.4	1.95
29.18	535.4	2.43	259.50	381.0	3.03
33.00	527.8	2.14	295	373.1	2.99
36.38	521.2	2.24	373	357.1	4.26
42.50	509.3	2.45			

proceeds beyond the formation of a dimer is shown by one experiment (No. 20) of which the initial pressure was 244.5 mm. and wherein the pressure

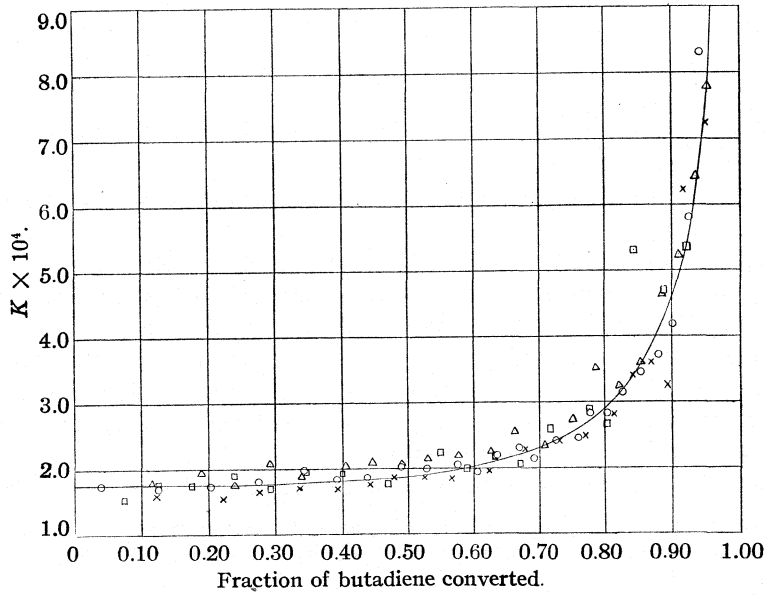


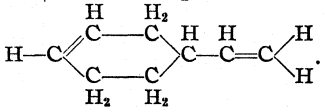
Fig. 1.—Rate constant *vs.* fraction of butadiene converted, 388°: ×, No. 15; △, No. 16; ○, No. 17; □, No. 18.

dropped to 40.0 mm. after a period of forty-five hours. It was observed that the colorless condensate obtained upon cooling to room temperature a reaction vessel containing a sample whose pressure had dropped below half

value, was more viscous than that obtained for shorter experiments; in a few very prolonged cases heavy oils were formed, and in one extreme instance the cell became coated with a brown iridescent film.[15] The normal condensate, certainly consisting chiefly of dimer, was capable of reëvaporation to the original pressure. It is significant that this vapor phase reaction gives as a product a dimer which is quite stable, and that the primary association is so much more rapid than any of the subsequent processes. This is quite different from usual polymerizations wherein isolation of so relatively simple a product is generally difficult due to much more rapid secondary steps, indicative of the presence of extremely reactive molecules, which leads to long chain reactions. However, some liquid phase reactions (mentioned hereinafter) have definitely yielded dimers.

A study was made of the pressure increments corresponding to the deviations from the strictly bimolecular rate as computed for the early part of the reaction to see if these deviations might be kinetically interpreted, but due to the experimental errors in determining small pressure changes for relatively long time intervals, the effort yielded only semi-quantitative results.

Only one reference on the dimerization of 1,3-butadiene has been located. Hoffmann (with Tank)[16] heated butadiene under pressure and obtained as a product a substance to which they ascribed the formula



It is claimed that this structure was confirmed by ozonization but unfortunately no experimental details or analyses are given.

Harries[17] and Ostromuislenskii[18] reported that they obtained 2,6-dimethyl-1,5,7-octatriene upon carefully controlled polymerization of isoprene. Wagner-Jauregg[19] claims on the basis of further experimental evidence that the material obtained by these two workers was identical with the *m*-menthadiene of Aschan.[20] It is interesting that also in the case of the polymerization of butadiene a dimer is obtained, and that the material may undergo further reaction.

In an effort to determine the precise composition of the dimer formed,

[15] It may be recorded that one sample of pure liquid butadiene sealed in a tube and left undisturbed for one year, lost its extreme mobility and became very viscous; a white solid appeared in the liquid.

[16] Hoffmann with Tank, *Z. angew. Chem.*, **25**, 1465 (1912).

[17] Harries, *Ann.*, **383**, 206 (1911).

[18] Ostromuislenskii, *J. Russ. Phys.-Chem. Soc.*, **47**, 1928 (1915).

[19] Wagner-Jauregg, *Ann.*, **488**, 176 (1931). See also Whitby and Crozier, *Canadian J. Research*, **6**, 203 (1932), for an extensive review and criticism of work on dimerization of isoprene.

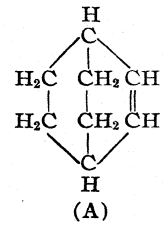
[20] Aschan, *Ann.*, **439**, 221 (1924); *Ber.*, **57**, 1959 (1924).

the products of Runs 39, 40 and 41 (see Table III) were removed from the reaction system at periods corresponding to approximately 70% conversion of monomer to dimer; after this interval the secondary polymerization becomes much more prominent and the product is undoubtedly a mixture. The material obtained up to 70% conversion is probably quite pure. The gases in the reaction vessel were frozen out with liquid air in an auxiliary trap separated from the main system by a stopcock; the liquid was then carefully purified by repeated vaporizations, recondensations and removal of gases which could be pumped off when the sample was at room temperature. The light, colorless liquid obtained was then fractionally distilled *in vacuo* and the last third rejected; a slight light yellow gummy residue was present in each of the three cases. The amounts of the final product were very small, in some cases being only a small fraction of a cc.; nevertheless a very excellent set of determinations was made upon these samples by Miss Gertrude M. Ware under the supervision of Professor J. B. Conant (Table II).[21]

TABLE II

Run	d_{25}	n (in Na light)	$\frac{n^2-1}{n^2+2}\frac{M}{d}$
39	0.867	1.469	34.75
40	.848	1.461	34.30
41	..	1.460	...

d_{25} is the density, n the refractive index and the last column gives the molecular refractivity, R, assuming the compound to be C_8H_{12} (M = 108). Calculated values of R for the various possible structures are as follows: for C_8H_{12} tricyclic, 32.55; dicyclic, one double bond, 34.28; open chain, two double bonds, 36.02; open chain, three double bonds, 37.74. While too great weight must not be given the data, due to the inherent errors, these figures indicate clearly that the compound in question is a dicyclic unsaturated hydrocarbon, for example (A). This structure may be derived from that proposed by Hoffmann.[16] A distinction between the two (and, indeed, any other possible structure, such as may be arrived at by considering 1,4-addition at the conjugated double bonds) could only be made by a chemical analysis of the product, and it is proposed that this will be done in the near future. This unexpected conclusion is borne out by a consideration of the density figures in Table II.



(A)

The densities of cyclopentadiene, cyclohexane, cyclohexadiene, methylcyclohexene and dimethylcyclohexadiene (monocyclic C_8H_{12}) are all below 0.830. The addition of another cyclic system increases the density considerably, as campholene (monocyclic C_9H_{16}), 0.803, and nopinane (dicyclic C_9H_{16}), 0.861, show.

[21] For the results given in Table II and aid in their interpretation, the author is deeply indebted to Professor Conant and Miss Ware.

Thus the data may be assumed to give, in the early part of the reaction, rate constants which represent the velocity of the association resulting in dimer formation. To obtain the average constant for a particular temperature, constructions of the type of Fig. 1 were made and an averaging curve plotted with extrapolation to 0% conversion. In Table III is presented a concise summary of data obtained in experiments with starting pressures in the range 100 to 720 mm.

TABLE III

Expt.	Temp., t, °C.	Initial pressure, mm.	$k \times 10^5$ (mm.$^{-1}$ min.$^{-1}$)	Comment
19	326	632.0		
20	325	245.2	2.50	80-cc. vessel
21	326	105.9		
11	341	700.0		
12	341	154.4	4.15	80-cc. vessel
13	343	356.3		
22	370	720.0	10.0	80-cc. vessel
23	370	221.1		
39	370	389.1	11.3	320-cc. vessel
40	370	375.1	11.1	320-cc. vessel
41	370	407.2	10.7	320-cc. vessel
15	388	378.0		
16	388	378.0	17.5	80-cc. vessel
17	388	720.0		
18	388	206.0		
24	370.5	241.0	9.8	80-cc. packed cell
25	370	211.2	10.9	80-cc.; 198.2 mm. propane added
27	371	111.5	10.5	80-cc.; 590.6 mm. propane added
26	371	192.7	10.1	80-cc.; 478.3 mm. nitrogen added
28	373	198.0	13.0	80-cc.; 8.9 mm. oxygen added
29	370.5	317.6	10.3	80-cc.; hexaphenylethane

Figure 2 is a plot of $\log_{10} k$ against $1/T$ for the experiments listed above with the exception of the last six ($k = Ae^{-E/RT}$). The slope as drawn corresponds to an energy of activation of 24,700 calories; this value is presumably accurate to within 1000 calories. Application of the equation $k = AT^{-1/2}e^{-E/RT}$ (k in pressure units), which is the more exact relationship, gives for E a value $RT/2$ calories greater, namely, 25,300.

The homogeneity of the reaction was tested both in preliminary runs and, as indicated, by No. 24. In this case a cell filled with lengths of Pyrex tubing was used; the net volume was the same as in Nos. 22 and 23 (80 cc.) while the surface area was 675 sq. cm. as compared to 120, a 5.6-fold increase. No significant change in rate is revealed. This is an interesting variation from the results of Pease,[8] who found a retardation of the ethylene polymerization by glass packing.

Added gases showed no effect. Tank propane at pressure ratios to that

of the butadiene of 1/1 and 5.5/1 caused no acceleration in rate. Similarly 99% pure nitrogen in a ratio 2.5/1 to butadiene was without evident result. These three experiments had exactly the same general trend as others at the temperature 371°; the rate constant gradually increased after a relatively long interval of constancy. Two runs were made wherein more butadiene was added during the course of the polymerization. No. 41 was one of these (see Table III) and the other, No. 6 (not given), showed the same trend. After 21.70 minutes, during which the rate constant increased from 10.7×10^{-5} (extrapolated value) to 12.3×10^{-5} for a pressure decrease corresponding to 49% conversion to dimer, 163.1 mm. of additional reactant was quickly added; the plot of k against time shows an unbroken

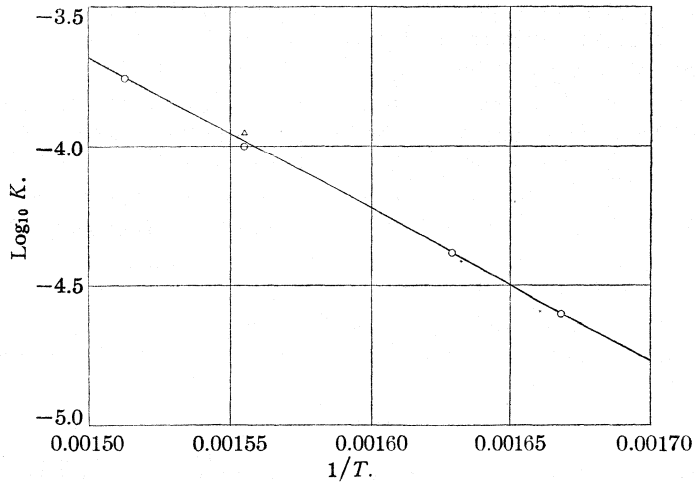


Fig. 2.—Log rate constant *vs.* $1/T$: △, 320-cc. vessel; ○, 80-cc. vessel.

trend; the change of k is quite unvaried and progresses slowly, being 47.8×10^{-5} at 92.85 minutes for a calculated residual pressure of butadiene of 49.5 mm. This effect would indicate that in all probability the secondary polymerization is one involving the association of molecules of dimer with monomer. Likewise the group of runs with "added gas" shows that molecules of quite diverse character are incapable of changing the rate.

The work of Conant and Peterson[22] shows conclusively that peroxides are extremely active catalysts in the promotion of the polymerization of isoprene at high pressures (3000–12,000 atm.). In order that the effect of oxygen might be determined, Run 28 (Table III) was made and it is seen that the rate is not radically altered by the presence of a considerable amount of oxygen. Traces of oxygen or of peroxides might have a very important effect and to examine this point, No. 29 was performed. Hexa-

[22] Conant and Peterson, THIS JOURNAL, **54**, 628 (1932).

phenylethane has a strong tendency to react with oxygen and was used with success by Conant and Peterson to lessen greatly the amount of peroxides in their isoprene, so that the rate was decreased ten-fold. Liquid butadiene was condensed on a sample of freshly prepared hexaphenylethane[23] and allowed to remain in contact with the solid for several minutes. The liquid was vaporized and its polymerization velocity determined. Even this treatment failed to alter the rate and it may reasonably be assumed that the general reaction is uncatalyzed.

The results of the low-pressure experiments are given in Table IV. Because of unsteadiness in the diaphragm gage it was necessary to increase progressively the temperature so as to obtain readable differences in pressure in sufficiently short time intervals. It was found that the precision of the measurements decreases greatly with decrease in pressures, as was indicated by the irregular plots of pressure *vs.* time. Runs 30 to 33 were quite consistent. For Runs 34 to 37, the averaging curve (pressure *vs.* time) was drawn in each case and the rate constant computed for several times in the interval over which the measurements were made. This procedure is not very satisfying and the values obtained are admittedly open to suspicion. Run 37 was of but 120 minutes' duration and only very approximate, and it was concluded that further extension of the pressure range was not feasible. Run 38 at the same temperature but with a "packed" cell of five times greater surface revealed that decomposition occurred under these conditions; blackening of the tubing slowly developed.

TABLE IV

Expt.	Temp., °C.	Initial pressure, mm.	Exptl. $k \times 10^{+5}$ (mm.$^{-1}$ min.$^{-1}$)	Extrap. $k \times 10^{5}$
30	380	105.5	15.0	
31	381	67.1	14.8	
32	381	29.22	15.5	14.0
33	381	32.78	15.2	
34	382	6.92	15	
35	394	2.98	20	20.4
36	414	2.53	60	35.8
37	436	1.50	290	62.2

In the last column is listed the value of k as determined by extrapolation of the curve of Fig. 2 which is expressible by the equation $\log k = -5390\,(1/T) + 4.394$. The experimental values of k for Nos. 36 and 37, coupled with the described behavior of No. 38, show definitely that the reaction is no longer simple beyond 394° and these data are not interpretable. It is to be observed that in the pressure range studied no falling off of the rate constant is noted.

[23] This material was received from Professor James B. Conant and Mr. B. F. Chow, and to them the author expresses his indebtedness.

Discussion

The slope of the curve in Fig. 2 corresponds to an energy of activation of 24,700 cal. for the reaction $2C_4H_6 \longrightarrow C_8H_{12}$. The Maxwellian distribution factor for molecules possessing in one degree of freedom this amount of energy at a temperature of 614°K. is 1.66×10^{-9}. The number of collisions per cc. in each second is given by the equation[24]

$$Z = 2N^2\sigma^2\sqrt{\frac{\pi kT}{m}}$$

wherein N is the number of molecules per cc., σ the diameter and m the mass of each particle. At $T = 614$°K. and a concentration of one mole per liter, a value of the diameter of 4.5×10^{-8} cm. gives $Z = 8.10 \times 10^{31}$. If each collision of suitably activated molecules results in reaction, the rate of disappearance of butadiene should be given by $2Z$ times the exponential since two molecules take part in each collision; this product is equal to 4.44×10^2 in liter moles^{-1} sec.$^{-1}$. The value of k determined by experiment is 2.65×10^{-2} expressed in liter moles^{-1} sec.$^{-1}$. The ratio of the observed and calculated rates is 1/16,800. If the value of 25,300 calories for E is used, the ratio becomes 1/10,300. These ratios, coupled with the data of Pease[8,11] that the efficiency of the ethylene polymerization is 1/2000 and for the hydrogenation of ethylene, 1/10, strongly indicate the dependence of the efficiency upon the size and complexity of the molecule. As Kassel points out,[9] although he conclusively shows the possibility with a high probability of the formation of association complexes by collisions of large molecules wherein energy and quantum conditions are satisfied, his treatment naturally neglects the determination of the total efficiency which will be dependent upon specific factors.

Thus the process may be considered as precisely the reverse of the unimolecular mechanism. The following series illustrates the idea

Complex $\longleftrightarrow$ Activated complex $\longleftrightarrow$ Unstable complex $\longleftrightarrow$ Activated products
(1) (2) (3) (4)

Unimolecular course: (1) $\longrightarrow$ (4)

(1) $\rightleftharpoons$ (2) Activation by collision and concurrent deactivation
(2) $\rightleftharpoons$ (3) Redistribution of energy
(3) $\longrightarrow$ (4) Dissociation

Bimolecular course: (4) $\longrightarrow$ (1)

(4) $\rightleftharpoons$ (3) Association upon collision of suitably activated molecules; dependent upon orientation. Reversible
(3) $\rightleftharpoons$ (2) Redistribution of energy
(2) $\longrightarrow$ (1) Stabilization upon collision.

The unimolecular course need not be discussed. The bimolecular or reverse reaction consists in the steps as listed. Two suitably energy-rich particles may, if properly oriented, combine with each other. This quasi-

[24] Tolman, "Statistical Mechanics," Chemical Catalog Co., N. Y., 1927, p. 242.

molecule may immediately decompose, or the excess energy may be redistributed among the various bonds, giving a more stable complex whose life would be sufficiently long to permit final stabilization by another collision. It may be further assumed that this stabilization will occur on every collision. It is essentially the assumption made in the unimolecular reaction theory and which has proved to be so useful. That no falling off of the rate (transition to a third order course) has been observed even at 3 mm. pressure, is perhaps not astonishing. The product formed here is of the same degree of complexity as azoisopropane, in the case of which no falling off of the rate has been detected even at 0.8 mm. pressure.[25]

The fact that the hydrogen–ethylene reaction occurs on every tenth collision is excellent evidence in favor of Kassel's contention that for polyatomic molecules, quantization rules present no serious obstacles for association processes. Then, *a fortiori*, these limitations should be even less binding in the process of the production of yet more complex molecules such as butylene and the dimer here formed. Thus one is led to the conclusion that the lower yields observed in these cases are primarily due to a steric factor: the more complex are the associating molecules, the more precise must be their relative orientation at the moment of collision to achieve reaction.

It is planned to continue these polymerization studies to test further these ideas.

The Vapor Pressure of 1,3-Butadiene

After the completion of the polymerization experiments, there remained a considerable quantity of butadiene and inasmuch as the vapor pressure–temperature dependence had never been measured and there was immediately available the necessary apparatus, it was decided to determine the relationship.

The temperatures were measured by means of a triple junction copper–constantan thermopile in the circuit of the potentiometer used in the previous study. The instrument was calibrated by the use of the melting points of ammonia (−77.7°), mercury (−38.87°), carbon tetrachloride (−22.9°), carbon disulfide (−111.6°) and the ice point; the warm set of junctions of the thermopile was kept in ice water. All of these five points lay on a smooth curve. The butadiene was carefully redistilled three times before use and was then brought into a trap in immediate communication with a mercury manometer.

The data are given in Table V. Each point was checked, some as many as three times.

The plot of $\log_{10} p$ against $1/T$ is shown in Fig. 3; the equation of the line is $\log_{10} p = -1275\ (1/T) + 7.615$. The heat of vaporization as determined therefrom is 5844 cal. The boiling point is found to be −4°.

[25] Ramsperger, THIS JOURNAL, **50**, 714 (1928).

TABLE V

VAPOR PRESSURE OF 1,3-BUTADIENE

Pressure, mm.	Temp., °C.	Pressure, mm.	Temp., °C.
9.2	−81.9	442.7	−17.0
11.0	−79.1	772.4	− 3.1
156.9	−38.5	862.6	+ 0.5
327.5	−24.0		

Another experiment was performed to determine the melting point. Butadiene frozen with liquid air was allowed to warm slowly in a stirred chilled bath of gasoline, wherein the thermopile was immersed; the melting point of the solid was found to be −105° (average of two experiments).

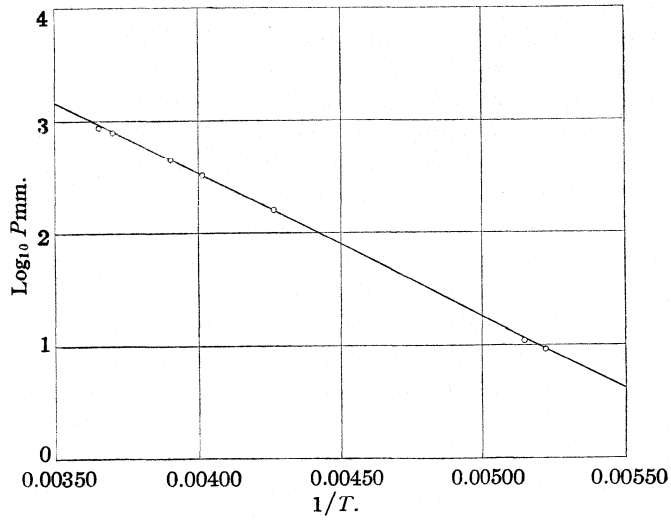


Fig. 3.—Vapor pressure of 1,3-butadiene.

The author is pleased to take this opportunity to extend to Professor G. B. Kistiakowsky his very sincere thanks for the active aid and stimulation received during the period of our recent association.

Summary

1. The kinetics of the thermal homogeneous polymerization of 1,3-butadiene have been investigated over the pressure range 720 to 1.5 mm. and a temperature interval of 326 to 436°. The reaction follows a strictly bimolecular course over the greater portion of the association.

2. The rate is expressible by the formula $\log_{10} k = -568_0 (1/T) + 7.673$ (k in liter·mole^{-1} sec.$^{-1}$).

3. The kinetic mechanism is discussed.

4. The vapor pressure–temperature dependence of 1,3-butadiene has

been measured in the interval -82 to $0°$; the equation is $\log_{10} p = -1275 (1/T) + 7.615$. ($p$ in mm.); m. p. $= -105°$; b. p. $-4°$.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE FIVE-ELECTRON PROBLEM IN QUANTUM MECHANICS AND ITS APPLICATION TO THE HYDROGEN–CHLORINE REACTION

BY G. E. KIMBALL AND H. EYRING

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Calculations of Rollefson and Eyring[1] point to the probable formation of Cl_3 molecules when chlorine atoms collide with chlorine molecules. To determine from perturbation theory whether such triatomic molecules react more rapidly with hydrogen molecules than do chlorine atoms requires a knowledge of at least the five-electron problem, since five valence electrons change partners in the process. It has been suggested recently by Franck and Rabinowitz[2] and more explicitly by Bodenstein[3] that the reaction $H + Cl_2 + H_2 = 2HCl + H$ might be an essential step in the photochemical combination of hydrogen and chlorine. To treat this reaction we again require a knowledge of the five-electron problem.

In the first part of the present paper we have used Slater's[4] method to solve the problem of five electrons with spin degeneracy and have given the rules for finding the eigenfunction corresponding to an arbitrary number of valence bonds between designated atoms. The energy levels can of course be found for more than five or six electrons but the labor becomes extremely great. In the second part of this paper we examine the reactions which might be expected to play important roles in the hydrogen–chlorine reaction.

The Five-Electron Problem.—We shall assume that the reader is familiar with Slater's treatment of the three- and four-electron problems, and shall use the same notation. We refer those desiring a fuller treatment than that given here to the thesis by one of us (G. E. K.).

If the eigenfunctions of the five electrons are $a(1)$, $b(2)$, $c(3)$, $d(4)$, $e(5)$, then the product $a(1)\, b(2)\, c(3)\, d(4)\, e(5)$ is a solution of Schrödinger's equation when the atoms are far apart. Any one of the 120 eigenfunctions obtained by permuting the electrons will likewise be a solution. As the atoms approach one another certain linear combinations of these eigenfunctions will form the "zero order" approximation to the solution.

[1] Rollefson and Eyring, THIS JOURNAL, **54**, 170 (1932).

[2] Franck and Rabinowitz, *Z. Elektrochem.*, **36**, 794 (1930).

[3] Bodenstein, *Trans. Faraday Soc.*, **27**, 413 (1931).

[4] Slater, *Phys. Rev.*, **38**, 1109 (1931).

Although the form of the eigenfunctions a to e will not appear explicitly in the solution, they may be thought of as those linear combinations of the available atomic eigenfunctions which lead to the lowest energy for the system. The evaluation of the resulting integrals from spectroscopic data avoids the difficult application of a variation method and the resulting computation.

Our problem is essentially simplified by introducing the Pauli principle at this point. Each of the electron eigenfunctions a to e is multiplied by a spin eigenfunction α or β, α representing a spin of $+1/2$, β a spin of $-1/2$. The total number of eigenfunctions resulting is $2^5 \times 120 = 3840$, but Pauli's principle immediately limits us to the 32 possible antisymmetric combinations of the form

$$\psi = \frac{1}{\sqrt{5!}} \sum \pm P(a\alpha(1)b\alpha(2)c\beta(3)d\beta(4)e\alpha(5)) \qquad (1)$$

the sum being taken over all possible permutations P of the indices 1, 2, . . . 5 each multiplied by $+1$ or -1 as the permutation P is even or odd. The factor $1/\sqrt{5!}$ approximately normalizes ψ. The summation in (1) is frequently written as a determinant.

The first order energy levels are given by the 32 roots of the secular equation formed from these 32 eigenfunctions, but since eigenfunctions corresponding to different total spins do not combine, the secular determinant is already factored into the product of six determinants of orders, 1, 5, 10, 10, 5 and 1, corresponding to total spins of 5/2, 3/2, 1/2, $-1/2$, $-3/2$ and $-5/2$. The energies of the five doublet states (one of which corresponds to the lowest energy) are five of the ten roots of the tenth order determinant corresponding to a total spin of 1/2. The ten eigenfunctions forming the basis of this determinant are indicated as follows

	a	b	c	d	e		a	b	c	d	e
ψ_1	α	α	α	β	β	ψ_6	α	β	α	β	α
ψ_2	α	α	β	α	β	ψ_7	β	α	α	β	α
ψ_3	α	β	α	α	β	ψ_8	α	β	β	α	α
ψ_4	β	α	α	α	β	ψ_9	β	α	β	α	α
ψ_5	α	α	β	β	α	ψ_{10}	β	β	α	α	α

(2)

Each ψ_i corresponds to an eigenfunction of the type (1) in which the electronic eigenfunction at the top of the column is multiplied by the spin eigenfunction indicated. For example, eigenfunction ψ_5 is the particular eigenfunction given in (1).

By taking linear combinations of the ten eigenfunctions (2) the secular equation can be reduced even further. The three sets of linear combinations may be regarded as representing the system of five atoms with two valence bonds, one valence bond and no valence bond. In order to find these linear combinations we define a function $\delta_{mn}(K)$ for each eigen-

function ψ_K, and each pair of electron eigenfunctions ab, ac, etc., as follows: $\delta_{mn}(K)$ is $+1$ if the spin of m is α and the spin of n is β in ψ_K, -1 if the spin of m is β and that of n is α, and 0 if the spins of m and n are the same. Then if we wish a linear combination of the eigenfunctions representing the system with bonds between a and b, and c and d, the desired eigenfunction is $\sum_{K=1}^{10} \delta_{ab}(K)\,\delta_{cd}(K)\,\psi_K$. There are fifteen such eigenfunctions representing two valence bonds, but only five are linearly independent. We choose the following

$$\begin{aligned}
\varphi_1 &= {}^1/_2(\psi_6 - \psi_8 + \psi_9 - \psi_7)\\
\varphi_2 &= {}^1/_2(\psi_8 - \psi_9 + \psi_4 - \psi_3)\\
\varphi_3 &= {}^1/_2(\psi_3 - \psi_{10} + \psi_7 - \psi_5)\\
\varphi_4 &= {}^1/_2(\psi_2 - \psi_8 + \psi_{10} - \psi_4)\\
\varphi_5 &= {}^1/_2(\psi_6 - \psi_{10} + \psi_4 - \psi_1)
\end{aligned} \tag{3}$$

There are four linearly independent eigenfunctions of the type $\sum_K \delta_{mn}(K)\,\psi_K$ corresponding to the system with one valence bond. Those we have chosen are

$$\begin{aligned}
\varphi_6 &= \frac{1}{\sqrt{6}}(\psi_3 - \psi_4 + \psi_6 - \psi_7 + \psi_8 - \psi_9)\\
\varphi_7 &= \frac{1}{\sqrt{6}}(\psi_2 - \psi_4 + \psi_5 - \psi_7 + \psi_8 - \psi_{10})\\
\varphi_8 &= \frac{1}{\sqrt{6}}(\psi_1 - \psi_4 + \psi_2 - \psi_4 + \psi_3 - \psi_{10})\\
\varphi_9 &= \frac{1}{\sqrt{6}}(\psi_1 - \psi_7 + \psi_2 - \psi_9 + \psi_3 - \psi_{10})
\end{aligned} \tag{3}$$

Finally, corresponding to the system with no bonds, there is

$$\varphi_{10} = \frac{1}{\sqrt{10}}(\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6 + \psi_7 + \psi_8 + \psi_9 + \psi_{10}) \tag{3}$$

It is now found that the φ's corresponding to different numbers of bonds do not combine. The energies we wish are those of the system with two valence bonds. These are the five roots of the secular equation

$$|\,H_{ij} - Wd_{ij}\,| = 0 \tag{4}$$

where

$$H_{ij} = \int \varphi_i^*\, H\varphi_j\, d\tau \qquad (i,j = 1,2,3,4,5)$$

$$d_{ij} = \int \varphi_i^*\, \varphi_j\, d\tau$$

and

$$H_{ij} = H_{ji}$$

If we denote the integral called by Slater $(abcde\,|\,H\,|\,abcde)$ by Q, and the integrals of the type $(abcde\,|\,H\,|\,bacde)$ by ab, and neglect the small integrals involving more than one interchange, and, moreover, assume that the eigenfunctions $a, b, \ldots . e$ are orthogonal. the elements H_{ij} are

$$
\begin{aligned}
H_{11} &= Q + ab + cd - {}^1/_2(ac + ad + ae + bc + bd + be + ce + de)\\
H_{22} &= Q + ab + ce - {}^1/_2(ac + ad + ae + bc + bd + be + cd + de)\\
H_{33} &= Q + ac + bd - {}^1/_2(ab + ad + ae + bc + be + cd + ce + de)\\
H_{44} &= Q + ac + be - {}^1/_2(ab + ad + ae + bc + bd + cd + ce + de)\\
H_{55} &= Q + ad + be - {}^1/_2(ab + ac + ae + bc + bd + cd + ce + de)\\
H_{12} &= -{}^1/_2Q + de + {}^1/_4(ad + ac + ae + bc + bd + be) - {}^1/_2(ab + cd + ce)\\
H_{13} &= -{}^1/_2Q + ad + bc + {}^1/_4(ae + be + ce + de) - {}^1/_2(ab + ac + bd + cd)\\
H_{14} &= {}^1/_4Q + {}^1/_4(ab + ac + bd + be + cd + ce) - {}^1/_2(ad + ae + bc + de) \qquad (5)\\
H_{15} &= {}^1/_4Q + {}^1/_4(ab + ad + bc + be + cd + de) - {}^1/_2(ac + ae + bd + ce)\\
H_{23} &= {}^1/_4Q + {}^1/_4(ab + ac + bd + be + cd + ce) - {}^1/_2(ad + ae + bc + de)\\
H_{24} &= -{}^1/_2Q + ae + bc + {}^1/_4(ad + bd + cd + de) - {}^1/_2(ab + ac + be + ce)\\
H_{25} &= {}^1/_4Q + {}^1/_4(ab + ac + ad + be + ce + de) - {}^1/_2(ae + bc + bd + cd)\\
H_{34} &= -{}^1/_2Q + de + {}^1/_4(ab + ad + ae + bc + cd + ce) - {}^1/_2(ac + bd + be)\\
H_{35} &= {}^1/_4Q + {}^1/_4(ac + ad + ae + bc + bd + be) - {}^1/_2(ab + cd + ce + de)\\
H_{45} &= -{}^1/_2Q + cd + {}^1/_4(ab + ae + bc + bd + ce + de) - {}^1/_2(ac + ad + be)
\end{aligned}
$$

while the d_{ij} are simply the coefficients of Q in the H_{ij}. These integrals may be found from the spectroscopically determined potential energy curves for diatomic molecules if the eigenfunctions are on different atoms. If two eigenfunctions are on the same atom the integrals may be obtained from the atomic spectrum. This manner of evaluating the integrals probably partially compensates for the approximation involved in neglecting the lack of orthogonality of the eigenfunctions.

In this way we can assign definite numerical values to all the quantities occurring in equation (4) for any configuration of five univalent atoms. By constructing a graph of the determinant on the left side of equation (5) against W, the roots may be obtained to any desired degree of approximation. The lowest root is the desired energy of the configuration. Such calculations have been carried out in certain interesting cases.

The solution of the problem of n electrons may be carried out in the same way. After forming the 2^n antisymmetric eigenfunctions of the type (1), we pick out the set of lowest spin S ($S = 0$ if n is even; $S = {}^1/_2$ if n is odd). From this set of $n!/[(n/2 + S)!\ (n/2 - S)!]$ eigenfunctions, ψ_K, we now take the linear combinations $\sum_K \delta_{mn}(K) \ldots \delta_{rs}(K)\,\psi_K$ corresponding to the maximum number of bonds. From these we pick the largest possible set of linearly independent combinations, $\varphi_1 \ldots \varphi_f$, where $f = (2S+1)n!\Big/\left(\frac{n}{2}+S+1\right)!\left(\frac{n}{2}-S\right)!$, and set up the secular equation on these f eigenfunctions. In this way the six-electron problem has been carried through.[5] The solutions of the seven- and eight-electron problems involve fourteenth order secular equations even after all of this reduction has been carried out.

Application.—The application of this theory must be treated with some care. Because of the uncertainty in determining the ratio of coulombic

[5] Sherman and Eyring, THIS JOURNAL, **54**, 2661 (1932).

to interchange energy, the absolute value of any activation energy is rather unreliable. If the coulombic part of the energy of a diatomic molecule is taken to be 10% of the total, the results will in general be too high. Nevertheless, if all the activation energies are calculated on this basis, it is very improbable that the relative magnitudes will be wrong (except in very close cases). The theory in its present state may be used to greatest effect in deciding which of a number of possible reactions between a given set of reactants is the most likely to take place. For example, Eyring[6] showed that the reaction between H_2 and Cl_2 goes more rapidly through the atoms than by the direct reaction. A similar result holds for the reaction of H_2 and Br_2, but H_2 and I_2 react more easily directly.

In constructing the Morse curves used in the calculation which follows we have used the constants

	r_0	ω_0	D	D'
HCl	1.28	2940.8	101.5	105.7
Cl_2	1.98	565	57.0	57.8
H_2	.74	4375	101.5	107.5
OH	.98	3660	113	118

Here r_0 is the distance between atoms in the normal state; ω_0 the corresponding vibrational frequency in wave numbers; D is the heat of dissociation in kg. cal. and D' is D plus a half quantum of vibrational energy.

The applications we shall make are to some of the reactions which have been proposed to account for the observed phenomena of the photochemical reaction between hydrogen and chlorine. Here the primary process is certainly

$$Cl_2 + h\nu = 2Cl \qquad (1)$$

The chlorine atoms are not formed in the same state, for one is in the normal $^2P_{3/2}$ state while the other is in the excited $^2P_{1/2}$ state, the energy of excitation amounting to 2.5 kg. cal. This energy is not enough, however, to change any of our conclusions. Now it has been shown by Rollefson and Eyring[1] that at room temperature most of these chlorine atoms react with chlorine molecules

$$Cl_2 + Cl = Cl_3 \qquad (2)$$

The question immediately arises, is the chain carried on by Cl or Cl_3? The reaction

$$Cl + H_2 = HCl + H \qquad (3)$$

was one of those studied by Eyring, who found an activation energy of 14 kg. cal. The potential energy surface has been drawn completely, and is shown in Fig. 1. It will be seen that the activation energy is 16 kg. cal. (The difference between this value and that given by Eyring is due to his use of an approximation formula.) In order to compare this activation energy with that of the reaction

$$Cl_3 + H_2 = Cl_2 + HCl + H \qquad (4)$$

[6] Eyring, THIS JOURNAL, 53, 2537 (1931).

the energies of two corresponding points on the potential energy surfaces were found. The Cl_3 molecule has the three Cl atoms in a straight line with a separation practically equal to the distance between Cl atoms in Cl_2. The configurations which were chosen were, therefore, of the form

$$\underset{}{Cl}\text{——}\underset{a}{Cl}\text{——}\underset{b}{Cl}\text{——}\underset{c}{H}\text{——}\underset{d}{H}$$

In the first configuration the distances were $a = 1.74$, $b = 1.74$, $c = 1.28$, $d = 0.76$ Å. The activation energy of this configuration was found to be 31 kg. cal., whereas for the system Cl–H–H with the same distances the activation energy was 22 kg. cal. The other configuration had $a = 1.74$, $b = 1.74$, $c = 1.45$, $d = 0.90$ Å. The energy was found to be 20.5 kg. cal., against 16 kg. cal. for Cl–H–H. These figures indicate that the activation energy of reaction (4) is higher than that of reaction (3) by about 5 kg. cal. The accuracy of this result is probably not high, but the conclusion that reaction (3) is the faster of the two is quite certain.

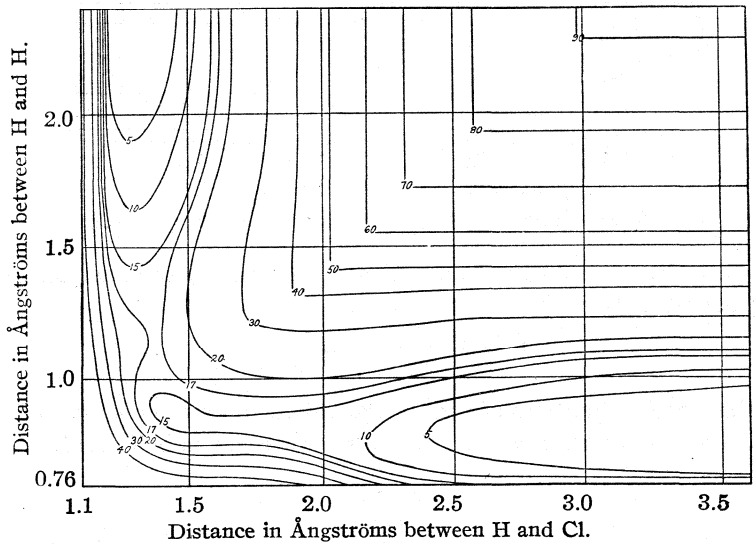


Fig. 1.—Potential energy in kg. cal. of the system H–H–Cl.

The activation energy of reaction (3) seems rather high for such a fast reaction as the hydrogen–chlorine reaction is known to be. In order to avoid this difficulty a mechanism has been proposed by Franck and Bodenstein[2,3] in which the hydrogen atoms formed at some stage in the chain (either from (3) or some reaction involving H_2O) react by

$$H + Cl_2 + H_2 = 2HCl + H \qquad (5)$$

rather than by

$$H + Cl_2 = HCl + Cl \qquad (6)$$

Now reaction (6) was found by Eyring to have no activation energy, and the complete potential energy surface (Fig. 2) shows an activation energy

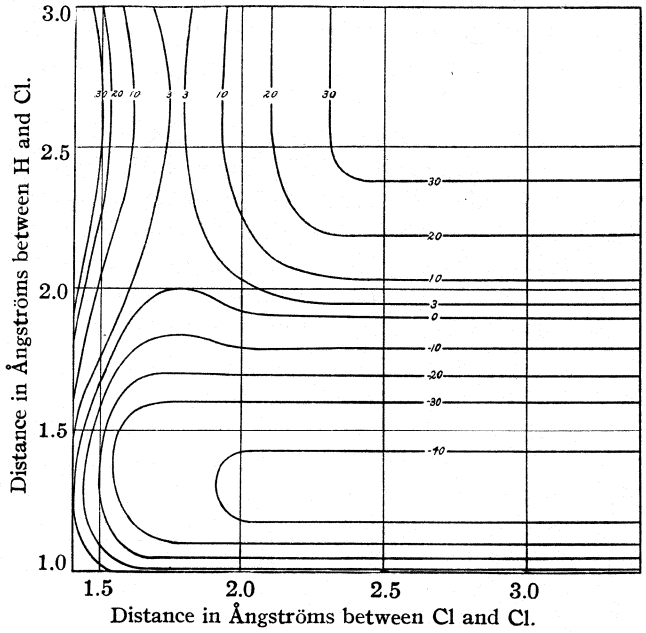


Fig. 2.—Potential energy in kg. cal. for the system H–Cl–Cl.

of only 3 kg. cal. In order to investigate reaction (5) the energies of the configurations of the type

$$\underset{a}{\text{H}}\text{——}\underset{b}{\text{Cl}}\text{——}\underset{c}{\text{Cl}}\text{——}\underset{d}{\text{H}}\text{——}\text{H}$$

were calculated. The zero of energy was taken to be the energy of H, H_2 and Cl_2 at a large distance apart. The results are shown in Table I.

TABLE I

Configuration	Distances, Å. a	b	c	d	Energy, kg. cal.
1	1.28	1.74	2.30	0.76	−37
2	1.28	1.74	1.90	.76	−16
3	1.28	1.74	1.61	.76	−16
4	1.28	1.74	1.28	.76	− 5
5	1.28	2.04	1.28	.76	−11
6	1.28	2.49	1.28	.76	−15
7	2.50	1.74	1.28	.76	19

In order to interpret these results let us consider a complex H–Cl–Cl with the distances $a = 1.28$, $b = 1.74$. When the complex has reached this configuration, it is easily seen from Fig. 2 that reaction (6) has to all

intents and purposes already taken place. Most of the energy of the reaction has been converted into kinetic energy. If now a hydrogen molecule is brought up to the complex we first reach configuration 1. As the hydrogen molecule comes nearer the system passes through configurations 2, 3 and finally 4. During this process the potential energy of the system is always less than zero, so that it might be thought that configuration 4 could be reached. A closer analysis shows that this is not the case. When the hydrogen molecule first arrives, the rest of the system is not stationary. The kinetic energy of the system consists mainly of translational energy of the Cl atom and HCl molecule separating. Now in order to prevent the system from flying apart, the hydrogen molecule must stop this motion. In order to do this a large momentum is necessary. Since the mass of the chlorine atom is 17.5 times that of the hydrogen molecule, this requires that the velocity of the hydrogen atom be 17.5 times that of the chlorine atom. Since such a velocity would correspond to an energy of some 350 kg. cal., we must conclude that it is practically impossible to reach configuration 4.

Configurations 5 and 6 indicate that conditions are not greatly improved by allowing the Cl to separate a little from the HCl. Since it seems impossible to make reaction (5) proceed after the system has passed the point of activation for reaction (6), the only hope for reaction (5) is that the presence of a hydrogen molecule will lower the energy of the point of activation. But configuration 7 shows that instead of being lowered the energy is raised by some 16 kg. cal., and we must conclude that reaction (5) cannot take place.

In 1927 a series of experiments was carried out by Coehn and Jung[7] which led them to believe that complete desiccation of a hydrogen–chlorine mixture prevented the reaction in visible light. In order to explain this phenomenon many reaction chains were suggested which involved water at some step. Recently attempts to duplicate this result have been made in Bodenstein's laboratory,[8] and have failed to find any such effect. Nevertheless, we have carried out some calculations on the reaction of Cl atoms with water. These calculations are less certain than the others, for the potential energy curve for the molecule Cl–O is not known. However, it was found that a large variation in this curve made little change in the activation energy, since the largest interaction energy amounted to some 4 kg. cal. Since one of the hydrogen atoms of the water molecule remains with the oxygen atom throughout the reaction, its effect, and that of the valence electron of the oxygen binding this hydrogen atom to it, was neglected. The water molecule was, therefore, treated as an hydroxyl molecule. Fig. 3 shows the potential energy of the system Cl–H_2O when the

[7] Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1927).

[8] Private communication.

Cl, O and the H which takes part in the reaction lie in a straight line. In this case there is a deep hollow, showing that a molecule (ClH_2O) may be

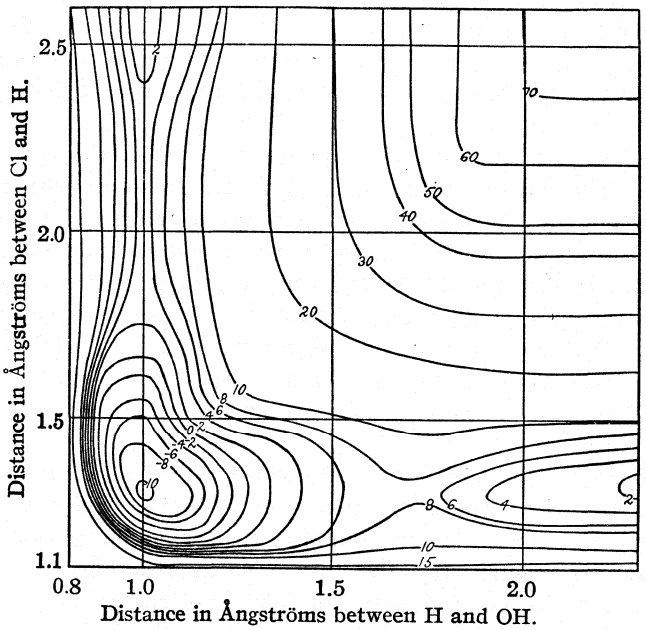


Fig. 3.—Potential energy in kg. cal. of the system Cl–H–OH.

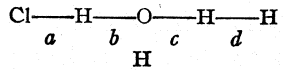
formed. The reaction $Cl + H_2O = ClH_2O$ has an activation energy of 4 kg. cal. With an activation energy of 8 kg. cal. the reaction

$$Cl + H_2O = HCl + OH \qquad (7)$$

can take place. The reaction

$$Cl + H_2O + H_2 = HCl + H_2O + H \qquad (8)$$

has also been suggested. In order to estimate its activation energy the energies of the configurations



were calculated. The energies are shown in Table II.

TABLE II

Distances, Å.				
a	*b*	*c*	*d*	Energy, kg. cal.
1.28	0.98	0.98	0.76	25
1.28	0.98	1.20	0.76	15
1.28	1.40	0.98	0.76	25

The activation energy must, therefore, be in the neighborhood of 25 kg. cal. (The activation energies of reactions (7) and (8) were calculated

using a value of 104 kg. cal. for the heat of dissociation of the OH bond. The value 113 kg. cal. is probably better. This would raise the activation energy of each reaction by about 9 kg. cal.)

Since the reaction of OH with H_2 is known to be slow (we find an activation energy of 8 or 17 kg. cal. according to whether the heat of dissociation of OH is taken to be 104 or 113 kg. cal.) it does not seem possible that water can be of any assistance to the hydrogen–chlorine reaction.

If all the activation energies we have obtained were numerically correct, it would appear that it was impossible for hydrogen and chlorine to combine at all at room temperature. Nevertheless, we do not claim any great accuracy for these figures A change in the ratio of coulombic energy to interchange energy from 9:1 to 6:1 would lower the activation energy of reaction (3) to the neighborhood of 7 kg. cal., which would agree quite well with experiment. The other activation energies would also be lowered, but all in approximately the same ratio. The conclusions that reaction (3) goes faster than reaction (4), and (6) faster than (5), would not be changed. It would, therefore, seem that if the hydrogen–chlorine reaction proceeds through any of the reactions we have considered, it must go by the Nernst chain

$$Cl + H_2 = HCl + H$$
$$H + Cl_2 = HCl + Cl$$

Summary

1. Slater's method of finding the energy of three and four atoms has been extended to five monovalent atoms, and the general method is outlined.

2. By means of this result the activation energies of the reactions

$$Cl_3 + H_2 = Cl_2 + HCl + H$$
$$H + Cl_2 + H_2 = 2HCl + H$$
$$Cl + H_2O + H_2 = HCl + H_2O + H$$

have been calculated. The results indicate that none of these reactions takes part in the photochemical reaction between hydrogen and chlorine.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE ANATOMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A DEVICE FOR INCREASING THE EFFECTIVENESS OF FREEZING MIXTURES[1]

BY RAYMOND C. ARCHIBALD

RECEIVED MAY 24, 1932 PUBLISHED OCTOBER 5, 1932

The difficulty in obtaining temperatures below $-15°$ with sodium chloride–ice mixtures in the laboratory is well known. The device pictured here was designed to overcome this difficulty. The apparatus consists of two concentric cylinders made of 8-mesh per inch (3-mesh per cm.) wire screen with a common bottom of the same material. This is made to fit easily inside of a standard one gallon wide-mouthed vacuum food jar. Crushed ice is placed in the vacuum jar and rock-salt (sodium chloride) in the annular space in the basket. The jar is then filled well up in the basket with brine or water. If water is used to start, rather than brine, the ice tends to cake together at first. If one breaks this cake after a few minutes, however, the action proceeds as if brine were used. Convection starts immediately, the dense, concentrated brine moving downward next to the walls, and the colder, more dilute, brine rising in the center.

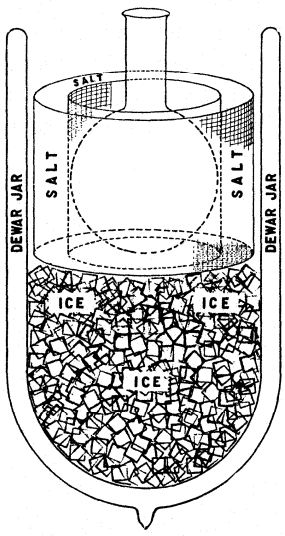


Fig. 1.—A device for obtaining temperatures close to the eutectic temperature of salt–ice mixtures. Material used is 8-mesh wire screen. A 500-cc. flask is pictured.

In tests made on this device the temperature of the brine in the center space dropped to $-18°$ in ten minutes, and to $-20.5°$ within thirty minutes after starting. It held this temperature approximately until practically all the ice had melted, which, starting with the vacuum jar half full of ice, was about twenty-four hours when the top was covered with a folded towel to keep out air currents. It is not necessary to have the jar covered in order to reach the low temperature obtained here.

A test was also made using an ordinary tin can of the proper size (a 5-lb. ether can) instead of the vacuum jar. In this case it cooled somewhat more slowly, reaching $-13°$ after ten minutes, and $-18°$ after thirty minutes. The minimum temperature, -18 to $-18.5°$ was held for about two hours, after which time the ice was gone. If the can were insulated with sawdust, its performance would doubtless approach that of the vacuum jar.

[1] While the author has no patent or other limitation on the use of this idea, it is perhaps of interest that the Central Scientific Company, Chicago, Illinois, has agreed to make these devices in various sizes on order.

The ice used for these tests was crushed, averaging 1 or 2 centimeters in dimensions. When a single large piece of ice was used the temperature dropped very slowly, reaching $-14°$ in one and one-half hours. A lower temperature would probably be reached if sufficient time were given. If snow or shaved ice were used the cooling would probably be rather slow also, since the packing of the snow would hinder convection.

The inside cylinder of the basket is made to take a 500-cc. flask or an 800-cc. beaker. As a test, using the vacuum jar, 500 cc. of ethyl alcohol was put in a flask at room temperature, and the flask placed in the already cold brine. At the end of half an hour the alcohol was lightly stirred for a moment and its temperature was read as $-17°$. At the end of the first hour the temperature was down to $-20.5°$. During the observations the temperature dropped as low as $-20.8°$ and it might have approached the eutectic temperature of $-21.1°$ even more closely.

Obviously this device may also be used with other salts and mixtures of salts. However, temperatures below $-30°$ are difficult to obtain with calcium chloride (either alone or with the aid of sodium chloride) because of the unfavorable heat relations and because of the decreased convection due to the greatly increased viscosity.

This device is a double application of the "dissolving cone" principle.[2] A further modification has been successfully used for many years by Professor W. C. Bray of the Chemistry Department for maintaining unstirred water-baths close to 0°. Since water has a maximum density at about 4°, Professor Bray uses a screen or cage to hold the crushed ice near the bottom of the 0° bath.

[2] "The Laboratory," Fisher Scientific Co., Pittsburgh, Pa., Vol. V, No. 1, p. 10, 1932.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY]

FURTHER STUDIES IN THE RARE GASES. I. THE PERMEABILITY OF VARIOUS GLASSES TO HELIUM[1]

BY WM. D. URRY[2]

RECEIVED MAY 27, 1932 PUBLISHED OCTOBER 5, 1932

During the course of a research[3] on the computation of the age of iron meteorites by the "Helium method"—the ratio of helium to uranium and thorium—it was necessary to determine the loss of helium on heating for

[1] The following paper presents the results of experiments on the diffusion of helium and hydrogen through Pyrex glass, Jena 16''' glass, soda glass and lead glass. The results are discussed from a theoretical standpoint in formulating a theory of the mechanism of the diffusion process.

[2] Henry E. Johnston Scholar at the Johns Hopkins University.

[3] Paneth and Urry, *Z. physik. Chem.*, **A152**, 127 (1931).

several hours in a vacuum at 1000°. This loss was surprisingly low, being in no case greater than 6.0% of the total helium content. It therefore became of interest to ascertain if possible how the radioactively produced helium is so tightly bound in the iron–nickel structure and eventually to apply the principle to the minerals, basalts, etc., which have recently been microanalyzed for helium, radium and thorium. Before attempting to make measurements on such factors as adsorption, solubility and diffusion of helium through crystalline substances, these factors have been determined for supercooled liquids.

The diffusion of helium through many types of glass is now a well-established fact. Paneth and Peters,[4] who have showed an extremely sharp differentiation between the diffusion of helium and neon through hot glass, have ably summarized the literature on the diffusion effects. Apart from the work of Williams and Ferguson,[5] who have made a few measurements at comparatively high temperatures through silica glass, no attempt has been made to determine accurately the effect of the variables, pressure, temperature and constitution of the glass.

Experimental

The apparatus shown in Fig. 1 is sealed at A to the "Analysis apparatus" for the study of minute quantities of the rare gases, developed in the laboratory of Professor Paneth and used by the author in several series of researches. In its present form it is best described in a lecture publication to the Bunsen Gesellschaft, 1928, forming "Heliumuntersuchungen."[3,6] The apparatus is also connected to the pumping system through stopcock 1. C represents the diffusion apparatus, immersed in water, of exactly similar construction to the palladium oven described in the above publication. D is a heating coil wound on a separate tube. B is a tube of the glass whose permeability to gases is to be measured and is fitted to the vacuum mantle through a glass

[4] Paneth and Peters, *Z. physik. Chem.*, **B1**, 253 (1928). About 1% of neon is the maximum present after diffusion through glass contrasted with the ratio of neon to helium in the atmosphere of 3 to 1.

[5] Williams and Ferguson, THIS JOURNAL, **44**, 2160 (1922). Richardson and Ditto, *Phil. Mag.*, **22**, 704 (1911), observed a diffusion of helium and neon from the atmosphere through quartz at 1000°. The statement of Williams and Ferguson that this is improbable and that the helium may come from the quartz itself should, however, be corrected. A quartz tube is surrounded by a vacuum mantle and heated for several hours until helium is no longer spectroscopically visible. Air is then let into the jacket and within thirty minutes or less the helium spectrum appears. That this is not due to leakage can be shown by the absence of neon as described in the publications in the following footnote. Moreover, Paneth and Peters have observed a continuous diffusion of helium from the atmosphere through soda glass.

[6] Paneth and Peters, *Z. physik. Chem.*, **134**, 353 (1928); Paneth and Peters, *ibid.*, **B1**, 170 (1928); Paneth and Peters, *ibid.*, **B1**, 253 (1928); Paneth, Gehlen and Peters, *Z. anorg. allgem. Chem.*, **4**, 175 (1928); Paneth, *Z. Elektrochem.*, **9**, 83 (1928); Paneth, Petersen and Chloupek, *Ber.*, **62**, 4, 801 (1929). Paneth and Urry, *Mikrochemie*, 233, "Emich-Festschrift" (1930); Paneth and Urry, *Z. physik. Chem.*, **A152**, 110 (1931).

joint E. By the use of a standard interchangeable ground-glass joint at E, various tubes B of different glasses may be inserted. These tubes are connected to the helium supply through the ground-glass joint F. In order that C may be easily removable, a ground-glass joint connects C with stopcock 2 and the analysis apparatus. A platinum–platinum-rhodium thermocouple sealed through the ground soda glass cap G passes down the center and touches the inner wall of B, giving the temperature of the tube. H is an aluminum electrode, the use of which is described later. The rest of the apparatus constitutes the helium supply to the inside of B which supply may be shut off at stopcock 3. I is the manometer for pressure readings from 5 mm. upward. K is a McLeod gage for pressure readings from 10^{-3} to 5 mm. L is a charcoal tube shut off by stopcock 4 from the main lead and from the helium store M by stopcock 5. Manometer N checks the pressure in the store. Stopcock 6 shuts off the calcium oven used in the purification of the helium.

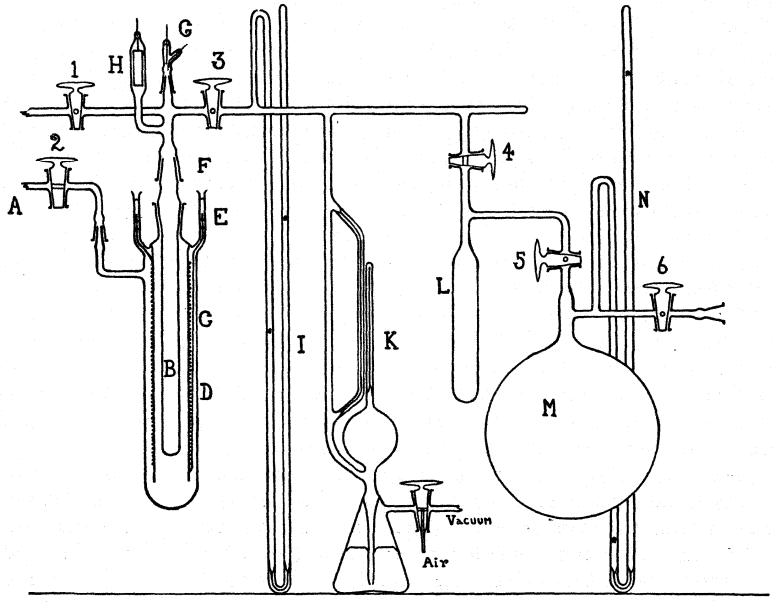


Fig. 1.

Procedure

The Purification of the Helium.—The apparatus on the "Helium side" including the calcium oven and the leads to the helium bomb are completely evacuated through stopcock 1 and the charcoal activated. The apparatus is then flushed out with electrolytic oxygen,[6] stopcock 4 shut off and helium streamed over the calcium at 350°, previously heated in a vacuum, until about 760 mm. is indicated by N. The supply tube is then shut off and by alternately immersing the charcoal tube L and another charcoal tube at the incoming end of the calcium oven in liquid air, a circulation of the gases over the calcium is brought about. After three to four hours stopcock 6 is shut off and the charcoal tube L immersed in liquid air for four hours. Stopcock 5 is then shut and the charcoal evacuated and activated once more through 4. To obtain a given pressure in B, L is once again immersed in liquid air and stopcock 5 carefully turned to admit a small quantity of helium into L. With stopcock 1 shut

and 3 and 4 open, B fills with helium to a pressure given by I or K. After adsorbing for two hours 4 is shut and the liquid air removed. The experimental order is so arranged as to start with a pressure of about 200 mm. and to pump off through 1 small quantities of helium as the next lower pressure is required. By drawing small amounts of this helium through a separate lead into the "Analysis apparatus" it was found that the spectrum of this gas gave no neon and no hydrogen lines, only the helium lines being visible—0.001% of neon in helium is visible under the conditions of the spectroscopic analysis described previously.[6] It is also arranged that the apparatus from 1 to 5 can be filled with electrolytic air-free hydrogen purified by adsorption of any oxygen in L.

Control Experiments.—To test for possible leakage in tube B or in C, tube B is filled with air at atmospheric pressure. The "Analysis apparatus" and C, stopcock 2 being open, are flushed out with oxygen, evacuated and shut off from the pumping system. Maintaining 2 open, the tube B is heated for ten to twelve hours at 290°. It is then cooled off, stopcock 2 shut, and the residual gases examined spectroscopically in a 0.1-mm. capillary on the McLeod gage, after purification as previously described.[6] If any leakage occurs, the residual rare gases must be in the same proportion as found in the atmosphere. In such control experiments, however, only pure helium was observed due to a diffusion of the helium through the glass from the atmosphere varying from 10^{-7} to 10^{-9} cc., depending upon the glass of which B is constructed and the duration of the heating.[7] To demonstrate that there is no accumulation of helium from any extraneous source during the progress of an experiment, tube B is connected to the pump through 1 as is C through the "Analysis apparatus" and heated for ten hours to drive out any helium in the glass. The "Analysis apparatus" is then shut off from the pump, stopcock 2 left open, and the evacuated tube heated for a further period of four hours, whereupon less than 10^{-10} cc. of helium or neon is present.[8]

A Diffusion Experiment.—Tube B is filled to a given pressure of helium and heated to the temperature at which the experiment is to be conducted for about six hours, after which time equilibrium conditions are reached. During this period C is left open to the "Analysis apparatus," which in turn is continuously on the pumping system. The tube B is again cooled to room temperature, the "Analysis apparatus" and C are flushed out with oxygen and evacuated and the pumping system shut off but stopcock 2 left open. One of the "Analysis apparatus" charcoal tubes is immersed in liquid air to produce a standard vacuum as the zero point of the diffusion. In about five minutes the tube attains the working temperature, which can be maintained within 3–4° between 150 and 300° and somewhat closer below 150°. Exactly at the end of 120 minutes the heater D is switched off and the liquid air removed. After fifteen minutes more the entire apparatus is once again at room temperature. Stopcock 2 is shut off and the gases are treated as previously described. The McLeod gage is run up and the helium spectroscopically viewed. If neon free and spectroscopically pure, the helium is measured as described in previous publications.[9] The tube B is again heated

[7] The gases from the heating coil D then also contained $< 10^{-10}$ cc. of neon and therefore $< 4.10^{-6}$ cc. of air, after the preliminary heating before the first control experiment.

[8] The heating coil D therefore contained no helium.

[9] See the previously mentioned publications of Paneth and co-workers, especially "Heliumuntersuchungen VIII," for an accurate method of measurement. In order to determine the total helium by diffusion, the ratio of the McLeod volume to the total volume of the "Analysis apparatus" including C must be determined as outlined in the above publication. According to the amount of helium expected, a McLeod capillary can be chosen of the correct diameter to give a suitable length of gas column. They are easily interchangeable in one glass-blowing operation.

at the same temperature for six hours with C open to the pump and the experiment repeated. This usually gave the same result, showing that after heating for six hours with a vacuum on the one side equilibrium had been established. The factors recorded in each experiment are the total helium diffusing, the temperature, the time of diffusion (120 minutes) and the pressure in B when at the working temperature and at the room temperature. The factors recorded for each series are the length and the internal and external diameters of the tube B and hence the wall thickness = 1.0 mm. average thickness for all specimens. An allowance is made in calculating the surface for the closed hemispherical end of B. The results have been checked at decreasing pressures from 200 to 0 mm. and at increasing pressures up to 200 mm.

Theoretical

Consider the diffusion process, representing the apparatus diagrammatically in Fig. 2. A represents the "Analysis apparatus" initially at a high vacuum. B represents the glass wall through which the diffusion occurs and C the helium reservoir. Suppose c_1 is the saturation concentration at the wall in contact with the helium and c_2 the concentration on the wall in contact with the evacuated apparatus. The rate of accumulation of helium in A will be dependent primarily on two factors—the rate of evaporation from the c_2 surface $= k_1 c_2$ and the rate of condensation on the same surface $= -k_2 p$, if the concentration of the helium on the surface is sufficiently low. When these two factors are equal and opposite, the pressure in A is fixed and the diffusion of helium no longer occurs. The pressure in A is then the "vapor pressure" of helium in glass but as long as c_2 is less than c_1 these two factors cannot be equal, owing to an increase in c_2 by diffusion in the glass phase which we shall assume obeys Fick's law. Equilibrium is then reached when the glass wall is saturated throughout its thickness, $c_2 = c_1$ and the rate of evaporation = the rate of condensation. The pressure of helium in A may then be termed the "vapor pressure" of helium in glass at the concentration $c_2 = c_1$, and the volume Q of helium in A at N. T. P. is now independent of time. It will at once be seen that the time required to reach this state will depend on the size of A. $pV = Q \times 760$, where V is the volume of A. Therefore $p = k_3 Q$, where $k_3 = 760/V$. Figure 3 diagrammatically represents the increase of Q with time (1) and on the same diagram is shown the change in concentration c_2 with time (2). Curve 3 shows the increase with time of c_2 if no evaporation occurred, that is, if the diffusion process finished at the glass surface in contact with A and is the curve given by Fick's law. Thus at first, owing to evaporation, c_2 tends greatly to decrease but at the same time tends greatly to increase by the oncoming helium in the glass phase and will

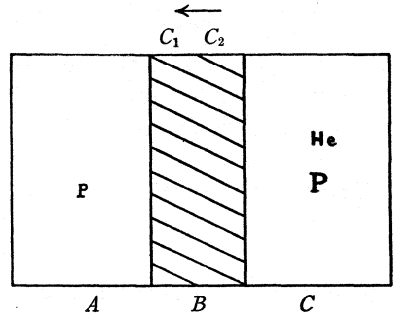


Fig. 2.

take a course roughly shown by the lower portion of Curve 2. As Q increases, however, the rate of condensation greatly increases and the net evaporation is smaller. c_2 starts increasing again and dQ/dt falls off. Hereafter dQ/dt approaches zero and c_2 approaches c_1 until the equilibrium state is reached. The two points on the Q–T curve were experimentally realized, the diffusing times being ten and thirty hours, while the volume of A was about 700 cc.

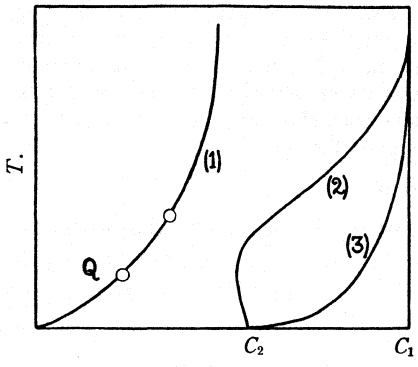


Fig. 3.

Hence the time required to come to such a state of equilibrium is practically speaking infinite. If we observe what occurs in a period of two hours from zero time, we note that over this period c_2 remains almost constant. It will be shown how this was experimentally verified. Hence a period of 120 minutes was chosen for the diffusion time.

What is actually determined is the relation of Q to the pressure P of helium in the tube B.

The concentration c at any plane x after a time t is given by

$$\frac{dc}{dt} = \frac{D d^2c}{dx^2}$$

where D is the diffusion coefficient.[10] On integrating, expanding into a

[10] Andrews and Johnston, THIS JOURNAL, **46**, 640 (1924) have dealt with the integration of the above equation for several cases, the full equation for the case under consideration being

$$\frac{c_1 - c}{c_1} = \frac{4}{\pi} \sum_{m=1}^{m=\infty} \frac{\cos\left[\frac{(2m-1)\pi x}{a}\right]}{(2m-1)(-1)^{n+1}} e^{-(Dt/a^2)(2m-1)^2\pi^2}$$

and hence after a given time t, c_2 is directly proportional to c_1. On differentiating equation (1)

$$\frac{dc_2}{dt} = \frac{D\pi^2}{a^2}(c_1 - c_2)$$

giving the rate of increase of c_2 with time due to diffusion in the glass phase. To determine what concentration c_2 exists previous to the commencement of an experiment and after pumping for six hours on A, during this time $p = 0$ and the condensation is zero. The increase in c_2 is given by

$$\frac{dc_2}{dt} = K(c_1 - c_2), \text{ where } K = \frac{D\pi^2}{a^2} \qquad (3)$$

The decrease in c_2 due to evaporation is given by

$$-\frac{dc_2}{dt} = k_1 c_2 \qquad (4)$$

and at equilibrium $c_2 = \bar{c}_2$, the initial concentration for a diffusion experiment. From equations (3) and (4) we obtain

series and neglecting the higher terms, putting $x = a$, the thickness of the glass wall, and therefore $c = c_2$ and collecting the separate constants under one constant, we obtain

$$\frac{c_1 - c_2}{c_1} = Ae^{-Dt\pi^2/a^2} \tag{1}$$

or, when t is constant as in these experiments

$$\frac{c_1 - c_2}{c_1} = Ae^{-B} \text{ and } \log (c_1 - c_2) + B = \log Ac_1$$

Putting $\log E = B$

$$c_2 = c_1\left[1 - \frac{A}{E}\right] \tag{2}$$

Thus Q is directly proportional to the saturation concentration on the reservoir wall c_1. If Henry's law were obeyed in this particular case, then $c_1 = \overline{K}P$, where P is the helium pressure in the tube B, and hence $Q =$ const. $\times P$. Since this is not the case, the results are discussed with reference to phenomena at the c_1 surface, since $c_1 \neq \overline{K}P$.

$$\bar{c}_2 = \frac{Kc_1}{(K - k_1)} \tag{5}$$

If the diffusion coefficient is smaller than the evaporation coefficient, then the concentration c_2 is zero at the commencement of the experiment and the oncoming helium is immediately evaporated off the c_2 surface. Consider the concentration c_{2t} on the c_2 surface at a given time t after the experiment has been started, taking the complete surface of the tube to express the concentration terms, then

$$c_{2t} = \bar{c}_2 - Q_t + c_t \tag{6}$$

Q_t being the net quantity evaporated in time t and c_t the increase in concentration due to the diffusion in the glass phase. The increase in concentration due to the diffusion in the glass phase $= (dc/dt)_{2t} = K(c_1 - c_{2t})$. The condensation on the c_2 surface, proportional to the pressure $= (dc/dt)_{2t} = k_2p$. The evaporation off the c_2 surface proportional to the concentration $= (dc/dt)_{2t} = -k_1c_{2t}$. Then

$$\frac{3dc_{2t}}{dt} = K(c_1 - c_{2t}) + k_2k_3Q_t - k_1c_{2t} \tag{7}$$

remembering that $p = k_3Q_t$. By putting $c_{2t} = f(t^n)$, equation (7) can be brought into an integrable form and the desired relation between Q_t and c_1 obtained.

The following experiments, however, verify the fact that c_{2t} does not vary and therefore is equal to $\bar{c}_2$ for the 120 minutes. After attaining equilibrium, a 120-minute diffusion was run giving a certain value for Q. The "Analysis apparatus" was pumped out and a second 120-minute run made immediately. This gave the same value for Q, a third run immediately after the conclusion of the second also gave the same value. c_{2t} and c_t are both functions of c_1 and therefore of $\bar{c}_2$ and hence from equation (6) if $\bar{c}_2$ were to vary Q_t would also vary. Q_t, however, was the same in all three experiments and therefore the initial concentration on the c_2 surface must have been the same. Hence the concentration during the course of the first experiment could not have changed, since the final concentration which is the initial for the following experiment must have been the same as the initial concentration of the first experiment. Then equation (7) becomes $0 = K(c_1 - \bar{c}_2) + k_2k_3Q - k_1\bar{c}_2$ and substituting for $\bar{c}_2$ from equation (5)

$$Q = \frac{2k_1Kc_1}{(K - k_1)k_2k_3} \tag{8}$$

TABLE I

(A) PYREX GLASS

P, mm.	t, °C.	Q^a	P, mm.	t, °C.	Q^a
175.0	283	5642	55.0	125	265
175.0	220	2711	55.0	81	128
175.0	172	1452	47.0	283	1759
175.0	125	699	29.0	283	1115
175.0	81	338	20.0	283	828
175.0	20	112	20.0	220	404
153.0	283	5020	20.0	172	213
125.0	283	4150	20.0	125	109
125.0	220	2032	20.0	81	53
125.0	172	1082	10.0	283	436
125.0	125	541	10.0	220	215
125.0	81	264	9.0	283	401
100.0	283	3429	5.5	283	268
100.0	221	1695	5.5	220	133
98.0	172	803	5.5	172	64
97.0	125	401	5.5	125	26
95.0	81	223	5.5	15	6
65.0	283	2320	1.2	283	57
55.0	283	2005	0.098	283	18
55.0	220	994	0.022	283	3
55.0	172	525			

(B) LEAD GLASS

P, mm.	t, °C.	Q^a	P, mm.	t, °C.	Q^a
209.0	283	200.5	45.0	283	80.9
160.0	283	173.5	20.0	283	49.7
129.0	283	143.5	9.2	283	33.0
80.0	283	113.0			

(C) SODA GLASS

P, mm.	t, °C.	Q^a	P, mm.	t, °C.	Q^a
185.0	283	69.3	43.5	283	23.6
140.0	283	53.1	10.0	283	9.7
93.5	283	43.3	10.0	283	10.36
47.0	283	24.2	10.0	283	9.7

(D) JENA 16''' GLASS

P, mm.	t, °C.	Q^a	P, mm.	t, °C.	Q^a
204.0	283	55.3	121.0	283	37.0
202.0	221	21.4	79.0	283	29.2
201.0	172	7.8	50.0	283	18.8
200.0	134	3.1	45.0	283	19.3
194.0	22	0.2	12.0	283	8.9
175.0	283	46.9	11.0	283	7.3

[a] The value of Q is given in units of 10^{-12} cc. and is the volume of helium, reduced to N. T. P., diffusing through a unit area of wall equal to 1.0 sq. cm. of thickness 1.0 mm. per second.

Baxter, Starkweather and Ellestad[11] have determined the loss in weight of a Pyrex globe containing 75 cm. pressure of helium at 20° with an internal surface of 500 sq. cm. After attaining a constant daily loss, 0.0047

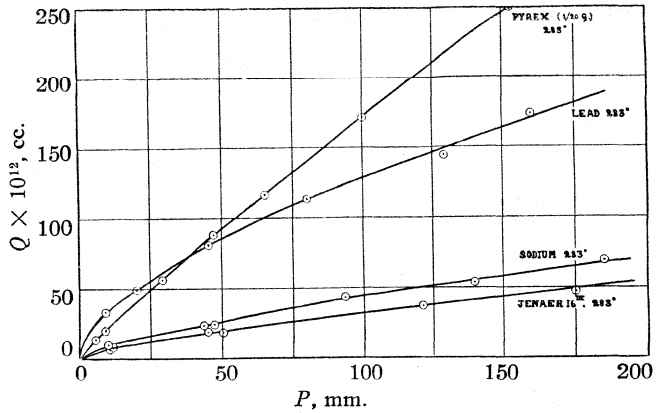


Fig. 4.—The relation between Q and P at 283°, for four types of glass (Pyrex glass; $^1/_{20}$ diminished).

mg. of helium leaked out per twenty-hour hours, approximately equal to 6.8×10^{-10} cc. per second per sq. cm. per mm. wall at room temperature. By extrapolation of the data in Table I, 4×10^{-10} cc. at 20° c for 750 mm. of helium through a 1-mm. Pyrex wall into a vacuum is obtained. The partial pressure of helium in the atmosphere being of the order of 5×10^{-6} mm., these two results are comparable and of good agreement. If the logarithm of Q is plotted against log P, straight lines result and $Q = \alpha P^n$. Similarly for a given pressure $Q = \beta T^m$, where T is the absolute temperature.

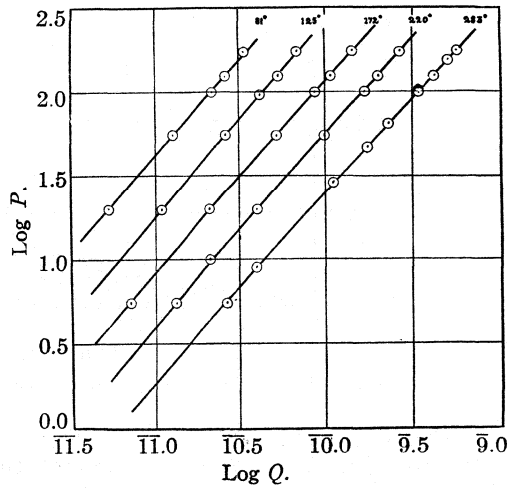


Fig. 5.—The log-log isotherms for the diffusion of helium through Pyrex glass.

Table II gives the values of α and β and of m and n for the four glasses studied.

Since the value of α is the value of Q for $P = 1$ mm., a comparison of α for the various glasses gives the relative diffusion through the various types of glass at 1 mm. pressure. On account of the variation of n for the

[11] Baxter, Starkweather and Ellestad, *Science*, November 23, p. 516 (1928).

TABLE II[12]

t, °C.	Pyrex glass $Q = \alpha P^{0.88}$ α	Lead glass $Q = \alpha P^{0.56}$ α	Soda glass $Q = \alpha P^{0.64}$ α	Jena 16''' glass $Q = \alpha P^{0.66}$ α
283	58.2×10^{-12}	8.8×10^{-12}	2.2×10^{-12}	1.6×10^{-12}
220	29.5	.....	.....	.....
172	15.7	.....	.....	.....
125	7.9	.....	.....	.....
81	3.7	.....	.....	.....
P, mm.	$Q = \beta T^{6.09}$ β			$Q = \beta T^{9.02}$ β
202.0	.....	.....	.....	3.24×10^{-36}
175.0	10.00×10^{-28}	.....	.....	.....
100.0	5.96	.....	.....	.....
20.0	1.50	.....	.....	.....
5.5	0.32	.....	.....	.....

different glasses, however, the relative diffusion through the various types of glasses will vary with pressure.

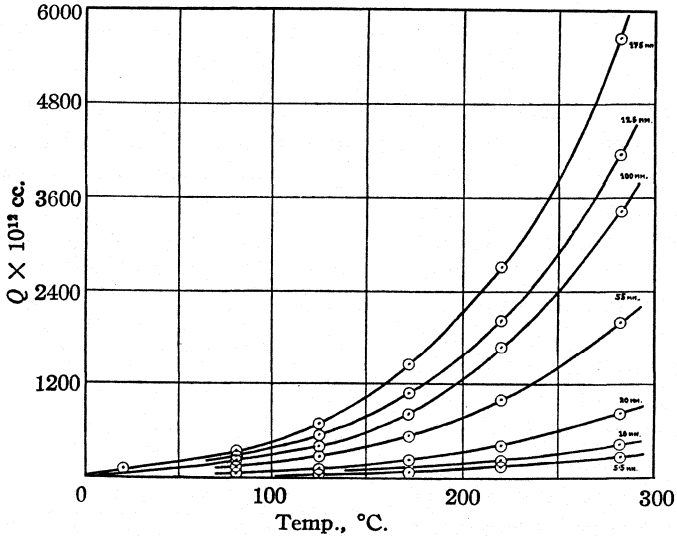


Fig. 6.—The variation of Q with temperature for various pressures.

Although glasses of as widely different composition as possible were used, no significant connection between the composition and the relative diffusion rate can be found. Table III gives the analyses of the glasses.

It will be noticed that the glasses of highest and lowest silica content have a higher permeability than those of medium content. Such physical constants as density, viscosity and dielectric constant also cannot be correlated. The values of n for the various glasses, however, are proportional, within the

[12] With the exception of Pyrex glass, which was selected from a new laboratory stock, the glasses were supplied by Hanff and Buest, Berlin, Germany.

TABLE III

	SiO_2	Na_2O	K_2O	CaO	B_2O_3	As_2O_3	PbO	ZnO	Mn_2O_3	Al_2O_3,Fe_2O_3
Pyrex glass	80.75	4.1	0.1	0.3	12.0	0.4	..	...	...	2.20
Lead glass	56.0	...	12.1	...	...	...	31.2	...	...	0.70
Soda glass	69.0	11.1	...	12.5	...	...	..	...	...	7.4
Jena 16'''	67.3	14.0	...	7.0	2.0	...	..	7.0	0.2	2.5

experimental limits, to the percentage of $SiO_2 + B_2O_3$, as may be seen from Table IV.

TABLE IV

Type	$SiO_2 + B_2O_3$	n calculated	n found
Pyrex	92.75%	0.88	0.88
Lead	56.00	.53	.56
Soda	69.00	.655	.64
Jena 16'''	69.30	.66	.66

We have seen that under the conditions of the experiments the quantity of helium measured Q must be directly proportional to the concentration on the wall in contact with the helium, c_1. If Henry's law were obeyed Q is proportional to c_1, is proportional to P. Now suppose that the helium is first adsorbed on the glass surface c_1 and passes into the glass phase only through this adsorbed phase. We should then have in general $Q \propto c \propto P^n$.

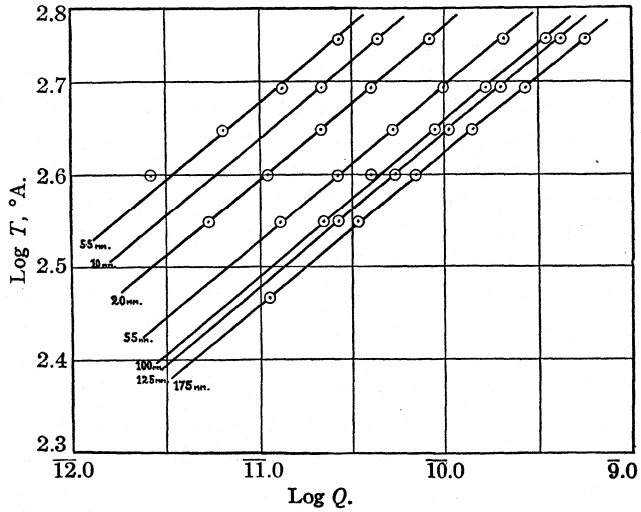


Fig. 7.—The log-log isobars for Pyrex glass.

Paneth and Peters[4] found that if a helium-containing glass is heated in a vacuum until $< 10^{-10}$ cc. is given off, by the addition of 3 mm. of hydrogen and reheating for a short period a further spectroscopically detectable amount of helium is obtained. With a helium-free Pyrex glass, the diffusion rate of hydrogen was obtained in a similar manner to the helium

determinations. Table V shows the relative diffusion rates of helium and hydrogen.

TABLE V

	Pressure, mm.	Temp., °C.	Q^a
Hydrogen	7.0	283	18×10^{-12}
Helium	7.0	283	320×10^{-12}

[a] Denotes the volume of helium in cc. diffusing per second per sq. cm., per mm. wall.

Since the diffusion of hydrogen into the glass during a short period is negligible compared to that of helium, it seems reasonable to propose that the hydrogen replaces an adsorbed layer of helium in much the same way as replacement takes place on charcoal. Moreover, if glass, previously heated in hydrogen until no more helium is given off, is left for twenty-four hours in the air, and reheated in hydrogen for a short while, helium and a little neon are given off. On heating again a practically neon-free helium is obtained. Thus helium is preferentially adsorbed from the atmosphere and the much smaller amount of neon quickly replaced by hydrogen when heated. Glass tubes of 50 sq. cm. surface when filled for one hour with neon and helium in the air ratio (3 to 1) and then pumped out, give on heating 10^{-5}–10^{-6} cc. of helium and very little neon. After the third fractional heating a neon-free helium is obtained.

More significant perhaps is the fact that instead of heating, the electric discharge in hydrogen can be used to bring about the same effect. Experiments described in the following pages show that the rate of diffusion of hydrogen (and helium) is not affected by a discharge through the glass wall, whether a high frequency 800,000 volt discharge or a 60 cycle 20,000 volt discharge. This being the case and remembering that the walls are at water cooled temperatures and therefore the rate of diffusion of hydrogen about 50 times smaller than in Table V, the observed effect must be a surface phenomenon.[13] If hydrogen can replace the adsorbed helium layer on a glass surface, which adsorbed layer is itself very stable, not being removed at 400° in a vacuum, then by the addition of an excess of hydrogen to the helium in the reservoir the helium adsorbed layer is partially displaced and the concentration in the first layer c_1 decreased, Q being correspondingly decreased. This was found to be the case, as may be seen from Table VI.

That the diffusion rate is not affected by a discharge through the glass was also shown. A Tesla coil using a 2 KV, 60 cycle, 2 kilowatt transformer for supply was connected to the electrode H. One of the heating

[13] A repetition of Paneth and Peters' experiment showed that 10^{-8} cc. of helium can be removed from an otherwise apparently helium-free Pyrex glass surface in twenty-two minutes using 18,000 volt, 60 cycle discharge in 5 mm. of hydrogen; temperature of the walls, 10°.

coil leads was earthed.[14] The calculated voltage output of the Tesla coil was 800,000 volts. At low frequency the transformer was connected to H and one lead of the heating coil. Table VI gives the results obtained, the experiments being conducted as previously over two hours.

TABLE VI

Expt.	Composition and pressure of gas in tube B, mm.	Temp., °C.	Q^a	Remarks
3A	5.5 He	283	275×10^{-12}	
12A	5.5 He	283	275	
13A	5.5 He	283	277	
14A	5.5 He			
	+ 5.5 H_2	283	275	
15A	5.5 He			
	+27.5 H_2	283	268	
7A	12.0 He	283	522	
8A	12.0 He	283	522	H. F. discharge
9A	12.0 He	283	522	L. F. discharge
21A	7.0 H_2	283	18	
22A	7.0 H_2	283	20	H. F. discharge
23A	7.0 H_2	283	17	L. F. discharge; atomic hydrogen visible

[a] Q being in the same units as in the foregoing tables.

In the case of hydrogen the total diffusion rate is so small that accurate measurements could not be made but the mean value shows that any effect is very small. The "clean-up effect" of hydrogen in helium is another example where a layer of hydrogen is adsorbed entirely on the glass surface since the discharge does not affect the very low rate of diffusion of hydrogen into the glass and the hydrogen is sometimes removed in a matter of seconds in a thoroughly outgassed 0.2-mm. capillary. With helium, neon and the rare gases, however, no "clean-up effect" occurs.

Williams and Ferguson,[5] in attempting to find the solution to the problem that helium diffuses 22 times faster than hydrogen at 760 mm. pressure and 500° through silica glass,[15] measured the relative solubility of these two gases in glass and found them not to differ appreciably. Supposing, however, that hydrogen is very strongly bound in the surface as we have seen is likely to be the case,[16] then, on outgassing the glass to determine the amount "dissolved," the main body of hydrogen would be that adsorbed or absorbed in the surface. With helium, however, where the time allowed

[14] The discharge did not affect the heating but had to be shut off when making temperature readings with the thermocouple.

[15] See also Table V through Pyrex glass.

[16] The same authors could detect no diffusion of hydrogen through Pyrex or Jena glass at 760 mm. and 640°, probably owing to a limited sensitivity, but the glass blackened. This latter fact appears to point to the presence of at least physico-chemical forces between the hydrogen and the glass.

for saturation was sufficient for quite a large diffusion into the glass, the "solubility" would be the chief factor. This result, then, instead of increasing the difficulties of the solution of the problem, may itself be a solution. The hydrogen being bound very strongly in the surface layer cannot to any great extent diffuse into the glass; the helium, being less strongly bound, diffuses.

The value of n in the equation $Q = \alpha P^n$ indicates the relative strength of the forces holding the adsorbed gas in the surface. On turning to Table IV, we see that the value of n decreases proportionately to the decrease in the silica + boric oxide content.[17] As the percentage of the metals and therefore of the metallic atoms in the surface increases, so the relative strength of the forces holding the gas in the surface increases. The other constant, α, which cannot be correlated in any way with the composition or physical properties of the glass, varies enormously for the four types of glass. Two factors obviously play an important part in fixing α, (1) the true surface of a given measured surface of the glass, (2) the true solubility in the bulk of the glass. Thus upon the extent of the true surface depends the concentration of the adsorbed layer and hence c_1. Nothing can be said at present, however, of the relative effect of these two factors on the constant α. An attempt will be made to determine the extent of the true surface by the radioactive indicator method of Paneth and Vorwerk.[18] That the solubility may substantially vary is to be expected from analogous experiments on the solubility in mixed liquid solvents of varying composition. That the true surface will vary is equally apparent from the very different composition, melting point, annealing and drawing temperature of each glass tube studied.[19]

The change of permeability with temperature agrees very closely with the equation $Q = \beta T^m$. In order to determine the chief factor affecting the increase of permeability with increasing temperature, the following series of experiments were conducted. The rate of diffusion was determined for six temperatures at one pressure, running the experiments consecutively and only evacuating a few minutes before each determination, working from 283° down to room temperature and back again to 283°. A second series was then made but after each determination the tube B was held for six hours at the next temperature, C being on the pump. The two series of results were identical within the experimental limits. If considerable changes in the concentration conditions at the different temperatures occur, these two series cannot give the same results since in the first set of determinations no time is allowed for a readjustment of such changes on going

[17] It may be of interest to note that these two elements are the only ones present in glass forming volatile hydrides.

[18] Paneth and Vorwerk, *Z. physik Chem.*, **101**, 445, 480 (1922).

[19] See "International Critical Tables," Vol. II, pp. 92–101.

to the next lower or next higher temperature, whereas in the second series a period of six hours is allowed for the attaining of any new equilibrium conditions. Thus the chief factor involved in the change of permeability with temperature must be the rate of change of the diffusion coefficient D with temperature in the glass phase, this being independent of concentration and adsorption changes. In this respect the relative diffusion may be related to the viscosity of the medium since Cohen and Brun[20] found the Stokes–Einstein equation to hold approximately for the diffusion of one organic liquid into another

$$D = \frac{RT}{N}\frac{1}{6\pi\eta r}$$

where η is the viscosity of the medium and r the radius of the diffusing atom or molecule.

Assuming r to be independent of temperature $D\eta = KT$, or for helium through various glasses at one temperature, $D\eta = K'$, where η and D are the viscosity and diffusion coefficient for each particular glass. Owing to a lack of viscosity data for glass below 500°, this question must be dealt with after a study of the viscosity of glasses at comparatively low temperatures.

Further work is in progress dealing with the diffusion and adsorption of the rare gases through and on crystalline bodies.

Summary

1. A method of determining accurately the rate of diffusion of helium, neon and hydrogen through glass at comparatively low temperatures and pressures is outlined and the results are given for Pyrex glass, lead glass, soda glass and Jena 16''' glass.

2. The results are discussed in the light of previous experiments on the helium content of glasses, outgassing effects and the "clean-up effect."

3. It is concluded that in the process of diffusion through glass, helium and hydrogen are first adsorbed on the glass surface and solubility and diffusion proceeds from this adsorbed or absorbed (in the case of hydrogen) layer. This theory may be extended to other gases equally well.

4. In the above conclusion lies an explanation of the hitherto inexplicable contrast between the rates of diffusion of hydrogen and helium through glass.

BALTIMORE, MARYLAND

[20] Cohen and Brun, *Z. physik. Chem.*, **103**, 404 (1923).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

EQUILIBRIUM IN SYSTEMS COMPOSED OF SULFUR DIOXIDE AND SODIUM, POTASSIUM OR AMMONIUM THIOCYANATE

BY H. W. FOOTE AND JOSEPH FLEISCHER

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In a previous investigation,[1] we have determined the composition of the solid phases and the vapor pressure relations in two-component systems composed of sulfur dioxide and an alkali (or ammonium) iodide. We give below the corresponding results obtained on systems containing thiocyanates instead of iodides. The methods, apparatus and procedure were the same in both investigations and were described in detail in the earlier one.

Sodium Thiocyanate and Sulfur Dioxide.—Sodium thiocyanate forms a bright yellow compound having the composition $NaCNS \cdot 2SO_2$ when brought in contact with liquid sulfur dioxide. The compound is rather insoluble in the liquid, yielding a pale yellow solution. The composition of the compound was determined by allowing the saturated solution to evaporate at a pressure of one atmosphere of sulfur dioxide at two temperatures where the vapor pressure data given below showed that only the pure compound could exist in equilibrium. The following results were obtained.

NaCNS, g.	SO_2, g.	Ratio NaCNS : SO_2	Temp., °C.
5.316	8.11	1:1.93	−8.0
2.450	3.79	1:1.96	0.0

The observed vapor pressures of the two univariant systems are given in the table.

I		II	
$NaCNS \cdot 2SO_2$–Solution–Vapor		$NaCNS \cdot 2SO_2$–NaCNS–Vapor	
T, °C.	P, cm.	T, °C.	P, cm.
−21.40	44.5	−21.30	9.1
12.20	69.2	9.70	23.2
2.75	103.5	0.00	49.9
0.00	115.9	+7.00	79.8
		10.50	102.0
$\text{Log } p = 6.954 - \frac{1335.5}{T}$		$\text{Log } p = 9.396 - \frac{2290.4}{T}$	
$\Delta H = 6100$		$\Delta H = 10{,}500$	

The results are plotted in Fig. 1. Ephraim and Kornblum[2] reported that sodium thiocyanate does not absorb sulfur dioxide to form a compound at 0° and one atmosphere pressure. Our results show that the addition

[1] Foote and Fleischer, THIS JOURNAL, **53**, 1752 (1931).

[2] Ephraim and Kornblum, *Ber.*, **49**, 2007 (1916).

product is stable under these conditions. It is not unlikely, however, that the absorption of the vapor is slow, as is often the case with solids. There is no difficulty in obtaining the compound by the method we have described.

Potassium Thiocyanate and Sulfur Dioxide.—Ephraim and Kornblum[2] investigated this system and recognized the fact that two compounds exist, to which they assigned the formulas $KCNS \cdot SO_2$ and $KCNS \cdot 0.5SO_2$. They did not, however, give the data on which these formulas are based. In the present investigation, it has been found that on standing for some hours in contact with liquid sulfur dioxide, potassium thiocyanate is converted, with apparent increase in volume, to a pale yellow compound which crystallizes in needles. The saturated solution has a bright yellow color though the compound is not readily soluble, as shown by the fact that the vapor pressure curve of the saturated solution lies only slightly below that of liquid sulfur dioxide.

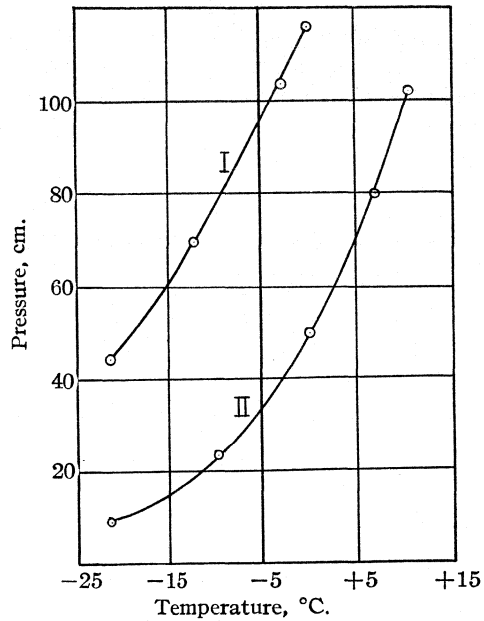

Fig. 1.—$NaCNS-SO_2$: Curves I and II represent, respectively, the systems $NaCNS \cdot 2SO_2$–solution–vapor and $NaCNS \cdot 2SO_2$–NaCNS–vapor.

The compound was prepared in pure condition by allowing the saturated solution, in contact with excess of solid, to evaporate at 0° and atmospheric pressure. The following results were obtained.

KCNS, g.	SO_2, g.	Ratio, KCNS : SO_2
3.225	4.155	1:1.95
4.875	6.438	1:2.00

The compound therefore has the formula $KCNS \cdot 2SO_2$. We found no indication of the 1:1 compound mentioned by Ephraim and Kornblum. Evaporation of sulfur dioxide from the compound at 20° and atmospheric pressure—conditions under which the vapor pressure measurements show that a lower compound is stable—left a bright yellow solid as residue. This reaction, however, takes place slowly. The following data were obtained after allowing the bulb containing the higher compound to stand several days at room temperature, the excess of sulfur dioxide escaping meanwhile at atmospheric pressure through the mercury bubbler.

KCNS, g.	SO_2, g.	Ratio, KCNS : SO_2
3.225	1.327	1:0.62
4.875	2.020	1:0.63

It is probable that the formula of this compound is $KCNS \cdot 0.5SO_2$ as stated by Ephraim and Kornblum, the high sulfur dioxide content of the residue being due to the slow rate of dissociation of the higher compound. The following tables contain the vapor pressure data of the three univariant systems.

I

$KCNS \cdot 2SO_2$–Solution–Vapor

T, °C.	P, cm.
−21.30	44.5
14.50	61.9
7.50	84.2
0.00	114.3

$$\text{Log } p = 6.825 - \frac{1301.5}{T}$$

$\Delta H = 5950$

II

$KCNS \cdot 2SO_2$–$KCNS \cdot 0.5SO_2$–Vapor

T, °C.	P, cm.
−10.00	18.3
0.00	37.1
+11.00	73.8
14.50	91.2
16.60	102.9

$$\text{Log } p = 9.353 - \frac{2126.4}{T}$$

$\Delta H = 9750$

III

$KCNS \cdot 0.5SO_2$–KCNS–Vapor

T, °C.	P, cm.
0.00	2.85
12.00	7.0
19.00	11.2
20.85	12.9
24.00	15.4

$$\text{Log } p = 9.475 - \frac{2461.6}{T}$$

$\Delta H = 11{,}270$

The results are plotted in Fig. 2.

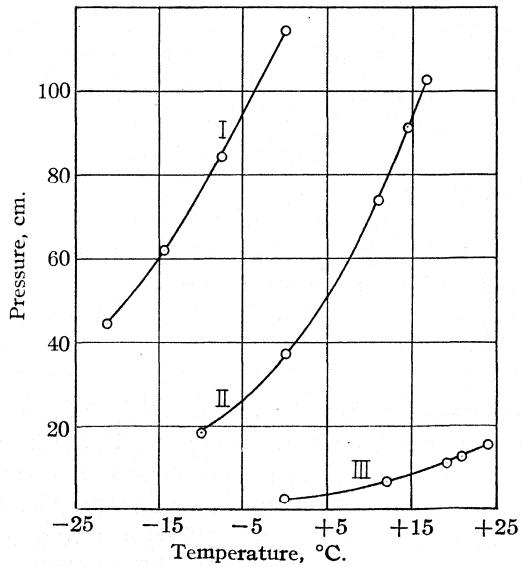

Fig. 2.—KCNS–SO_2: Curves I, II and III represent, respectively, the systems $KCNS \cdot 2SO_2$–solution–vapor, $KCNS \cdot 2SO_2$–$KCNS \cdot {}^1/_2SO_2$–vapor, and $KCNS \cdot {}^1/_2SO_2$–KCNS–vapor.

Ammonium Thiocyanate and Sulfur Dioxide.—This salt is more soluble than the potassium salt in liquid sulfur dioxide. The saturated solution has the color of an aqueous dichromate solution, quite different from the yellow color of the solutions of the sodium and potassium salts.

Isothermal evaporation of solution at a pressure somewhat below that of the saturated solution left a residue of transparent yellow cubes of composition corresponding to the formula $NH_4CNS \cdot SO_2$. The data are given in the table, together with the temperatures and pressures at which the evaporation was carried out.

NH_4CNS, g.	SO_2, g.	Ratio $NH_4CNS:SO_2$	T, °C.	P, cm.
5.812	4.460	1:1.02	−16	40
4.667	4.061	1:1.03	−10	50
4.012	3.534	1:1.05	− 2	77

The compound floats on the saturated solution and therefore has a lower density than the latter. The existence of lower compounds was disproved by the fact that at a constant temperature practically all the sulfur dioxide was removed at constant pressure. Furthermore, evaporation of the solution at +7° and atmospheric pressure left a residue containing only 0.03 mole of sulfur dioxide per mole of thiocyanate.

The compound decomposes to a liquid and a solid phase when warmed slightly, showing the existence of a transition temperature. This temperature was found to be +2.4° from the intersection of the vapor pressure curves of the three univariant systems given below. The solubility of $NH_4CNS \cdot SO_2$ in liquid sulfur dioxide increases with rising temperature, which is the case with all the other addition compounds investigated, while the solubility of NH_4CNS (above the transition point) decreases, as it does for all the other simple iodides and thiocyanates investigated.

Vapor Pressure Data of the Three Univariant Systems

I		II		III	
$NH_4CNS \cdot SO_2$–Solution–Vapor		$NH_4CNS \cdot SO_2$–NH_4CNS–Vapor		NH_4CN_2–Solution–Vapor	
T, °C.	P, cm.	T, °C.	P, cm.	T, °C.	P, cm.
−20.40	41.5	−20.90	20.1	+3.00	94.7
19.75	42.6	−12.60	35.2	4.00	98.7
16.50	48.0	− 7.50	49.6	4.50	100.7
13.20	55.3	− 4.60	59.9	5.70	105.7
7.70	68.1	0.00	80.1	6.40	108.5
5.90	72.4			7.20	112.4
3.50	78.9				
0.00	87 4				
		$\text{Log } p = 9.178 - \frac{1987.0}{T}$		$\text{Log } p = 6.931 - \frac{1368.0}{T}$	
		$\Delta H = 9100$		$\Delta H = 6250$	

The results are plotted in Fig. 3.

Ephraim and Kornblum found no absorption of sulfur dioxide by ammonium thiocyanate at 0° and atmospheric pressure. Our data confirm

this observation, since the dissociation pressure in system II above is greater than atmospheric at 0°.

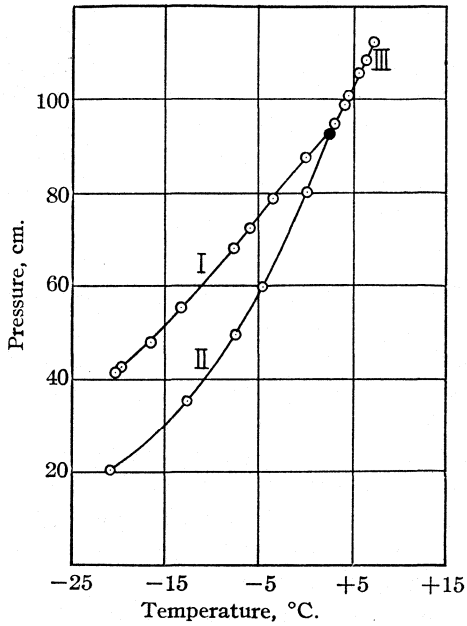

Fig. 3.—NH_4CNS–SO_2: Curves I, II and III represent, respectively, the systems $NH_4CNS \cdot SO_2$–solution–vapor, $NH_4CNS \cdot SO_2$–NH_4CNS–vapor, and NH_4CNS–solution–vapor. The black dot represents the invariant system.

Summary

The composition of the solid addition products and the vapor pressure curves limiting the stability of these compounds have been determined between the maximum limits of −20 and +25° for the two-component systems of sulfur dioxide with sodium, potassium and ammonium thiocyanates. The investigation supplements a previous one on similar systems with alkali iodides.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

PHOTOCHEMICAL STUDIES. XIV. THE DECOMPOSITION OF NITROUS OXIDE SENSITIZED BY MERCURY VAPOR

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The reactions of nitrous oxide have been the subject of numerous recent publications,[1] while its Raman spectrum[2] and its infra-red[3] and ultraviolet[4] absorption spectra have also been studied. Various suggestions have been made as to the structure of the nitrous oxide molecule.[1,5] The direct photochemical decomposition[6] and the decompositions initiated by alpha particles[7] and cathode rays[8] have also been investigated. Taylor and Marshall[9] studied the behavior of nitrous oxide in the presence of excited mercury, both with and without added hydrogen. Finally, the rate of thermal decomposition has been thoroughly investigated so that a more or less satisfactory explanation of the homogeneous thermal reaction is possible.[10]

It would not be within the scope of the present article to review the literature of nitrous oxide critically and we shall confine ourselves to a detailed mention of only those works which are intimately related to the present problem. The study of the decomposition of nitrous oxide initiated by excited mercury atoms should be of more than passing interest because of the possibility of at least two different primary steps and because the interaction of excited mercury with all of the gases, with perhaps one exception, which may be formed during the reaction has already been the subject of previous investigation.

I. Experimental

The nitrous oxide used in the present experiments was a commercial product. It was bubbled slowly through concentrated potassium hydroxide, dried by standing over phosphorus pentoxide and purified finally by fractional distillation with liquid air, only the middle fraction being retained for use. It was stored in a system free from stopcocks and wax joints. The reaction vessel was of fused quartz sealed to the line

[1] *Cf.* W. A. Noyes, Sr., THIS JOURNAL, **50**, 2902 (1928); **53**, 2137 (1931).

[2] See Kohlrausch, "Der Smekal-Raman Effekt," Julius Springer, Berlin, 1931, pp. 126, 180.

[3] Plyler and Barker, *Phys. Rev.*, **38**, 1827 (1931); see also Bailey and Cassie, *ibid.*, **39**, 534 (1932).

[4] Wulf and Melvin, *ibid.*, **39**, 180 (1932).

[5] *Cf.* Pauling, THIS JOURNAL, **53**, 1386 (1931); see also Bailey and Cassie, Ref. 3.

[6] Macdonald, *J. Chem. Soc.*, 1 (1928).

[7] Wourtzel, *Le Radium*, **11**, 289 (1919).

[8] Gedye, *J. Chem. Soc.*, 3016 (1931).

[9] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[10] For review see Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, 1932, pp. 227–31; Musgrave and Hinshelwood, *Proc. Roy. Soc.* (London), **A135**, 23 (1932).

by a graded seal. In the later part of the work two nearly identical reaction systems were used in such a way that variations in the intensity of the mercury arc lamp could be ascertained by using one as a control.

The vapor pressure of mercury in the reaction vessel was maintained constant by separating the vessel from the rest of the system by a trap immersed in an ice-water bath. The pressures were read on a McLeod gage. During the runs both the total pressure and the pressure of the residual gas after condensation with liquid air were measured. The latter pressures were corrected for the cooling of the trap by a constant factor obtained by filling the system with air.

Both the reaction vessel and the lamp were placed under water. In the early runs it became apparent that the light intensity was so high that the rate of reaction seemed to be determined by the rate of diffusion of mercury into the illuminated zone. For the major portion of the work Corex glass screens were placed between the reaction vessel and the lamp.

In certain experiments nitric oxide was added. This gas was prepared by the method previously described.[11]

II. Results

(a) The Absorption Spectrum of Nitrous Oxide.—The absorption spectrum of nitrous oxide has been studied by Leifson[12] and by Wulf and Melvin.[4] Neither of these authors found any banded absorption but only a continuum extending to wave lengths as long as 2300 Å. Wulf and Melvin[4] found, moreover, that nitric oxide bands appeared after exposure of the nitrous oxide to radiation from the hydrogen discharge tube, thus agreeing with Macdonald[6] that nitric oxide is one of the products of photochemical decomposition. It was not proved, however, that the nitric oxide was formed by the primary process although Wulf and Melvin consider this to be probable.

In the present work the absorption spectrum of nitrous oxide was photographed in a tube 3.6 meters in length at a pressure of one atmosphere. No bands could be located and the continuous absorption was found to begin at about 2250 Å., in good agreement with Wulf and Melvin.

These observations raise the question as to whether the present experiments deal with direct or sensitized decomposition of nitrous oxide. The pressures were, however, very low and Corex glass transmits very little radiation which would be absorbed directly by the gas. In addition, immersion of the trap in a carbon dioxide–ether mixture to reduce the vapor pressure of mercury to a low figure practically stopped the reaction. We feel justified in stating that the direct photochemical reaction is not of importance in these experiments.

(b) The Interpretation of the Pressure Measurements.—The following gases may possibly result from the decomposition of nitrous oxide: N_2, NO, O_2, NO_2, N_2O_3.[13] The last named would not be of importance in these experiments.

[11] Noyes, THIS JOURNAL, **53**, 514 (1931).

[12] Leifson, *Astrophys. J.*, **63**, 73 (1926).

[13] Melvin and Wulf, *Phys. Rev.*, **38**, 2294 (1931).

At the pressures used nitrogen, nitric oxide and oxygen should remain in the gaseous state at liquid air temperatures, whereas nitrogen dioxide and undecomposed nitrous oxide should condense to give negligible pressures. The reaction between nitric oxide and oxygen is of the third order[14] and should be exceedingly slow under the conditions of these experiments. Nitrogen dioxide might have been formed, however, when the pressure of gas uncondensed by liquid air was measured. Nitrogen dioxide reacts with liquid mercury[8] according to the equation $6NO_2 + 2Hg = 2Hg(NO_3)_2 + N_2$. As will be shown later the total reaction in the present experiments may be written $Hg + N_2O = HgO + N_2$ so that very little if any nitrogen dioxide has been formed as an intermediate. Its presence is, therefore, ignored. Oxygen reacts rapidly with excited mercury with the eventual production of mercuric oxide.[15] This gas could not be present to any appreciable extent as the results will be shown to indicate.

With the above facts in mind the total pressure during a run will be represented by the expression

$$P_t = P_{NO} + P_{N_2O} + P_{N_2} \quad (1)$$

Nitric oxide has a vapor pressure large enough so that it would not be condensed by liquid air at the low pressures prevailing in these experiments.[11] When mixtures of nitrous and nitric oxides were studied it became evident that condensation of the nitrous oxide removed a considerable portion of the nitric oxide from the gas phase. In fact some of the results indicated the existence of a definite compound $NO \cdot N_2O$ (or N_3O_2) stable at liquid air temperatures. Definite proof of the existence of this compound could not be obtained, but the results showed that approximately one molecule of nitric oxide is removed from the gas phase per molecule of nitrous oxide condensed. The extent of the removal will depend somewhat on conditions. The pressure of the gas uncondensed by liquid air will be given by

$$P_f = P_{N_2} + (1 - x)P_{NO} \quad (2)$$

where x is the fraction of the nitric oxide removed from the gas phase. When the nitrous oxide is present in large excess, x may be taken equal to unity.

If we consider part of the reaction to have proceeded according to the equation $Hg + N_2O = N_2 + HgO$ and the rest according to $N_2O = NO + {}^1/_2 N_2$, we may obviously write

$$P_{NO} = 2(P_t - P_i) \quad (3)$$

[14] See Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, London, 1926, p. 110.

[15] Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926); Noyes, THIS JOURNAL, **49**, 3100 (1927); Leipunsky and Sagulin, *Z. physik. Chem.*, **B1**, 362 (1928); **B3**, 215 (1929); Noyes, *ibid.*, **B2**, 445 (1929).

where P_i is the initial pressure of nitrous oxide. When the nitrous oxide is in excess we may write

$$P_{N_2O} = 2P_i - P_t - P_f \quad (4)$$

When the nitric oxide is in excess

$$P_{N_2O} = {}^1/_2(P_t - P_f) \quad (5)$$

(c) **The Change of Pressure during Reaction.**—Figure 1 shows typical curves of total pressure and pressure of gas uncondensed by liquid air as a function of time. It will be noticed that the curves both pass through maxima and at the end of the run they become identical. The final pressure indicated on both curves is equal to the initial pressure of nitrous oxide within experimental error. This was always found to be true for reactions which were allowed to proceed to completion.

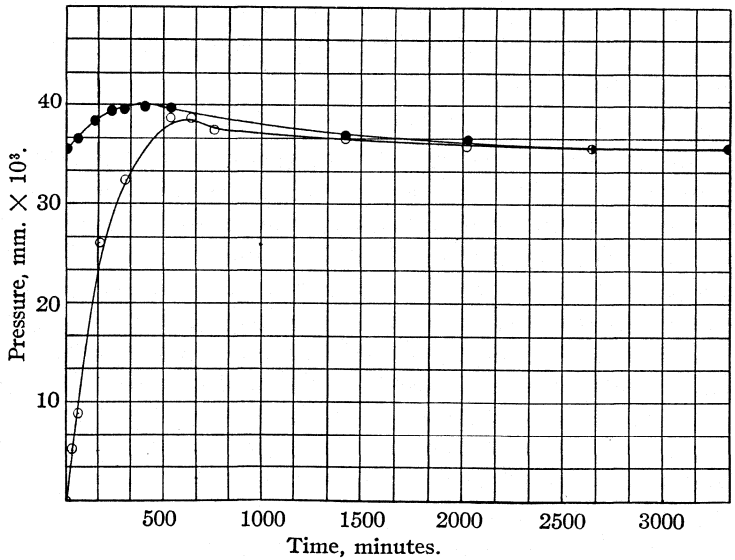

Fig. 1.—Lower curve, gas uncondensed by liquid air; upper curve, total gas.

These facts may be interpreted in the following manner. (1) The total net reaction is represented by the equation $Hg + N_2O = HgO + N_2$. (2) Nitric oxide is formed either by a primary or secondary reaction and reacts eventually with excited mercury to give mercuric oxide and nitrogen.[11] Side reactions leading to other final products must be relatively unimportant.

(d) **The Effect of Addition of Nitric Oxide.**—When nitric oxide was added to the nitrous oxide so that pressures of the two gases were both large, the total pressure decreased quite rapidly, thus indicating that nitric oxide was being decomposed more rapidly than it was being formed. When

the nitrous oxide was greatly in excess, this was still found to be the case, the pressure increase at the beginning being very slight or negligible followed by a fairly rapid decrease. Figure 2 shows variation of nitrous oxide pressure and of nitric oxide pressure in a system consisting initially of a mixture of the two gases.

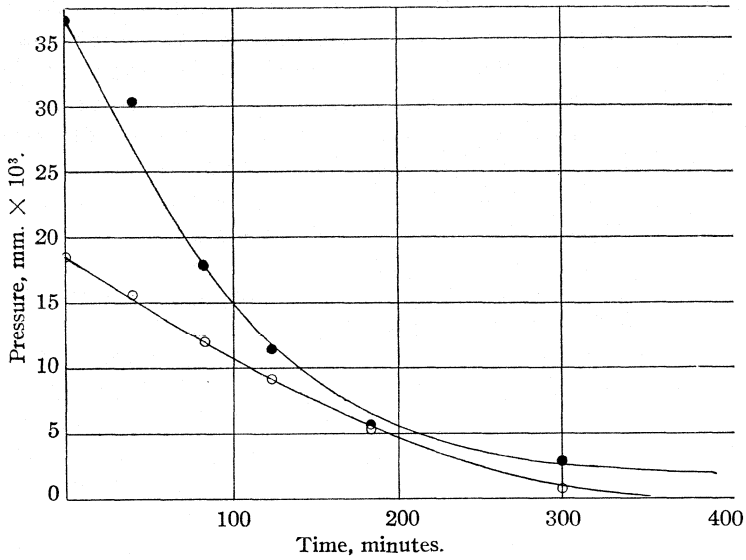

Fig. 2.—Upper curve, nitric oxide; lower curve, nitrous oxide.

(e) **The Relative Rates of Reaction of Nitrous and Nitric Oxides.**—The rate of decomposition of nitric oxide is markedly affected by impurities, particularly oxygen and nitrous oxide. When carefully purified nitrous and nitric oxides were compared, it was found that the initial rate of reaction of the former was about twenty times that of the latter at the same pressures.

(f) **Variation of Reaction Rate with Light Intensity.**—Only a qualitative study of the variation of reaction rate with light intensity was made. As stated above the rate without a Corex filter was so rapid that it may have been determined by the rate of diffusion of mercury vapor into the illuminated zone. This was further verified by a study of the rate of reaction as a function of the initial pressure of nitrous oxide. The transmission of Corex was determined and it is safe to say that the rate is at least approximately proportional to the light intensity.

(g) **The Quenching of Mercury Vapor Fluorescence by Nitrous Oxide.**—Only a qualitative study of the quenching of mercury fluorescence by nitrous oxide was made. The method has been described previously.[11] The results did indicate a very high degree of quenching and a very large probable cross section.

III. Discussion of Results

(a) **The Primary Process.**—The possible primary actions of excited mercury on nitrous oxide may be represented by the equations[16]

$$Hg(2^3P_1) + N_2O = NO(^2\Pi) + N(^4S) + Hg(1^1S_0);\ E = 0.3 \pm 0.3\ \text{v.} \quad (6)$$

$$Hg(2^3P_1) + N_2O = N_2(^1\Sigma) + O(^3P) + Hg(1^1S_0);\ E = 3.0\ \text{v.} \quad (7)$$

Electronic excitation of either the nitrogen or nitric oxide molecules would be impossible, although either might separate with a certain amount of vibration energy.[17] Certain higher levels of the nitrogen and oxygen atoms might be of importance. For nitrogen all doublet and quartet levels seem to be too high. For oxygen the ^1D level at 1.9 volts might be formed.[8]

Two principles may be used as guides for the prediction of the most probable primary step, although neither of them is applicable in a simple way to systems as complex as the one under consideration: (1) the principle of conservation of spin angular momentum.[18] Reaction (7) or the corresponding reaction involving formation of a ^1D oxygen atom, would best obey the requirements of this principle. The change in electron spin of the mercury atom would, apparently, favor the formation of ^3P oxygen atoms. It seems more necessary, however, for both fragments to have the same spin. (2) Kallmann and London[19] and Rice[20] have shown that good resonance is essential to a high probability of energy transfer in collisions of the second kind. Thus equation (6) would be more probable than equation (7) unless in the latter case either the nitrogen molecule or the oxygen atom were in a high energy level.

The molecule of nitrous oxide is linear[3] and unsymmetrical.[1,3] It may have the structure N=N=O or be resonating, according to Pauling, between the structures N—N≡O and N≡N—O. Its electron structure is probably similar to that of carbon dioxide, which, according to Mulliken,[21] is $\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4$, corresponding to a $^1\Sigma$ state for a diatomic molecule. A definite prediction as to the nature of the upper electron state is difficult,

[16] The energies of dissociation of nitrogen [Birge, *Phys. Rev.*, **34**, 1062 (1929); Tate and Lozier, *ibid.*, **39**, 262 (1932)] and oxygen [Herzberg, *Z. physik. Chem.*, **B10**, 189 (1930)] were taken as 8.7 and 5.1 electron volts, respectively. The heats of formation of nitrous oxide [Ramsperger and Waddington, *Proc. Nat. Acad. Sci.*, **17**, 104 (1931)] and nitric oxide [Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 560] correspond to 0.74 and 0.94 electron volt.

[17] For example, if the nitrogen molecules were formed in the tenth vibration level, nearly perfect resonance would be found. See "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, p. 415, for the data concerning vibration levels of nitrogen.

[18] Wigner, *Nachr. Götting. Ges.*, 375 (1927); see Bates, THIS JOURNAL, **54**, 569 (1932), for a discussion of the applicability of this principle to systems involving excited mercury.

[19] Kallmann and London, *Z. physik. Chem.*, **B2**, 207 (1929).

[20] Rice, *Proc. Nat. Acad. Sci.*, **17**, 34 (1931).

[21] Mulliken, *Phys. Rev.*, **40**, 60 (1932).

although repulsion seems to exist between the dissociation products at all distances since no bands are observed even at high pressures with long lengths of path. From this one would expect a dissociation into a ^1D oxygen atom and a normal nitrogen molecule to be most probable. It is not improbable that a shift of one of the π bonding electrons by the absorption of radiation would produce a change of this type.

Farkas, Haber and Harteck[22] find that nitrous oxide photosensitizes the hydrogen–oxygen reaction in the far ultraviolet. While these results may be interpreted in several different manners, these authors believe the reaction chains to be started by the initial production of oxygen atoms.

The evidence to be presented is somewhat inconclusive as to the nature of the primary step. If a chain is to be propagated, as seems necessary to explain the results of Macdonald,[6] it must be by reactions of the type $O + N_2O = O_2 + N_2$ (or 2NO) or $N + N_2O = NO + N_2$, unless a nitrogen molecule in a high vibration state is considered to be effective in this respect. Musgrave and Hinshelwood[10] use the reaction $O + N_2O = 2NO$ in interpreting the decomposition of nitrous oxide thermally at relatively low pressures.

Since one molecule of nitric oxide is not formed for each molecule of nitrous oxide decomposing even at the beginning of a run, the first step can hardly be (6) followed by $N + N_2O = NO + N_2$, unless some exceedingly probable reaction begins to use up nitric oxide immediately.

The behavior of mixtures of nitrous and nitric oxides indicates that nitric oxide is used up quite rapidly. Although nitric oxide alone decomposes with about one-twentieth the rate for pure nitrous oxide, in mixtures of the two gases its rate of disappearance is the larger of the two. This may be due partially to the fact that excited nitric oxide molecules[11] react more readily with nitrous oxide than with nitric oxide molecules and it may be due to reactions of the type $N + NO = N_2 + O$ or $O + NO = O_2 + N$. Even if the low recent value for the heat of dissociation of nitrogen (8.4 v.[16]) is assumed, the second of these reactions is endoenergetic to the extent of more than half a volt. It seems probable, therefore, that either ^1D oxygen atoms or nitrogen atoms are formed during the primary process. The data herein presented may be explained by assuming that both reactions take place simultaneously, but the data may best be interpreted by assuming the ^1D oxygen atoms.[23] Calculation of the probable energy of activation for a reaction of the type $O + NO = O_2 + N$, although subject to several uncertainties, indicates quite a low value.[24] This reaction does, however, violate the electron skin conservation rule.

[22] Farkas, Haber and Harteck, *Z. Elektrochem.*, **36,** 711 (1930).

[23] Herzberg [*Z. physik. Chem.*, **B17,** 68 (1932)] has recently come to the conclusion that probably $^1\Sigma$ nitrogen molecules and ^1D oxygen atoms are produced by direct optical dissociation.

[24] *Cf.* Eyring and Polanyi, *Z. physik. Chem.*, **B12,** 279 (1931).

Some experiments were performed in which oxygen was added to the nitrous oxide. Here the results indicate that oxygen catalyzes the reaction $2N_2O = 2NO + N_2$, in addition to forming mercuric oxide,[25] and that when the gases were cooled in the liquid-air trap, nitrogen dioxide was formed from the union of nitric oxide and oxygen. Plausible mechanisms for this process may be advanced, but it seems probable that oxygen atoms (probably in excited levels) do react with nitrous oxide to form nitric oxide. For reasons given above nitrogen dioxide is probably not formed in appreciable quantity in the absence of added oxygen.

(b) **The Rate of Decomposition of Nitrous Oxide.**—The pressure of excited mercury atoms in the steady state will be

$$P_{Hg}^{\circ} = k_1 I/(k_2 P_{N_2O} + k_3 + f(P_x)) \qquad (8)$$

where $k_1 I$ is the rate of increase of pressure of excited mercury atoms due to absorption of radiation of intensity I, k_2 is the constant for the bimolecular reaction between excited mercury atoms and nitrous oxide molecules, k_3 is the constant in the equation for the unimolecular rate of decay of excited mercury atoms by fluorescence and $f(P_x)$ is a term depending on the rate of quenching of mercury atoms by gases other than nitrous oxide. The rate of decomposition of nitrous oxide will be given by the equation

$$-dP_{N_2O}/dt = Mk_2 P_{Hg}^{\circ} P_{N_2O} \qquad (9)$$

in the absence of disturbing secondary reactions. M is the number of nitrous oxide molecules decomposing per molecule activated by collisions of the second kind with excited mercury. Equation (10) may be integrated if M is assumed to be constant and $f(P_x)$ is either known or assumed to be small compared to the other terms in the denominator of equation (8).

At the start of a run $f(P_x)$ is zero and other disturbing factors should be a minimum, so that by studying the initial rates of reaction at a series of pressures k_2/k_3 may be calculated. This ratio shows a fair degree of constancy from quite low pressures to pressures of several millimeters. The average value is 4.67×10^{-3}, if the unit of pressure is taken as 10^{-3} mm. Since k_3 is 9.7×10^6 sec.$^{-1}$, k_2 may be calculated. $1/k_2$ will be the mean time between collisions between excited mercury atoms and nitrous oxide molecules at a pressure of 10^{-3} mm. Using the familiar expressions of kinetic theory the value of σ^2, the square of the sum of the radii of the nitrous oxide molecule and the excited mercury atom may be calculated. The average value is found to be about 100×10^{-16} sq. cm. This value may be compared with those found by Zemansky[26] and by Bates[18] for other molecules by a study of their quenching of the fluorescence of mercury

[25] *Cf.* Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926); Noyes, THIS JOURNAL, **49**, 3100 (1927); Leipunsky and Sagulin, *Z. physik. Chem.*, **B1**, 362 (1928); **B3**, 215 (1929); Noyes, *ibid.*, **B2**, 445 (1929).

[26] Zemansky, *Phys. Rev.*, **31**, 812 (1928); **36**, 219, 919 (1930).

vapor. Suffice to say that this value is exceedingly large and agrees with the qualitative results presented above on the extent of quenching.

Integration of equation (9) gives

$$K_1(P_{N_2O} - P'_{N_2O}) + K_2 \log_e(P_{N_2O}/P'_{N_2O}) = t' - t \qquad (10)$$

if $f(P_x)$ is ignored. $K_1 = 1/Mk_1I$; $K_2 = k_3/Mk_1k_2I$. Thus $K_1/K_2 = k_2/k_3$. Equation (10) is found to be of the right general form to fit the data, as is shown in Fig. 3, where the smooth curve is calculated with arbitrary values of K_1 and K_2. The ratio of K_1 to K_2 calculated from a given run is much larger than k_2/k_3 found above and the introduction of a term corresponding to $f(P_x)$ only makes matters worse. The deviation is of such a nature that the logarithmic term is actually of less importance than theory would predict.

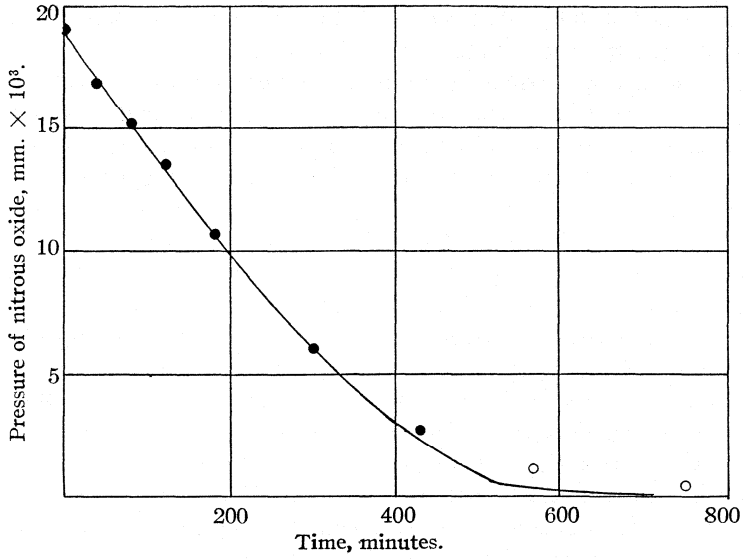

Fig. 3.

One is forced to one of two conclusions: (1) the effective cross section of the nitrous oxide molecule may be much larger than found above; (2) the products of the reaction may be instrumental in bringing about decomposition of nitrous oxide molecules. The former conclusion is entirely unreasonable, whereas the latter would involve a term accounting for a species of autocatalysis. This is to be expected in view of the behavior of mixtures of nitrous and nitric oxides. Previous work indicated that a nitric oxide molecule in a high rotation–vibration state may be produced upon collision with excited mercury atoms.[11] Even though Bates[18] has shown nitric oxide to quench strongly the fluorescence of mercury, this gas does not have much inhibiting action on the decomposition of nitrous oxide. It may be,

therefore, that the excited nitric oxide molecules react readily with nitrous oxide. Inclusion of these postulates makes it possible to arrive at an exact rate equation, but since undeterminable constants would at the same time be introduced, the result would have little theoretical significance. The qualitative conclusion here given is, however, further made reasonable by the facts in the following section.

(c) **The Variation of Total Pressure with Time.**—It is well known that there is no appreciable thermal reaction between nitrous and nitric oxides at room temperature. Experiment showed also no noticeable reaction at 100 or at 200°, thus indicating that activation of these molecules to the first few vibration levels is insufficient to produce reaction between them. We may, therefore, neglect both the thermal reaction between these gases and reaction between nitrous oxide molecules and molecules of nitric oxide which have been raised to the second vibration level through quenching 2^3P_1 mercury atoms to the 2^3P_0 state.

At the beginning of the run one finds between 0.3 and 0.5 molecule of nitric oxide to be formed for each molecule of nitrous oxide disappearing. If the equation found by Macdonald[6] for the direct reaction is identical with that followed by the sensitized reaction, the ratio should be 0.5.

At the point of maximum total pressure the rate of formation of nitric oxide should be equal to its rate of disappearance. If no disturbing influence intervenes, one could calculate, from the ratio P_{NO}/P_{N_2O} at this point, the ratios of the constants for the bimolecular reactions between these gases and excited mercury. The average value of P_{NO}/P_{N_2O} at the maximum is between three and four, although it shows some variation from run to run, and this may be compared with the fact that pure nitrous oxide decomposes about twenty times as rapidly as pure nitric oxide. Since all of the nitrous oxide does not decompose to give nitric oxide, this ratio should be actually between six and ten. On the other hand, when the reaction is nearly complete and the nitrous oxide has practically disappeared, the final pressure changes are very close to what one would predict for pure nitric oxide. This is further evidence that these gases influence each other during reaction.

(d) **Conclusions.**—The course of the reaction between excited mercury and nitrous oxide may be described as follows. (1) Either an excited oxygen atom and a nitrogen molecule or a normal nitrogen atom and a nitric oxide molecule are produced in the primary step. (2) The excited oxygen atom reacts with a nitrous oxide molecule to produce nitric oxide or the nitrogen atom reacts with nitrous oxide to produce nitrogen and nitric oxide. Both of the steps under (1) and (2) may take place simultaneously, but the initial formation of oxygen atoms seems probable. (3) Nitric oxide is used up either by collision with oxygen or with nitrogen atoms. (4) Nitric oxide molecules activated by collision with excited

mercury atoms react with nitrous oxide molecules. (5) Since the final equation of the complete reaction is $Hg + N_2O = HgO + N_2$, either ozone or excited oxygen molecules finally react with the mercury to produce mercuric oxide. This is considered to be a relatively fast reaction. The possibility of nitrogen dioxide is not considered to be of importance due to the fact that the final nitrogen pressure in long runs is equal to the initial nitrous oxide pressure. Some reaction of the type $NO_2 + Hg = HgO + NO$ may, however, take place in the gas phase. With nitric oxide and oxygen present, nitrogen dioxide would result when the gases are cooled in the liquid-air trap.

Summary

1. The total reaction between excited mercury and nitrous oxide may be represented by the equation $Hg + N_2O = HgO + N_2$.

2. Definite decision as to the nature of the initial step is not possible, although certain conclusions are drawn. The effects of adding oxygen and nitric oxide make identification of some steps possible.

3. As ascertained from reaction rate experiments the effective cross section of the nitrous oxide molecule as regards its interaction with excited mercury is very large.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE RAMAN SPECTRUM OF GERMANIUM TETRACHLORIDE

BY R. R. HAUN AND WILLIAM D. HARKINS

RECEIVED JUNE 6, 1932 PUBLISHED OCTOBER 5, 1932

The Raman spectrum of germanium tetrachloride was obtained by the method described in the next paper of this series. The frequencies of the Raman lines are given in Table I.

Considerable work, both experimental and theoretical, has been done upon the problem of the vibrational frequencies of molecules of the type

TABLE I

THE RAMAN LINES OF GERMANIUM TETRACHLORIDE

Raman lines, exciting lines and displacements in $cm.^{-1}$

Raman	Excit.	D	Raman	Excit.	D
22487 (1)	22938	451	23112 (5)	22938	174
22544 (10)	22938	394	23337 (6)	22938	399
22595 (1)	22995	400	24309 (6)	24705	396
22768 (6)	22938	170	24535 (2)	24705	171
22808 (6)	22938	130	24571 (2)	24705	134
23070 (5)	22938	132			

SUMMARY OF DISPLACEMENTS IN ORDER OF INTENSITY

397 (10), 132 (6), 171 (6), 451 (or 508) (1)

XY_4, which contain five atoms. Table II gives a comparison of the wave numbers for the tetrachlorides of carbon, silicon, titanium and tin, with those of germanium.

TABLE II

RAMAN FREQUENCIES OF TETRAHALIDES

	CCl_4(6)	$SiCl_4$(14)	$TiCl_4$(22)	$GeCl_4$(32)	$SnCl_4$(50)	CBr_4	$SnBr_4$
ω_2(?)	217 (8)	151 (5)	(120 (4))	132 (6)	104 (5)	123 (2)	64 (2)
ω_4(a)	313 (8)	221 (5)	(144 (1))	171 (6)	134 (6)	183 (4)	88 (4)
ω_1(?)	459 (8)	452 (10)	(386 (6))	397 (10)	366 (10)	265 (5)	220 (4)
ω_3(a)	760 (3)	607 (2)	(497 (2))	451 (1)	404 (6)	667 (3b)	279 (3)
	791 (3)			(or 508)			
	1537 (1)						

The data for all of the substances with the exception of germanium tetrachloride are taken from the compilation by Kohlrausch.[1]

In this table the chlorides are arranged in increasing order of the atomic numbers of the fourth group elements. The values for germanium tetrachloride appear to be too high in comparison with those of titanium and tin. However, this discrepancy is partly fictitious, since titanium belongs to another subdivision of group 4 of the periodic system[2] than germanium and tin. The normal term is $^3F_2$ for titanium, but $^3P_0$ for all of the other elements of this group.

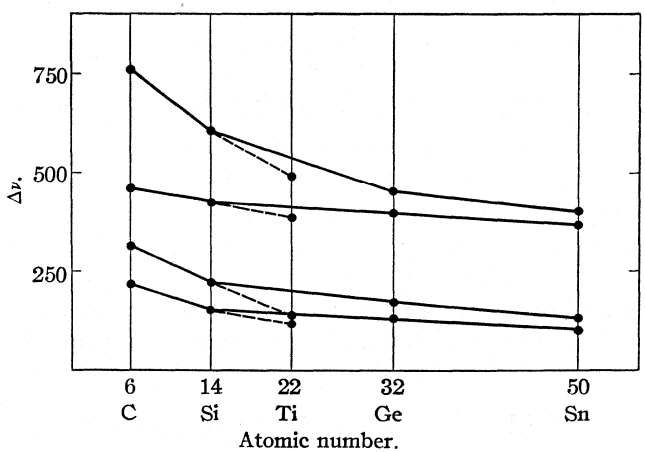

Fig. 1.—Raman frequencies for tetrachlorides (in cm.$^{-1}$). The highest frequency for germanium may be 508 cm.$^{-1}$ instead of the value plotted. If this is true the uppermost line is also linear from Si to Sn.

Figure 1 exhibits the following interesting relations: the wave numbers for any one of the types of frequencies (ω_1, ω_2, ω_3 or ω_4) are nearly linear

[1] Kohlrausch, "Der Smekal-Raman-Effekt," Berlin, 1931.

[2] Harkins and Hall, THIS JOURNAL, **38**, 169 (1916).

with respect to atomic number (1) for carbon, silicon and titanium, and (2) (except for W_3) for silicon, for germanium and tin.

The theory of the spectra of molecules of the type XY_4 has been developed for methane by Dennison[3] and for tetrahalides by Schaeffer[4] on the assumption of central forces. Trumpy[5] has shown that the three constants of the theory can be adjusted in such a way as to give a moderately good agreement with the observed data. Urey and Bradley[6] use a more accurate theory which considers forces which act along the "valence bonds," perpendicular to them, and also repulsive forces between the halogen atoms. Both Trumpy, and Urey and Bradley, obtain the poorest agreement in the case of titanium tetrachloride.

The frequencies ω_1 and ω_2 correspond to optically inactive vibrations which do not affect the electrical moment. The vibration for ω_1 is along the valence directions of the tetrahedron, and all the halogen atoms are supposed to move outward (or inward) simultaneously in such a way as to keep the resultant force upon the central atom equal to zero. In the vibration for ω_2 the halogen atoms are supposed to move on the surface of a sphere for which the atom X is the center. The frequencies ω_3 and ω_4 correspond to vibrations in which the symmetry of the molecule is not preserved, so the electrical moment is affected and ω_3 and ω_4 are optically active.

The writers are indebted to Professor Warren C. Johnson for the germanium tetrachloride, and to a Grant-in-Aid of the National Research Council for the spectrograph used in this investigation.

Summary

1. The Raman spectrum of germanium tetrachloride is found to correspond to four displacements of wave number with values as follows

$$\omega_2 = 132\ (6),\ \omega_4 = 171\ (6),\ \omega_1 = 397\ (10) \text{ and } \omega_3 = 451\ (1)$$

(with a possibility that ω_3 is 508). The numbers in parentheses denote the relative intensities, and ω_1 and ω_2 designate, according to the theory, optically inactive and ω_3 and ω_4, optically active frequencies.

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[3] Dennison, *Astrophys. J.*, **62**, 84 (1925).

[4] Schaeffer, *Z. Physik*, **60**, 586 (1930).

[5] Trumpy, *ibid.*, **66**, 790 (1930).

[6] Urey and Bradley, *Phys. Rev.*, **38**, 1969 (1931).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE VIBRATION OF ATOMS AT THE END OF ORGANIC MOLECULES: RAMAN EFFECT AND THE CARBON-CHLORINE BOND

BY WILLIAM D. HARKINS AND R. R. HAUN

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1. Introduction

This investigation is a continuation of a study[1] of the effect of the length of an organic molecule and of a splitting of the hydrocarbon chain upon the vibration of an atom attached at the end of the molecule.

In the spectra of the halides of the paraffins the Raman frequency which is on the whole by far the most intense is represented in wave numbers in cm.$^{-1}$ by the values 712, 603 and 522 for the methyl chloride, bromide, and iodide, and by 650, 566 and 500 for the corresponding normal compounds which contain more than one carbon atom.

These values may be supposed to give the frequency of (longitudinal) vibration of the halogen atom at the end of the molecule with respect to the adjacent —CH_2— group. This frequency is in the methyl halides 2.13×10^{13} per second between carbon and chlorine, 1.81×10^{13} between carbon and bromine and 1.60×10^{13} between carbon and iodine. If more than one carbon atom is present these values are reduced to 1.96×10^{13} for chlorine, 1.70×10^{13} for bromine and 1.53×10^{13} for iodine. For comparison it may be stated that the frequency of vibration of the carbon atom in diamond is 3.7×10^{13} per second according to the simple theory of Lindemann.

The equation which gives the energy (ϵ^v) of the vibrational quantum number v (= 0, 1, 2, 3, ...) is, for an electronic state (e)

$$\epsilon^v = hc[\bar{\omega}_e (v + 1/2) - \bar{\omega}_e x_e (v + 1/2)^2 + \ldots] \quad (1)$$

It may be assumed that these Raman lines are usually produced by a net decrease (or increase in anti-Stokes lines) of unity in the vibrational quantum number, and that the transitions occur either to or from the zero state. Under these conditions it is justifiable to use merely the first term in v of the above equation since the error introduced in this way is small, probably less than one per cent. If the final Δv is two, then the error is larger, but still relatively small. In this paper $\bar{\omega}$ will be used to represent a wave number in cm.$^{-1}$ and ω, a frequency in sec.$^{-1}$.

On the above basis it may be assumed that the mechanical frequency ω_0 is, for a value of $\Delta v = \pm 1$, related approximately by the equation

$$\Delta\nu = \omega_0 (v' - v'') = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2} (v' - v'') \quad (2)$$

[1] Harkins and Bowers, THIS JOURNAL, **53**, 2425 (1931).

to the Raman frequency ($\Delta\nu$), which is associated with the vibration. For $v' - v'' = \pm 1$ this becomes

$$\Delta\nu = \pm \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2} \qquad (3)$$

the equation of the classical theory, in which μ is the mutual mass ($1/\mu = 1/m_1 + 1/m_2$) of the bodies which vibrate, and f is the force constant in the equation $P = f\,x$, in which P is the restoring force and x the displacement. A discussion of the probable values of the (valence) force constant will be given after the data have been presented.

2. Experimental Procedure

The apparatus is essentially the same as that used by Harkins and Bowers. The substance to be investigated was put into a bulb which is sealed to the Raman tube. The system was evacuated and sealed off, and the liquid then distilled into the Raman tube. The tube was placed vertically in a cylindrical container and a set of "condensed" mercury vapor arcs placed alongside the tube. The Raman tube and lamps were kept cooled by a stream of distilled water, which had been cooled previously by passing through a coil kept in ice. In this way it was possible to prevent distillation back into the side bulb, and consequently to use liquids of lower boiling point than in the previous work. In general, the chlorides used suffer no photochemical decomposition so that it was not necessary to use the filters which were required with the bromides and iodides.

The scattered light passed through a window in the bottom of the container and was reflected by a right angle prism into the spectrograph. The instrument used was a large Steinheil three glass prism spectrograph, which gives large dispersion and consequently affords greater accuracy in the determination of the frequencies. The dispersion obtained was 6 Å. per mm. at 4000 Å. and 25 Å. per mm. at 5500 Å., which was the range over which the experiments were conducted. Since the range was small, not as many Raman lines were obtained as by some other experimenters, but it was not thought necessary to repeat the experiments with another setting of the instrument, since the important values were obtainable with one setting. The large dispersion also accounts for the absence of some of the weaker lines, since the intensity is decreased.

The approximate wave length of each line was first obtained by direct comparison with the spectrum of the iron arc. The more exact values were obtained by measuring with the comparator and the use of the Hartmann formula. These were converted to frequencies and the differences between these and all the possible mercury exciting frequencies were calculated. The assignment to exciting frequencies was based upon the recurrence of the same difference and also to some extent upon the relative intensities.

TABLE I

RAMAN LINES, EXCITING LINES AND DISPLACEMENTS IN CM.$^{-1}$

Raman		Exct.	Δ	Raman		Exct.	Δ	Raman		Exct.	Δ
Ethyl Chloride											
19969	(2)	22938	2969	21830	(2)	24705	2875	22280	(10)	22938	658
20008	(2)	22938	2930	21873	(2)	22938	1065	22601	(3)	22938	337
21740	(4)	24705	2966	21974	(1)	22938	964	24047	(6)	24705	658
21772	(4)	24705	2933								
***n*-Propyl Chloride**											
19982	(4)	22938	2956	22212	(8)	22938	727	24395	(1)	27353	2958
21486	(5)	22938	1452	22290	(10)	22938	648	24419	(1)	27353	2934
21749	(6)	24705	2957	22573	(8)	22938	366	24431	(1)	27388	2957
21773	(6)	24705	2933	23927	(1)	24705	779	24458	(4)	27388	2931
21834	(5)	24705	2872	23981	(2)	24705	725	24478	(3)	27353	2875
22151	(7)	22938	787	24058	(4)	24705	643				
***n*-Butyl Chloride**											
21738	(2)	24705	2967	22282	(10)	22938	656	24425	(8b)	27388	2964
21764	(2)	24705	2942	22613	(1)	22938	325	24451	(8b)	27388	2937
21802	(4)	24705	2903	22645	(1)	22938	293	24486	(8b)	27388	2903
21832	(6)	24705	2875	24050	(2)	24705	655	24356	(1)	27388	3032
22219	(2)	22938	719	24389	(5b)	27353	2964				
***n*-Amyl Chloride**											
19972	(2)	22938	2967	21738	(4)	24705	2967	22207	(8)	22938	731
19996	(2)	22938	2943	21764	(4)	24705	2941	22280	(10)	22938	658
20024	(2)	22938	2914	21797	(2)	24705	2908	22428	(1)	22938	456
20060	(4)	22938	2877	21835	(8b)	24705	2870	22588	(1)	23039	451
21489	(10b)	22938	1450	21968	(1)	22938	970	23253	(4)	24705	1452
21553	(3)	24516	2963	22046	(1)	22938	893	23977	(1)	24705	729
21631	(3)	24516	2885	22146	(1)	23039	893	24048	(8)	23705	657
								24145	(1)	25592	1447
Isopropyl Chloride											
20009	(1)	22938	2929	21835	(3)	24705	2870	22598	(6)	22938	340
21491	(1)	22938	1447	21876	(3)	22938	1062	23256	(1)	24705	1450
21679	(1)	22938	1259	21975	(1)	22938	963	23646	(1)	24705	1060
21716	(2)	24705	3026	22052	(5)	22938	886	23187	(1)	24705	888
21767	(5)	24705	2938	22320	(10)	22938	618	24088	(7)	24705	617
21787	(5)	24705	2918	22512	(6)	22938	427				
Isobutyl Chloride											
19958	(1)	22938	2980	21829	(3)	24705	2876	23973	(3)	24705	733
20058	(1)	22938	2880	21977	(1)	22938	962	24014	(2)	24705	691
21362	(1)	24335	2973	22117	(3)	22938	821	24140	(3)	24705	565
21483	(1)	22938	1455	22205	(10)	22938	733	24408	(1)	27388	2980
21602	(1)	22938	1336	22246	(9)	22938	692	24433	(1)	27388	2955
21723	(2)	24705	2982	22371	(2)	22938	567	24476	(1)	27388	2912
21754	(2)	24705	2951	22504	(2)	22938	434				
21791	(2)	24705	2915	22599	(1)	22938	339				

TABLE I (*Concluded*)

Raman		Exct.	Δ	Raman		Exct.	Δ	Raman		Exct.	Δ
Isoamyl Chloride											
19972	(3)	22938	2966	21978	(2)	22938	960	23879	(1)	24705	826
21484	(2)	22938	1454	22107	(4)	22938	832	23950	(1)	24705	755
21550	(1)	24516	2965	22183	(2)	22938	755	24049	(2)	24705	656
21596	(1)	24516	2920	22214	(2)	23039	826	24238	(1)	24705	412
21643	(1)	24516	2874	22279	(4)	22938	659	24356	(1)	27388	3032
21735	(8)	24705	2970	22380	(1)	23039	660	24388	(6)	27353	2965
21771	(4)	24705	2934	22521	(1)	22938	418	22423	(10b)	27388	2966
21834	(7)	24705	2871	22662	(1)	25592	2930	24458	(5)	27388	2930
								24483	(5)	27388	2870
***Sec.*-butyl Chloride**											
20010	(4)	22938	2928	22269	(2)	22938	670	23329	(2)	24705	1377
21489	(1)	22938	1449	22306	(1)	22938	632	24039	(1)	24705	667
21586	(1)	24516	2930	22333	(4)	22938	605	24100	(1)	24705	606
21724	(4)	24705	2981	22417	(1)	22938	522	24148	(1)	25592	1444
21776	(8)	24705	2930	22475	(2)	22938	463	24364	(3)	27388	3025
21829	(3)	24705	2876	22558	(2)	25592	3034	24420	(10b)	27388	2968
22094	(1)	22938	844	22609	(2)	25592	2983	24460	(10b)	27388	2929
***Tert.*-butyl Chloride**											
19295	(1)	20155	859	21581	(2)	23039	1458	22694	(2)	24705	1911
19471	(1)	20336	866	21725	(7)	24705	2980	24131	(1)	22592	1461
19952	(2)	22938	2986	21775	(8)	24705	2930	24143	(9)	24705	563
20007	(2)	22938	2932	22066	(1)	24516	2450	24363	(2)	27388	3026
20452	(4)	22938	2487	22126	(5)	22938	812	24405	(5)	27388	2983
20490	(1)	22938	2449	22369	(10)	22938	569	24421	(5)	27388	2967
20839	(2)	22938	2099	22565	(2)	25592	3026	24459	(9)	27388	2930
21479	(1)	22938	1460	22626	(2)	25592	2966				
***Tert.*-amyl Chloride**											
19954	(1)	22938	2984	22139	(1)	22938	799	22636	(1)	25592	2990
20000	(1)	22938	2938	22162	(1)	25093	2932	23256	(3)	24705	1449
21483	(4)	22938	1455	22320	(3)	22938	619	24142	(8)	24705	563
21728	(7)	24705	2977	22377	(8)	22938	562	24409	(10)	27388	2980
21773	(8)	24705	2933	22567	(3)	25592	3025	24451	(10)	27388	2938
21816	(2)	22938	1123	22602	(1)	22938	336				
Allyl Chloride											
19979	(2)	22938	2959	21716	(1)	23039	1323	23291	(3)	24705	1414
19910	(1)	22938	3029	21740	(7)	24705	2965	23411	(2)	24705	1295
21293	(9)	22938	1645	22201	(10)	22938	737	23447	(2)	24705	1258
21522	(5)	22938	1416	22346	(8)	22938	592	23501	(2)	24705	1204
21607	(1)	22938	1330	22523	(5)	22938	416	23771	(1)	24705	934
21639	(4)	22938	1299	22644	(4)	22938	295	23966	(7)	24705	739
21678	(8)	22938	1260	22695	(1)	24335	1640	24112	(3)	24705	593

3. Experimental Data

Table I shows the compounds used, the values of the Raman frequencies obtained, the exciting frequencies to which they have been assigned, and

the frequency displacements. The intensities given are rough estimates made by arbitrarily assigning an intensity of 10 to the strongest Raman line on each plate, and estimating a comparative value of the others on that plate in terms of it.

A summary of the various displacements for the above compounds is given in Table II. Following this, in Table III, are given the values attained by other workers for those compounds of the above series which

TABLE II

RAMAN DISPLACEMENTS IN CM.$^{-1}$ FOR A SERIES OF ORGANIC CHLORIDES (HARKINS AND HAUN)

Ethyl	*n*-Propyl	*n*-Butyl	*n*-Amyl	Isopropyl	Isobutyl
337 (3)	366 (8)	294 (1)	454 (1)	340 (6)	339 (1)
		325 (1)		427 (6)	434 (2)
658 (10)	648 (10)	655 (10)	658 (10)	618 (10)	566 (3)
					691 (9)
	726 (6)	(719) (2)	730 (8)		733 (10)
	783 (7)				821 (3)
			893 (1)	887 (5)	
964 (1)			970 (1)	(963) (1)	962 (1)
1065 (2)				1063 (3)	
				1259 (1)	1336 (1)
	1452 (5)		1450 (10)	1448 (1)	1455 (1)
2875 (2)	2872 (7)	2874 (5)	2877 (8)	2870 (3)	2878 (3)
		2903 (8)	2911 (2)	2918 (5)	2914 (2)
2931 (4)	2930 (6)	2939 (8)	2941 (4)	2934 (3)	
2967 (4)	2956 (6)	2964 (8)	2967 (4)		2953 (2)
		3032 (1)		3026 (2)	2980 (1)

Isoamyl	*Sec.*-butyl	*Tert.*-butyl	*Tert.*-amyl	Allyl
	463 (2)			295 (4)
415 (1)	(522) (1)		(336) (1)	416 (5)
657 (4)	605 (4)	566 (10)	562 (8)	593 (8)
	668 (2)		(619) (3)	
755 (2)	(632) (1)		(799) (1)	738 (10)
828 (4)	(844) (1)	(812) (5)		
		862 (1)		
(960) (2)				934 (1)
			(1123) (2)	1204 (2)
				1259 (8)
				1297 (4)
	(1377) (2)			1327 (1)
1454 (2)	1446 (1)	1460 (1)	1452 (4)	1415 (5)
		(1911) (2)		
2872 (7)	(2876 (3)	(2099) (2)		1645 (9)
(2920) (1)		2449 (1)		
2931 (5)	2929 (10)	2930 (9)	2935 (10)	
2965 (10)	(2968) (10)	2966 (2)	2978 (10)	2962 (7)
	2982 (4)	2983 (7)	2987 (2)	
3026 (1)	3029 (3)	3026 (2)	3025 (3)	3028 (1)

TABLE III

RAMAN DISPLACEMENTS IN CM.$^{-1}$ FOR ORGANIC CHLORIDES (FROM KOHLRAUSCH'S "DER SMEKAL-RAMAN EFFEKT")

Methyl	Ethyl	*n*-Propyl	*n*-Butyl	Isopropyl	Isobutyl	*Teri.*-butyl	Allyl
					157 (0)		
			302 (3)		238 (0)	299 (3)	301 (3)
	337 (5)	365 (4)	333 (4)	340 (3)	340 (1)	368 (3)	
	438 (½)	(418) (2)		426 (2)	433 (1)		408 (3)
			469 (2)	490 (0)	528 (0)		514 (1)
712 (10)	655 (10)	651 (5)	650 (8)	614 (5)	696 (3)	546 (6)	589 (4)
		725 (4)	722 (4)		738 (4)		735 (2)
			809 (4)		815 (1)	806 (3)	
		850 (2)	871 (3)		867 (0)		
		892 (2)	898 (1)	886 (2)			
	966 (4)		928 (½)		956 (2)		932 (2)
						1017 (1)	1032 (1)
1098 (2)	1071 (3)	1028 (3)	1055 (3)	1060 (2)			
		(1105) (0)	1107 (6)	1158 (1)	1107 (0)		1110 (1)
							1204 (3)
	(1276) (½)	(1289) (0)	1294 (4b)	1257 (2)	1230 (0)		1259 (3)
							1291 (2)
		(1339) (1)		1326 (1)	1322 (0)		1412 (3)
	1448 (4)	1446 (4b)	1464 (2)	1446 (4b)	1464 (2)	1445 (3sb)	1442 (1)
							1478 (3)
2815 (2)				(2828) (2?)			1641 (6)
	2875 (4b)	2873 (5)	2872 (3)	2864 (2)	2874 (5)	2893 (2b)	2882 (2?)
			2906 (5)	2917 (5)	2918 (0)		
	2930 (8b)	2935 (7)	2936 (4)	2932 (2)		2925 (6b)	
2955 (10)	2966 (8)	2957 (7)	2960 (5)	2964 (4)	2977 (5)		2954 (5b)
		2975 (0)					
		2998 (0)	3001 (0)				3021 (4b)
3024 (2b)		3019 (0)		3024 (0)			3087 (2b)

they have studied. These values have been taken from Kohlrausch's "Der Smekal-Raman Effekt," which contains a summary of all the results obtained by various workers up to June, 1931.

4. The Carbon–Chlorine Bond and the Vibration of Atoms at the End of an Organic Molecule. (a) Normal Compounds.—Contrary to the earlier opinion, the vibration of a bromine atom at the end of a paraffin chain has been shown to be an inner, rather than an outer, vibration.[1] That is, the vibration is largely that of the bromine atom and of the adjacent —CH_2— group. This was indicated by the fact that the fundamental wave number remains practically constant at 564 cm.$^{-1}$ as the length of the molecule is varied by a change from two to five in the number of carbon atoms. The same general constancy in frequency is found (Table IV) for the chlorine derivatives.

This table exhibits a considerable decrease of the vibration frequency at the carbon halogen bond, 54, 37 and 25 wave numbers for the chloride, bromide and iodide, respectively, as the number of carbon atoms is increased from one to two, but an approximate constancy with a further increase.

Propyl chloride appears to be somewhat anomalous in that its wave number is 10 units lower than that for ethyl chloride and 7 units lower

TABLE IV

TWO HIGHER FREQUENCIES ASSOCIATED WITH THE PRESENCE OF A HALOGEN ATOM

(1) Designates the fundamental frequency

(The numbers in parentheses represent the intensities)

	Cl (1)	Cl (2)	Δ	Br (1)	5r (2)	Δ	I (1)	I (2)	Δ
NORMAL									
Methyl CH_3X	712			603 (8)			522		
Ethyl CH_3CH_2X	658			566 (6)			497		
n-Propyl $CH_3CH_2CH_2X$	648 (10)	726 (6)	78	563 (6)	648 (4)	85	503	590	87
n-Butyl $CH_3CH_2CH_2CH_2X$	655 (10)	719 (2)	64	563 (5)	642 (2)	79	505	592	87
n-Amyl $CH_3CH_2CH_2CH_2CH_2X$	658 (10)	730 (8)	72	564	642	78			
ISO									
Isopropyl $(CH_3)_2CHX$	618 (10)			540					
Isobutyl $(CH_3)_2CHCH_2X$	691 (9)	733 (10)	42	572	612	60			
Isoamyl $(CH_3)_2CHCH_2CH_2X$	657 (4)	755 (2)	98	564	619	55			
SECONDARY									
Sec.-butyl $\begin{matrix}C_2H_5\\CH_3\end{matrix}\!\!>\!\!CHX$	605 (4)	668 (2)	63	533	612	79			
TERTIARY									
Tert.-butyl $(CH_3)_3CX$	566 (10)			538	615	77			
Tert.-amyl $(CH_3)_3CCH_2X$	562 (8)	619 (3)	57	No data					
UNSATURATED									
Allyl $CH_2{=}CHCH_2Cl$	593 (8)	738 (10)	145	535	695	160			

than that for butyl chloride. This effect is confirmed by the data of Dadieu and Kohlrausch,[2] and to some extent by those of West and Farnsworth,[3] who did not, however, investigate butyl chloride. The lower frequency associated here with the presence of three carbon atoms is not found for the bromide or for the iodide.

(b) Effect of a Branching of the Chains.—The branching of a hydrocarbon chain has a marked effect upon the frequency of vibration at the carbon–halogen bond. The relations which are exhibited are of considerable interest, and are outlined as follows where the comparisons are with respect to the frequency of the normal compounds. 1. A branching at the (α) carbon atom adjacent to the halogen atom causes a decrease of about 40 in the wave number of a chloride, and about 25 with a bromide. 2. A branching at the second (β) carbon atom causes (a) a considerable increase of frequency (about 40 wave numbers for the chloride and 16 for the bromide) if the chain divides into two (iso or secondary) at the second (β) carbon atom; (b) a large decrease of frequency, at least for tertiary amyl chloride ($\Delta\tilde{\omega} \simeq -100$) if the chain divides into three parts (tertiary) at the second (or β) carbon atom. 3. A branching of the chain into two methyl groups at the third (γ) carbon atom is associated with the same frequency as is found for the normal halide. 4. A double bond between the second and third carbon atoms in the allyl compounds is associated with a lowering of frequency of

[2] Dadieu and Kohlrausch, *Wien. Ber.*, **138**, 635 (1929).

[3] West and Farnsworth, *Trans. Faraday Soc.*, **27**, 145 (1931).

about 55 for the chloride and 30 for the bromide. That these frequencies are related to the presence of the halogen atom in the molecule is shown by the fact that they are not found in the corresponding paraffins.

5. A Higher Frequency (Wave Number about 730 cm.$^{-1}$) Associated with the Presence of a Chlorine Atom in the Molecule.—It is found that in addition to the fundamental wave number of about 657 cm.$^{-1}$ associated with the vibration of the halogen atom with respect to the adjacent —CH_2— group, there is a higher frequency, commonly about 80 wave numbers higher, which is related in an interesting and peculiar way to the presence of the halogen atom in the molecule. The wave number involved is about 730 cm.$^{-1}$ for either normal or iso derivatives of the paraffins (Table IV), but this frequency does not appear in the methyl or in the ethyl halide, and it is absent also for the isopropyl halide. It appears in the normal propyl and in the isobutyl halides, and in the secondary butyl derivatives. However, in the secondary compound the frequency is much lower (668 cm.$^{-1}$), but the fundamental frequency is also much lower (605 cm.$^{-1}$). The values given above are for the chlorides, but the bromides and iodides exhibit corresponding values. In the normal and iso halides the peculiar higher frequency does not appear until there are three carbon atoms in the chain, aside from those in a branch.

These relations give considerable interest to the presence or absence of the corresponding frequency in the case of the tertiary amyl halides. Here, unfortunately, the data do not entirely agree, since the frequency in question has not been found for the chlorine, but seems to have been found for the bromine derivative.

6. Lower Frequencies Possibly Associated with the Carbon–Chlorine Bond.—In general one or two additional frequencies, lower than the fundamental frequency, associated with the carbon–chlorine bond, are obtained with the compounds studied above. This is in agreement with the results obtained for the bromides by Harkins and Bowers, who sug-

TABLE V

LOWER WAVE NUMBERS CHARACTERISTIC OF THE CARBON–HALOGEN BOND (PROBABLY DUE TO A TRANSVERSE VIBRATION)

	Cl	Br	I
Ethyl	337 (4)	290	261 (8)
n-Propyl	366 (8)	312	285 (4)
n-Butyl	294 (1) 325 (1)	280	209 (2) 250 (3)
n-Amyl	....	219 436	
Isopropyl	340 (6)	297	
Isobutyl	339 (2)	303	
Isoamyl		288	
Tert-butyl	299 (3) 368 (3)		

D. K.

gested that these lower frequencies are due to a transverse vibration at the bond, while the fundamental frequency is due to a longitudinal vibration. A larger variation is seen in the values for the chlorides than for the bromides.

West and Farnsworth also consider frequencies of this order to be due to a transverse vibration.

These values are of the general order of half those for the more characteristic vibration, but the correspondence is not at all exact.

7. Frequencies Associated with the Carbon–Hydrogen Bond and the Double Bond.—The wave numbers for the organic halides which correspond to a vibration along the carbon–hydrogen bond exhibit in general four different values of about 2870, 2930, 2965 and 3030 cm.$^{-1}$. The first three of these are found in many other classes of derivatives, but the last is more prominent in chlorides and bromides than in most other classes of compounds. The remarkably small variation in these values in the derivatives of the paraffins will be exhibited in a later paper.

The frequency associated with the double bond in the allyl halides is 1645 cm.$^{-1}$ in the chlorides, and 1638 in the bromides.

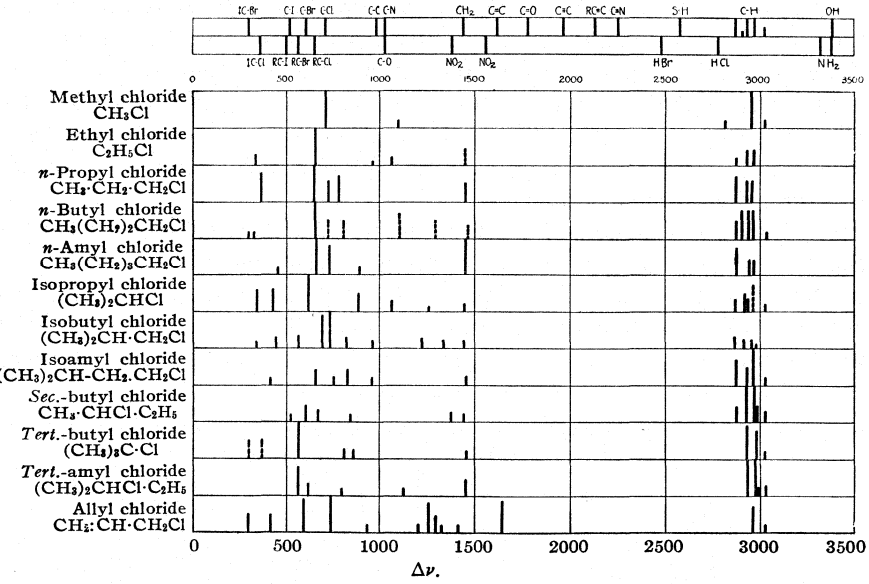

Fig. 1.—Raman frequencies for chlorides of the paraffins in cm.$^{-1}$.

8. The Raman Frequencies of Chlorides of the Paraffins.—The relations, which have already been discussed, are summarized in Fig. 1. At the top of this figure the most characteristic Raman frequencies for various derivatives of the paraffins are summarized. The first two frequencies on the left are assumed to be due to a transverse vibration at the

carbon–chlorine bond, and the next six to longitudinal vibrations for halides (RC–X) which contain more than one carbon atom, and also for those (C–X) which contain only one carbon atom.

9. The Strength of the Carbon–Halogen Bond.—It is customary to express the strength of a chemical bond for small displacements in terms of the force constant (f) in the equation.

The values of f as calculated in an earlier paper[1] for methyl halides are given in Table VI in order to establish a basis for discussion. These values relate to a vibration in the direction of the valence bond.

The force constant (a) is calculated in the ordinary way, and it is considered that the methyl group vibrates as a unit with respect to the halogen atom. In (b) a slight, somewhat arbitrary, allowance has been made for the fact that this is not strictly true.

TABLE VI

VALUES FOR THE CARBON–HALOGEN BOND

Compound	Wave no., $cm.^{-1}$	Frequency per second $\times 10^{-13}$	Force const. f $\times 10^{-5}$ dynes/cm. a	b	Amplitude $\times 10^{8}$ cm.		$\frac{1}{2}fa \times 10^{2}$	
CH_3Cl	712	2.135	3.136	3.02	6.7	11.6	2.0	3.5
CH_3Br	603	1.808	2.695	2.60	6.65	11.5	1.7	3.0
CH_3I	534	1.601	2.246	2.17	6.9	11.9	1.5	2.6

The force constant decreases from the chloride to the iodide. The values are much smaller than those of the single bonds listed by Dadieu and Kohlrausch which are, in 10^5 dynes per cm., equal to 4.31 for C–C in ethane, 4.96 for C–C in methyl alcohol, and 4.89 for C–N in methylamine.

Thus if f represents the strength of the bond, the carbon–halogen bond seems to be much weaker than the most common of the other single bonds found in organic compounds. That the strength of the bond decreases rapidly from chloride to bromide to iodide, is in agreement not only with the heats of dissociation but also with the other known relations.

The meaning of the amplitude a' is definite in the classical quantum theory, but loses this definiteness in the newer quantum mechanics.

Since

$$\epsilon = fa^2/_2 = (v + {}^1/_2)\omega_0 h$$

$$a = \left(\frac{2\epsilon}{f}\right)^{1/2} = \left(\frac{(2v+1)\,h\omega_0}{f}\right)^{1/2}$$

in which (ϵ) is the energy and ω_0 is the mechanical frequency. The values for this amplitude for $v = {}^1/_2$ and $v = {}^3/_2$ are given in Table IV.

Dadieu and Kohlrausch give the mean value of the force as $\frac{1}{2}fa$, and consider this to be more characteristic of the bond than the force constant.

Unfortunately equation (3) contains two variables, the force constant and the mutual mass (μ). Thus unless the masses of the vibrating bodies are known, the equation cannot be solved.

However, the equation and the data seem to indicate that the following conclusions are approximately true. (1) In general as the length of the normal hydrocarbon chain increases from two to five carbon atoms the strength of the carbon–halogen bond remains constant. (2) The Raman frequencies alone do not show whether or not the force constant for the carbon–halogen bond decreases from the methyl to the ethyl derivative, since the lower frequency for the latter may be caused by the increase of the mutual mass due to a damping of the vibration of the adjacent —CH_2— group by the remainder of the hydrocarbon chain. (3) A branching of the hydrocarbon chain seems to (a) in general lower the strength of the carbon–halogen bond, (b) increase the strength of the bond if two methyl groups are attached to the second (or β) carbon atom, (c) leave the strength of the bond the same as for the normal compound if the branching occurs at the third (or γ) carbon atom, or also presumably if it is more distant than this from the halogen atom.

The Raman wave number for butyl chloride is 655 cm.$^{-1}$ for the normal and 566 for the tertiary butyl chloride. If this lowering of frequency for the tertiary compound is due entirely to a decrease in the strength of the bond, and not to an increase of mutual mass due to the loading up of the α-carbon atom with three methyl groups, then the force constant is lower by about 25% in the tertiary compound.

There are chemical indications which confirm the idea that the bond is considerably weaker in the tertiary than in the normal halide. For example tertiary butyl halides are almost completely hydrolyzed by shaking with water at room temperature for about ten minutes, while the normal compound is hydrolyzed only slowly by hot water.

In general the ease of hydrolysis increases and the wave number of the Raman frequency decreases in the order: normal, iso, secondary, and tertiary compound. It seems that this is the order of decreasing strength of the halogen bond.

The exceptional case of the isobutyl halides, in which the increased frequency indicates an increased strength of bond, has been mentioned earlier. The Raman effect indicates that the strength of the carbon–halogen bond increases in the order isopropyl, normal, isobutyl halide. This is the order found by Kharasch and Flenner[4] in their study of the unsymmetrical mercuri-organic compounds.

The writers are indebted to a Grant-in-Aid of the National Research Council for the spectrograph used in this investigation.

Summary

1. It is found that the vibration at the carbon–chlorine bond in compounds of the type R–Cl, in which R is a paraffin radical, is an inner

[4] Kharasch and Flenner, THIS JOURNAL, **54**, 674 (1932).

rather than an outer vibration. That is, the vibration is largely between the chlorine atom and the adjacent carbon atom with its attached hydrogen atoms. This agrees with the conclusion of Harkins and Bowers concerning the vibration at the carbon–bromine bond.

2. The fundamental carbon–chlorine frequency, which probably corresponds to a longitudinal vibration in the direction of the straight line between the carbon and the chlorine nuclei is about 710 cm.$^{-1}$ for the methyl chloride and about 655 cm.$^{-1}$ for normal paraffin chlorides which contain two or more carbon atoms. This latter frequency is in general lowered considerably from 605 to 560 by a not too distant branching of the paraffin chain. In isobutyl chloride the frequency is higher (690), and in the isoamyl chloride it is the same as in the normal compound.

3. The strength of the carbon–halogen bond seems to be nearly constant as the number of carbon atoms in the molecule is increased from 2 to 5. It is possible that the bond is stronger in the methyl halides, but this is uncertain, since the large difference between methyl and other normal paraffin halides may lie wholly in a smaller mutual mass in the methyl halide.

4. The bond seems to be weaker in halides of the secondary, and still weaker in those of the tertiary derivatives. It is also weak in the isopropyl halides.

5. While according to (3) a branching of the hydrocarbon chain seems in general to weaken the carbon–halogen bond, the bond seems to be strengthened by the branching in isobutyl halides, and on the whole is left unaffected if the branching occurs sufficiently distant from the halogen atom, as in isoamyl halides, in which the branching occurs at the third (γ) carbon atom.

6. A frequency about 80 wave numbers higher than the most characteristic frequency of the halides is found to exhibit a very peculiar scheme of occurrence. For example it does not appear in normal paraffins which contain less than three, and with branched chains it does not appear if the number of carbon atoms is less than four. Whether this frequency is entirely absent or merely has a very low intensity has not been determined, but its intensity in the lowest compound in which it is found is in general high, for example 10 in isobutyl chloride, while the isopropyl compound exhibits no such frequency.

7. In general a frequency about half that of the fundamental frequency, seems to be associated with the carbon–halogen bond, probably with a transverse vibration.

CHICAGO, ILLINOIS

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

A REVISION OF THE ATOMIC WEIGHT OF SILICON. THE RATIO $SiCl_4:SiO_2$[1]

BY PHILIP F. WEATHERILL AND PERRY S. BRUNDAGE

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F. W. Clarke, in the fourth edition of his "Recalculation of Atomic Weights,"[2] gives a summary of the work on the atomic weight of silicon up to that time. Since the publication of Clarke's memoir, however, great advances have been made in the methods of purifying and handling silicon tetrachloride.

The first and, up to the present time, the most exhaustive study of the atomic weight of silicon, using the method of distillation in an all-glass vacuum apparatus, is that carried out by Baxter and his co-workers.[3,4] A determination of the ratios $SiCl_4$:Ag and $SiBr_4$:Ag gave, in the final series with each compound, respectively, Si = 28.067 and Si = 28.059, or an average value 28.063, on which the accepted value of 28.06 is based.

Hönigschmid and Steinheil,[5] using $SiCl_4$ which had been very carefully purified by A. Stock, by a method which has been described in connection with the purification of other compounds of this type,[6] determined the ratio $SiCl_4$:Ag. As the result of four very concordant values, they found Si = 28.105. An investigation of the purity of their silicon tetrachloride by the measurement of its vapor pressure at 0° showed that no change was taking place after four distillations.

By a novel method of determining the ratio $SiCl_4:H_2$, Stock and Kuss[7] found Si = 28.15. From the nature of this investigation the value obtained cannot be given the weight which is due the researches of Baxter and of Hönigschmid.

In the present work silicon tetrachloride was purified by repeated distillation in a vacuum, using fractionating columns filled with glass pearls. The pure material was taken off in sample bulbs of fused quartz, the bulbs broken in a platinum crucible under a partially frozen solution of pure hydrochloric acid, and the resulting silica gel dehydrated and weighed.

This ratio has been used before, most recently by Becker and Meyer,[8] but at that time the method of purification by repeated distillation in a

[1] From a dissertation submitted by Perry S. Brundage to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Clarke, Third Memoir, *Nat. Acad. Sci.*, **16**, 222 (1920).

[3] Baxter, Weatherill and Scripture, *Proc. Am. Acad. Arts Sci.*, **58**, 245 (1923).

[4] Baxter, Weatherill and Holmes, THIS JOURNAL, **42**, 1194 (1920).

[5] Hönigschmid and Steinheil, *Z. anorg. allgem. Chem.*, **141**, 101 (1924).

[6] Stock and Kuss, *Ber.*, **56B**, 1463 (1923).

[7] Stock and Kuss, *ibid.*, **56B**, 314 (1923).

[8] Becker and Meyer, *Z. anorg. Chem.*, **43**, 251 (1905).

vacuum had not been developed, and the method of taking off samples for analysis allowed more chance for error.

The Purification of Silicon Tetrachloride

With minor changes, the procedure followed that developed by Baxter and his coworkers.[3] Silicon tetrachloride, obtained from the General Electric Company, was repeatedly distilled in a vacuum, using fractionating columns containing glass pearls. A modification of the glass valve was adopted because it was felt that with the type used by Baxter (Fig. 1, A) there was danger of breaking the tube at *a*. The first type tried was that used by Hönigschmid and Chan[9] (Fig. 1, B). This, however, gave a cloud of extremely fine glass fragments which were carried throughout the apparatus when the thin-walled bulb at *b* (Fig. 1, B) was broken, so this was discarded in favor of the valve shown in Fig. 1, C. Here the hammer, *d*, weighted with mercury, breaks the spiral capillary *c*. In this type there seems to be little danger of breaking the apparatus and no fine fragments of glass are formed. The operation of this valve was very satisfactory.

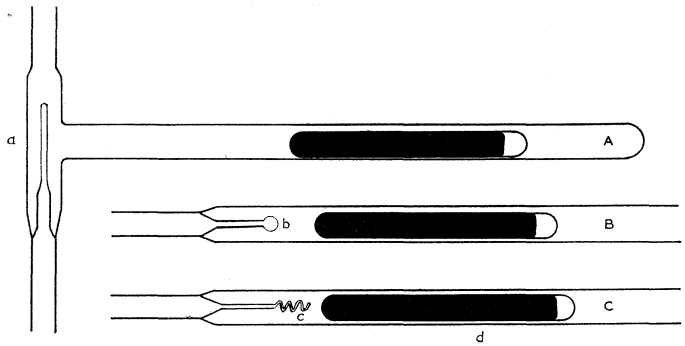

Fig. 1.

In pumping out the apparatus a mercury diffusion pump, backed by a rotary oil pump, was used. In all cases the apparatus was allowed to stand at least overnight, and readings on the McLeod gage were taken to be sure there was no leak. Phosphorus pentoxide was used as a drying agent in the McLeod gage.

After the start, where liquid air and carbon dioxide snow were necessary to remove the more volatile materials present, the distillation was carried out by cooling the receiver with an ice–salt mixture, the distillation flask being kept at room temperature. The distillation column was surrounded by a jacket which was kept cool by ice, so that there was a constant reflux of material over the glass pearls. In every distillation a small heavy fraction was left in the distillation flask and before sealing off this flask, the receiver was gently warmed, the distillation flask cooled and a small light fraction distilled back into it. In this way both a light and heavy fraction were removed at each distillation.

The best evidence for the purity of the material is the constancy of the value obtained from samples taken at rather widely separated points in the course of the distillations.

The number in the "Fraction of $SiCl_4$" column in Table I shows the number of distillations which were made before the material destined for analysis was taken off from the main line of distillation.

[9] Hönigschmid and Chan, *Z. anorg. allgem. Chem.*, **163**, 326 (1927).

Purification of Other Materials

Water.—Water from the laboratory still was twice redistilled, once from alkaline permanganate (which had been allowed to stand for some time) and once from very dilute sulfuric acid. The condensers were constructed of block tin tubes fitted to Pyrex flasks with constricted necks, which served as stills. The connections were made by a water seal, no cork or rubber being used. The water was distilled directly into the platinum crucible just before hydrolysis was started.

Hydrochloric Acid.—The best C. P. acid was diluted with an equal volume of pure water and distilled from a Pyrex flask through a quartz condenser, fitted to the constricted neck of the flask by a liquid seal. No cork or rubber or other material was used. The first and last thirds of the acid were discarded. The pure acid was distilled directly into the platinum crucible just before hydrolysis was started.

Phosphorus Pentoxide.—The ordinary C. P. material was sublimed in a current of pure oxygen in the usual way.

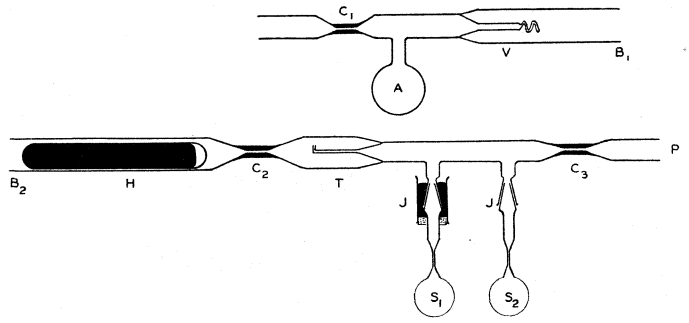

Fig. 2.

Method of Taking Samples for Analysis.—The apparatus used in taking samples for analysis is shown in Fig. 2. A large sampling bulb A with a valve V was sealed into the main distillation train, and after filling was sealed off at C_1. B_1 and B_2 were now sealed together and the whole system evacuated through P and sealed off at C_3. The valve V was then opened by allowing the hammer H to break the spiral capillary. The trap T was used to prevent any fragment of glass going into the sample bulbs S_1 and S_2.

One of the mercury seals used around the joints connecting the sampling bulbs to the rest of the apparatus is shown on S_1. The glass tube is held in place by a small cork so that the whole is easily removed.

The fused quartz sample bulbs S_1 and S_2 were then filled by cooling, and the slender capillaries sealed off with a very fine gas-oxygen flame.

The weight of the whole bulb and joint system was found before connecting it to the apparatus. After the bulb was sealed off from the joint, the weight of the joint was found, and thus the weight of quartz in the bulb itself. Subtracting this from the weight of the whole sealed sample gave the weight of $SiCl_4$.

After sealing off the samples and before opening the joints, bulb A was cooled in liquid air to remove all traces of silicon tetrachloride and capillary

C_2 sealed off. This prevented any possible deposition of silica on the joints, which were, however, momentarily dipped in sodium hydroxide, and then rinsed in acid to remove any trace that might have been left.

It is well known that quartz volatilizes rapidly on fusion. Experiments showed that it was necessary to keep the capillaries on the sampling bulbs very fine so that the loss of silica during the sealing off was not more than 0.01 or 0.02 mg. Experiments also showed that the joints could be cleaned completely from silica (from the silicon tetrachloride) and mercury, and that no appreciable amount of quartz was ground off from the joints during their use.

Weighings.—All weighings were made on a No. 10 Troemner balance with weights standardized to 0.01 mg. All weights were corrected to vacuum, the density of the air at the time of weighing being determined by readings of the barometer and the temperature and relative humidity in the balance case. For relative humidity measurements in the balance case, a hair hygrometer was used. This was checked frequently against a whirling psychrometer.

The density of dry air was plotted against pressure for a series of temperatures. The corrected barometric reading was modified by subtracting $0.38 \times$ v. p. $H_2O \times (H/100)$, where H is the relative humidity. This gave the pressure at which dry air would have the same density as the moist air at barometric pressure and relative humidity H. The graph was then entered on the proper isotherm, and from the pressure the density was determined. We have used other methods, such as weighing a standardized sealed bulb, but prefer the method outlined. It has the advantage that the readings are taken at the time of weighing rather than before or after, and seems to us easier.

The density of the weights was assumed to be 8.4; the density of fused quartz and of the silica formed by hydrolysis, 2.20. The densities of the sealed samples were determined separately for each sample by weighing in air and under distilled water in the usual way. All weighings were made by the method of substitution, except that in the standardization of weights the method of transposition was considered more convenient and so used. In weighing the platinum crucible in which hydrolysis was carried out, a similar platinum crucible weighing within 0.2 g. was used as a tare, and carried through the same heating treatment as the one in which hydrolysis occurred.

Analysis

Pure water and hydrochloric acid were distilled into a rather large platinum crucible and the quartz bulb with the sample of silicon tetrachloride put in this solution, which contained about 6 per cent. hydrochloric acid. The solution was then partially frozen by carbon dioxide snow, so that the bulb was held firmly to the bottom of the crucible. The bulb was

then broken under the liquid by tapping with a stiff platinum wire (which was left in the crucible).

The crucible and its contents, with the carbon dioxide snow, were transferred to a large casserole containing several pieces of cracked ice. The whole was carefully covered and allowed to stand overnight to allow the hydrolysis to proceed slowly as the temperature rose. The following morning the crucible contained a clear, smooth silica gel.

This gel was then slowly dehydrated, for several hours, in an air-bath, at 90 to 95°. After this treatment, which usually lasted overnight, the contents of the crucible had become a dry white flaky mass.

The crucible was then placed on a platinum disk in an electrically heated crucible furnace and ignited to constant weight.

Another similar furnace was connected in series and used to give the tare crucible the same ignition treatment.

The temperature was raised rather gradually, the usual times being one hour at 400°, one hour at 600°, two hours at 850°, two hours at 950° and finally at about 1080° until the weight became constant. Experiments showed that once a constant weight under this treatment was reached, further heating, even into the 1100° range, caused no further loss in weight.

Previous investigators used pure water, partially frozen, for this hydrolysis. In our preliminary experiments, however, we were unable to make the reaction take place so slowly that there was no appearance of spattering. While no material may be lost in such spattering, it seemed safer to use the hydrochloric acid solution where hydrolysis was much slower and no sign of spattering was visible.

The final heatings were carried out in a crucible furnace with a platinum winding. The Chromel A windings at first used gave out rapidly at the high temperatures used and caused much trouble, but once the platinum windings were put on, the furnaces worked perfectly.

The silica prepared in this way was uniformly white and flaky, and there was no evidence of adsorption during weighings. Apparently after prolonged treatment at the high temperature it is quite inactive. The purity of material so prepared has been the subject of investigations by Meyer,[10] who found no evidence of impurities present.

It was at first hoped that Pyrex bulbs would be satisfactory for the samples, but difficulties were found in their use. It was found that the heating necessary for dehydrating the silica gels caused a small loss in weight of the Pyrex glass from the bulb. This might have been corrected for partially by carrying an equal weight of Pyrex glass through the same treatment in the tare crucible, but a much greater trouble was found. During the dehydration at higher temperatures, reaction apparently takes place between the Pyrex and the contents of the crucible, and small spheres

[10] Meyer, *Z. anorg. Chem.*, **47**, 45 (1905).

of material are formed instead of the flaky solid given when quartz bulbs were used. The extent of this reaction was dependent upon the time rate of temperature change, and by a very gradual dehydration could be largely eliminated. Results computed for those analyses where such a reaction had taken place, gave markedly low values for the atomic weight of silicon, indicating a loss of some material. Since the analyses would always be open to question if Pyrex glass were used, it was necessary to make our sampling bulbs of fused quartz.

Results

The results of all analyses where sampling bulbs of fused quartz were used are given in Table I. With the exception of one sample which was lost during hydrolysis, every analysis that was started was carried to completion, and is recorded in the table. The atomic weight of chlorine is taken as 35.457.[11]

While the average rounds off to 28.103 in either case, we believe that those three analyses which are starred in the table should be given less weight than the others for the following reasons. Analyses 1 and 2 were the first ones run using fused quartz sampling bulbs, and these bulbs were so heavy that it was necessary to treat them very roughly in order to break them. This experience led to thinner bulbs for the remaining samples, and no further difficulty was encountered in breaking the remaining sample bulbs. Analysis 8 was in progress at a time when a great deal of difficulty was experienced with the furnace windings and the dehydration of the silica gel from this sample was twice interrupted for several days, so that it was subjected to much more handling than the others.

TABLE I

(Cl = 35.457)

Analysis	$SiCl_4$ vac. wt. g.	SiO_2 vac. wt. g.	Ratio SiO_2:$SiCl_4$	Atomic weight Si	Fraction of $SiCl_4$
1	2.11017	0.74587	0.353464	28.044*	XIII
2	2.53146	0.89563	.353800	28.132*	XIII
3	4.59854	1.62648	.353695	28.104	XV
4	2.86802	1.01447	.353718	28.110	XV
5	3.01710	1.06731	.353754	28.120	XV
6	2.90424	1.02706	.353642	28.090	XVII
7	2.55431	0.90357	.353743	28.117	XVII
8	2.80323	0.99175	.353788	28.129*	XVII
9	2.92542	1.03462	.353665	28.096	XVII
10	3.38901	1.19857	.353664	28.096	XVIII
11	2.10540	0.74458	.353653	28.093	XVIII
Average, including all analyses.....				28.103	
Average, omitting analyses 1, 2 and 8.....				28.103 ± 0.0027	

[11] "First Report of the Committee on Atomic Weights of the International Union of Chemistry," THIS JOURNAL, **53**, 1627 (1931).

In the remaining 8 analyses everything ran smoothly and there is no reason for preferring one analysis to any other.

Discarding those three analyses which were known to be subject to more possibility of error than the others, and which are recorded only for the sake of completeness, we have a value, based on 8 analyses, of Si = 28.103 ± 0.0027.

This is higher than the value 28.063 which Baxter[3] obtained from the ratios $SiCl_4$:Ag and $SiBr_4$:Ag. It is in excellent agreement with the value obtained by Hönigschmid and Steinheil,[5] Si = 28.105, from the ratio $SiCl_4$:Ag. It is difficult to explain this deviation, which is almost certainly much greater than the experimental error involved in either of the analytical methods. Each of the two rounded-off values, 28.06 and 28.10, has strong evidence in its support, since in each case different compounds have been used and have given results in good agreement. More experimental work obviously is needed.

Some previous atomic weight work has been criticized[12] because the exact terrestrial source of the material used was not known. It is interesting to note, therefore, that in accord with all other work on non-radioactive elements, investigations[13] have shown that silicon, regardless of its source, always has the same atomic weight and therefore the same isotopic composition.

Summary

Silicon tetrachloride, carefully purified by repeated distillation through efficient fractionating columns, in a vacuum in an all glass apparatus was hydrolyzed with a pure hydrochloric acid solution, and the ratio SiO_2:$SiCl_4$ determined. The mean of eight analyses gave the value Si = 28.103 ± 0.0027.

ANN ARBOR, MICHIGAN

[12] "Annual Reports of the Progress of Chemistry," The Chemical Society of London, 1924, Vol. XXI, p. 30.

[13] Jaeger and Dijkstra, *Z. anorg. allgem. Chem.*, **143**, 233 (1925); *Z. Electrochem.*, **32**, 328 (1926); Briscoe and Robinson, *Nature*, **117**, 377 (1926); Robinson and Smith, *J. Chem. Soc.*, 1262 (1926).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

THE QUANTUM EFFICIENCY OF THE PHOTOCHEMICAL DECOMPOSITION OF POTASSIUM PERSULFATE

BY R. H. CRIST

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The kinetic study of the photochemical decomposition of potassium persulfate has been reported previously.[1] The reaction $K_2S_2O_8 + H_2O = 2KHSO_4 + 1/2O_2$ is zero order in concentrated solution and pseudo unimolecular in very dilute solution (0.001 *M*), the temperature coefficient is low (1.0–1.15), the absorption starts at 3200 Å. and increases rapidly into the far ultraviolet, and the rate of the reaction is retarded very markedly by additions of sulfuric acid and less so by additions of potassium sulfate and potassium hydroxide. An effort was made to explain these latter results as a kinetic salt effect but with no definite conclusions. The present study gives some further facts for the reëxamination of this problem.

The primary object of this investigation was to determine the quantum efficiency of the reaction under different circumstances of electrolyte concentration and light frequency.

Apparatus and Procedure

The monochromator consisted of a 60° fused quartz prism 11.2 cm. on the side and 7.6 cm. high with fused quartz lenses 7.6 cm. high and 46 cm. focal length. A capillary mercury arc of special construction was used as the source and a Moll surface thermopile with a low resistance galvanometer served to measure the energy.

The lamp was substantially the same as described previously.[2] The most important change has been to put a transverse magnetic field across the arc and in the direction to displace the arc to the back wall. If the arc runs against the front air-cooled wall the quartz devitrifies very rapidly, if against the back wall the capillary remains clean in front except for a small brown deposit at the anode.[3] There is no white deposit as described by Daniels.[4]

Foreign gases were removed by gentle boiling at first and then heating the capillary to redness. A brown deposit formed which decomposed on further heating. The capillaries should be of pure fused crystal quartz instead of machine-blown quartz, which is of somewhat different composition.

The large Moll surface thermopile can be used as a surface instrument only when the energy density is the same throughout the area to be measured. In order to use it with

[1] Morgan and Crist, THIS JOURNAL, **49**, 16, 338, 960 (1927).

[2] Crist, *ibid.*, **52**, 4337 (1930); *J. Opt. Soc. Am.*, **21**, 690 (1931).

[3] The cooling was accomplished as before except that the larger stream of water struck the lamp somewhat below the upper end of the luminous arc. This served to reduce the fluctuations of the upper electrode. The copper gauze should cover slightly less than half the capillary, the best arrangement to be determined by experience. The gauze is supported by small wires from the upright part of the lower electrode. The capillary was 5 cm. long with the bore 3–3.4 mm. and the wall 1.8–2.2 mm. The arc burned on 5–5.5 amp. and 90–120 volts.

[4] Daniels and Heidt, THIS JOURNAL, **54**, 2383 (1932).

the divergent beam the whole surface was covered except for a 2.2-mm. slit over the junctions of the middle section, and the light was focused on the slit. The image width was smaller than the slit and a correction was made for the greater sensitivity in the central part of the slit from a plot of the deflections at regular intervals across the middle section. The calibration found was 27.4×10^{-8} watts per sec. or 3.93×10^{-6} cal. per minute.

The transmission of the measuring train, two crystal quartz lenses and the thermopile window was found by direct measurement to be 73%, that of the cell filled with water 91.6%.

Analytical Method.—The method of analysis used in the previous investigation was the ferrous sulfate–permanganate method for the determination of the undecomposed persulfate. The present method was the precipitation of the sulfate formed by the decomposition. Thermal decomposition of the persulfate made precipitation and digestion in a hot solution impossible as well as standing in the presence of the hydrogen-ion concentration usually recommended in barium sulfate precipitations. Consequently the solution to be analyzed was very slowly added to a well-stirred solution of about 50 cc. of 0.005 *M* barium chloride. The crystals obtained were very heavy and were filtered immediately. The method gave quite satisfactory results in the presence of persulfate ions.

Results and Discussion

The results of the investigation are given in Table I. The solutions used were 0.05 molar with respect to $K_2S_2O_8$ and the electrolyte concentration was as indicated. For the case of λ302 a correction for reflection from the rear wall of the cell was made. The light absorption by the persulfate is given in the third column, corrections having been made for the independent absorption of electrolytes where necessary. In the fourth column is the average intensity (deflections) for the period of the exposure.[5]

TABLE I

QUANTUM EFFICIENCY OF THE DECOMPOSITION OF POTASSIUM PERSULFATE IN THE PRESENCE OF ELECTROLYTES

Concn. in moles per liter; $K_2S_2O_8$ = 0.05 + electrolyte	Wave length in mμ	Light absorption	*I* (def.) incident on solution	Time, min.	Calories incident on soln.	Absorbed	Mole quanta × 10^5	Moles $K_2S_2O_8$ × 10^5	Moles / quanta
...	254	1.00	976	981	3.77	3.77	3.35	3.6	1.07
Na_2CO_3 0.005	254	1.00	1168	1905	8.75	8.74	7.78	7.5	0.96
...	265	0.965	5350	387	8.15	7.86	7.31	7.4	1.01
...	265	.965	4660	345	6.32	6.10	5.67	5.6	0.99
Na_2CO_3 0.05	265	.916	7230	320	9.10	8.33	7.75	7.9	1.02
KOH 0.05	265	.930	4750	280	5.23	4.87	4.53	5.1	1.12
H_2SO_4 0.01	265	.965	6430	260	6.55	6.32	5.88	5.0	0.85
...	302	.475	14290	220	12.34	6.00	6.37	6.4	1.01
...	302	.475	11180	242	10.62	5.16	5.48	5.7	1.04
Na_2CO_3 0.05	302	.455	6530	290	7.42	3.47	3.68	3.8	1.03
Na_2CO_3 0.05	302	.455	6440	341	8.63	4.02	4.27	4.4	1.03
H_2SO_4 0.01	302	.475	8630	259	8.78	4.26	4.51	3.8	0.84

[5] I (incident on solution)/I (thermopile) = (1/0.73) × 0.957 = 1.31, and one deflection = 3.93×10^{-6} calories per minute.

The photochemical reaction has been established in the previous papers,[1] as proceeding quantitatively according to the equation

$$S_2O_8^{=} + H_2O + h\nu \longrightarrow 2SO_4^{=} + 2H^+ + {}^1/_2O_2$$

The results in Table I show definitely a quantum efficiency of unity for the neutral and alkaline solutions. The absorption of active light is undoubtedly by the peroxide bond in the persulfate group. This would result in a dissociation and immediate reaction of the products with water or in an excited ion which would have an appreciable life period during which it could react with water or hydroxyl ions. It is difficult to explain even qualitatively the effects of neutral salts by the first process, and it has not been possible to account for their effect quantitatively if excited ions are assumed. An excited ion must collide with the reacting molecule during its life period and if this reaction were with water molecules the efficiency should be maintained unless the negative ions were readily able to take up the energy of excitation. This type of energy transfer has been investigated in the case of excited uranyl ions.[6] The ratio of the original fluorescence efficiency to that in the presence of the salt is proportional to the concentration of the salt. Persulfate solutions do not fluoresce as each excited ion results in reaction, but since the quantum efficiency is equivalent to fluorescence efficiency, the ratio of unity to the yield in the presence of electrolytes should be proportional to the concentration of electrolyte. The values used were calculated from the rate measurements in the previous papers[7] by assuming a value of unity for the lowest salt concentration and then obtaining the yield from the velocity constants. Plots were then made to see if $\gamma_0/\gamma_{(\text{electrolyte})}$ was proportional to the concentration of electrolyte. The points for potassium sulfate and potassium hydroxide fell on a somewhat curved line but those for sulfuric acid were widely off, which would suggest the operation of important additional factors. If the reaction were

$$[S_2O_8^{=}]' + OH^- \longrightarrow 2SO_4^{=} + H^+ + {}^1/_2O_2$$

then at sufficiently low concentrations of hydroxyl ion, the efficiency should decrease. Such an effect was analyzed kinetically but the equations did not approximate the observed rate. Some further information is available in the data. From Table I 0.05 *M* $K_2S_2O_8$ + 0.01 *M* H_2SO_4 gives a yield of 0.85 and from the rate study[7] the solution 0.00025 *M* $K_2S_2O_8$ + 0.01 *M* H_2SO_4 gave a calculated yield of 0.55. This would indicate that since the ratio of persulfuric acid to persulfate ion is very much larger in the second case the persulfuric acid is more stable than the persulfate ion, it being found in the previous papers that 0.01 *M* sulfuric acid did not change the absorption characteristics of the persulfate solution.

[6] West, Müller and Jette, *Proc. Roy. Soc* (London), [A] **121**, 294 (1928); Jette and West, *ibid.*, [A] **121**, 299 (1928); Wawilow, *Z. Physik*, **53**, 665 (1929).

[7] Morgan and Crist, THIS JOURNAL, **49**, 960 (1927).

It was thought that the efficiency of the reaction in the presence of sulfuric acid could be raised again by introducing relatively high concentrations of other "receptor" ions. Experiments showed that chloride ions are oxidized by persulfate when exposed, the dark reaction being very slow and autocatalytic. The chlorine produced was removed by a stream of oxygen, then absorbed in a potassium hydroxide solution and determined. In unstirred solutions the oxygen produced was very much less than before and the chlorine determined in the stirred samples was perhaps a third of the sulfate produced.[8] The results for various chlorides are given in Table II. The reduced yields for potassium chloride and hydrochloric acid are about the same and this would indicate that hydrogen ion has a much less effect than chloride, a result which could be attributed to the very high deactivating efficiency of chlorides.[6] Unfortunately the effect of potassium chloride in alkaline solutions could not be investigated for comparison with potassium sulfate and potassium hydroxide, since the oxidized chlorine would be retained as hypochlorites, etc., which are photosensitive with the wave lengths employed.

TABLE II

QUANTUM EFFICIENCY FOR PERSULFATE IN PRESENCE OF ELECTROLYTES

Concn. of electrolytes in moles per liter	Wave length in mμ	γ
KCl[a] 0.05	302	0.73
KCl 0.05	302	.67
HCl 0.05	302	.74
KCl 0.20 + H_2SO_4 0.001	302	.67
$HgCl_2$ 0.1 + H_2SO_4 0.001	302	.72

[a] This solution was unstirred and the absorption of light increased during the exposure, due to the chlorine for which a correction was made. The stirred solutions did not change in absorption when exposed.

Summary

The quantum efficiency of the persulfate decomposition has been found to be unity for neutral and alkaline solutions.

The effect of electrolytes and the mechanism of the reaction have been discussed.

The capillary mercury arc as a source of light has been further improved by deflecting the arc with a magnet.

NEW YORK CITY

[8] It was not possible to remove completely the chlorine from the exposed solution as several hours aeration did not remove the odor and some of the chlorine was probably retained in the solution by photochemical change to higher states of oxidation.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 21]

FLUOROCHLORIDES OF SILICON

BY WALTER C. SCHUMB AND E. LEE GAMBLE

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Although an extensive series of silicon mixed halides has long been known,[1] those containing fluorine as one constituent appear not to have been isolated. Interest in the preparation of such compounds is to be found in the fact that the analogous carbon compounds, such as difluorodichloromethane, have recently come into prominence as excellent refrigerants.

With the isolation of hexafluorodisilane, Si_2F_6, a convenient way[2] was open for the preparation of such mixed halides as SiF_3Cl, SiF_2Cl_2 and $SiFCl_3$, and in the present paper the isolation and the properties of the first two of these compounds, trifluorochlorosilane and difluorodichlorosilane, will be described.

When hexafluorodisilane and chlorine are mixed at room temperature there is no apparent reaction, but when the mixture is strongly heated at one point for a few seconds a mild explosion occurs, resulting in the formation of silicon tetrafluoride, trifluorochlorosilane and difluorodichlorosilane. When an excess of hexafluorodisilane is used in the reaction, amorphous silicon is formed at the same time as the gaseous products of the reaction.

The hexafluorodisilane used in this work was prepared by the action of zinc fluoride on hexachlorodisilane as previously described.[2] The apparatus as shown in Fig. 1 was adopted to carry out the reaction between hexafluorodisilane and chlorine. Condenser A was evacuated and hexafluorodisilane distilled into it, solid carbon dioxide and alcohol being used to cool this condenser. Dry chlorine was passed into condenser C, which was cooled by carbon dioxide and alcohol, and was thereby condensed to a liquid. With condensers A and C in liquid air, the entire system was completely evacuated. To measure out a known volume of hexafluorodisilane, the Dewar was removed from around condenser A, and the tube B allowed to fill with gas to a pressure of one atmosphere. The alcohol in the Dewar containing C was kept about $-35°$ or the approximate boiling point of chlorine; thus D could be filled with chlorine at a pressure of approximately one atmosphere. The hexafluorodisilane from B and the chlorine from D were next condensed in E by means of liquid air and the stopcocks to B and D closed. The Dewar surrounding E was then removed and the mixture of hexafluorodisilane and chlorine distilled into the explosion chamber F. When there was no more solid or liquid in E the stopcock between E and F was closed and the flame of a small blast burner applied to F at one point, whereupon in fifteen to thirty seconds a mild explosion would take place in F. This explosion was accompanied by a flash of light and a whistling noise. The products of the reaction were then completely removed from F by condensing them out in G, which was cooled by liquid air. The process of filling the chamber F and exploding the mixture therein was then repeated until all the hexafluorodisilane had been brought into reaction.

[1] See, for example, Friend, "A Textbook of Inorganic Chemistry," Vol. V, p. 198.

[2] Schumb and Gamble, THIS JOURNAL, 54, 583 (1932).

Although the explosions in F were never sufficient to do any damage to the apparatus it was thought advisable to wrap this combustion tube with wire gauze. The chamber B for measuring out the hexafluorodisilane had a volume of about 150 cc., D for measuring the chlorine a volume of about 300 cc., and the combustion chamber about 600 cc. Thus about two volumes of chlorine were mixed with one volume of hexafluorodisilane and exploded under a total pressure less than atmospheric.

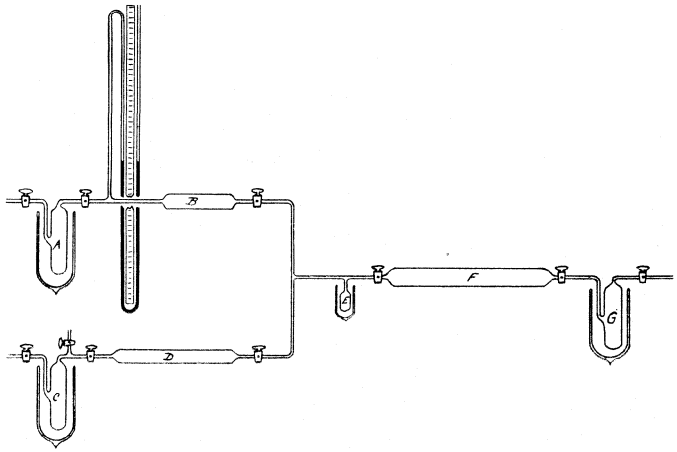

Fig. 1.

To remove the excess of free chlorine from the mixture of the gases, the products of combustion were transferred to an evacuated flask containing mercury and shaken occasionally until no further decrease in pressure was observed on the manometer attached to the flask. The removal of chlorine in this way appeared to be complete in about twenty-four hours.

To separate the mixture of silicon tetrafluoride, trifluorochlorosilane and difluorodichlorosilane, the fractionation apparatus as shown in Fig. 2 was used. In the construction of this apparatus certain features of the precision type columns developed by Podbielniak[3] in the separation of highly complex mixtures of hydrocarbons were adopted.

The column was a 7-mm. Pyrex tube 65 cm. high, the lower 20 cm. being vacuum jacketed. A spiral made of small copper wire, about five turns to the inch, and fitting snugly to the inside of the column served to conduct the capillary films of condensed liquid back to the bulb. The upper 45 cm. of the column was surrounded with a jacket containing carbon dioxide and alcohol. This cooling of the column was so effective that the temperature of the escaping gases varied only slightly from the sublimation temperature of carbon dioxide. The manometer M_1 registered the pressure in the column; the rate at which the gases were distilled was controlled by the adjustment of stopcock S. From the change of pressure observed on manometer M_2 while the gases were being collected in a 100-cc. bulb (D) the rate of flow could be established quite accurately. The evacuated one-liter globes B, C and F and the two-liter globe E served to hold the gas fractions as they were collected; the tube G, cooled by liquid air, served to condense all the gases which were to be collected during the intervals when the pressure was not constant. As the temperature of the gases leaving the column was almost constant, the

[3] Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

change in pressure on M_1 served as a guide in determining where the fractions should be cut.

After the elimination of the free chlorine as above described, the mixture of silicon tetrafluoride, trifluorochlorosilane and difluorodichlorosilane was transferred quantitatively from the flask to the small bulb A at the bottom of the column by means of liquid air. A was then placed in a carbon dioxide–alcohol bath until most of the silicon tetrafluoride had distilled; the carbon dioxide bath was then gradually lowered, the gases being collected at the rate of about 600 cc. per hour.

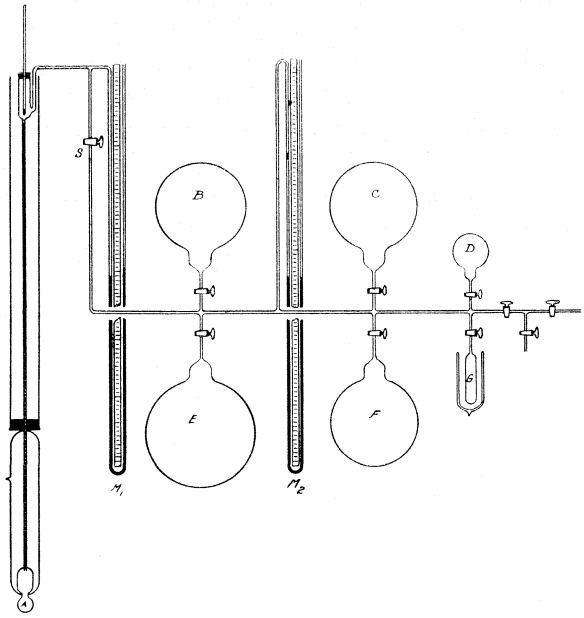

Fig. 2.

This procedure yielded three fractions of approximately the same volume, together with a very small amount of higher boiling material.[4] As a check upon the composition of each of these fractions, their molecular weights were determined by the gas density method. A globe of known weight and volume (495.58 cc.) was attached to the end of the fractionation apparatus and thoroughly evacuated. The fraction the molecular weight of which was to be determined, was drawn into G by means of liquid air and then admitted to the globe to be weighed. The temperature of the room was taken as the temperature of the gas (after standing for twenty minutes) and the pressure was taken from manometer M_2. The first fraction gave the molecular weight of 103.6; the theoretical value for SiF_4 is 104.06. The results of three determinations on the second fraction were 121.5, 121.7 and 121.3, which are in reasonable agreement with the theoretical value for SiF_3Cl, 120.52. The results of three determinations on the third fraction were 138.9, 138.4 and 138.7; calcd. for SiF_2Cl_2, 136.97.

Under ordinary conditions trifluorochlorosilane and difluorodichlorosilane are

[4] Because of the difficulty of purifying the small quantity of this higher boiling residue, its composition was not definitely established, but it is probable that a little of a third fluorochloride, $SiFCl_3$, was contained therein.

gases with very pungent odors, resembling that of silicon tetrafluoride. They are readily hydrolyzed on coming into contact with the moisture of the air. Trifluorochlorosilane boils at −70.0° and melts at −138°; difluorodichlorosilane boils at −31.7° and melts at −144°.

Vapor Pressures.—The apparatus and method used for measuring the vapor pressures of trifluorochlorosilane and difluorodichlorosilane were essentially the same as previously used in work[5] with sulfur hexafluoride. In taking the measurements for trifluorochlorosilane over the temperature interval below that which could be obtained with carbon dioxide and alcohol, the bath was chilled by the addition of small lumps of solid alcohol, which had been frozen by means of liquid air. The purity of the samples was assured by obtaining check readings of the vapor pressure with variable amounts of liquid, *i. e.*, with part of the sample being withdrawn from the apparatus between readings. Figure 3 shows the results obtained for the vapor pressures of trifluorochlorosilane and difluorodichlorosilane when the reciprocal of the absolute temperature is plotted against the logarithm of the pressure.

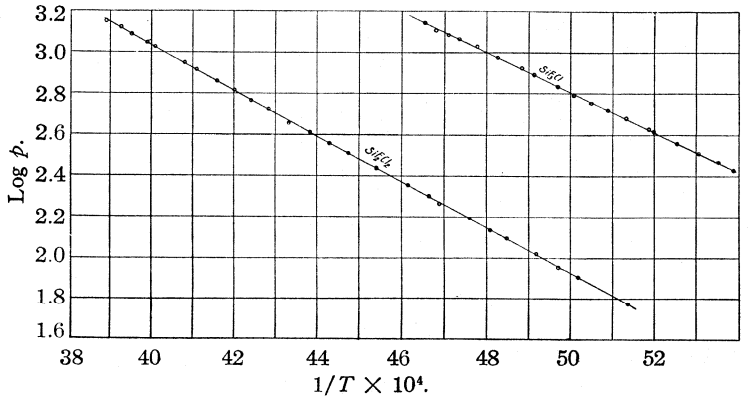

Fig. 3.

The vapor pressure of these two liquids is represented by the following empirical equations; for trifluorochlorosilane

$$\log p = 7.6440 - \frac{967.16}{T}$$

and for difluorodichlorosilane

$$\log p = 7.4832 - \frac{1111.1}{T}$$

In the following tables are shown the values of the observed pressure (expressed in mm. of mercury at 0°) and the values as calculated from the above equations at the same temperature.

[5] Schumb and Gamble, THIS JOURNAL, **52**, 4302 (1930).

TRIFLUOROCHLOROSILANE

Temp., °C.	P obs., mm.	P calcd., mm.	Temp., °C.	P obs., mm.	P calcd., mm.
−86.3	293.0	292.8	−72.0	683.0	683.3
−83.6	342.8	346.9	−69.3	796.1	791.2
−81.8	386.4	387.4	−65.8	955.2	951.5
−80.7	416.0	414.2	−65.6	959.6	961.6
−78.2	481.5	477.6	−63.6	1066.	1065.
−75.1	581.5	574.6	−61.2	1198.	1202.
−73.3	637.1	635.9	−57.9	1409.	1412.

DIFLUORODICHLOROSILANE

Temp., °C.	P obs., mm.	P calcd., mm.	Temp., °C.	P obs., mm.	P calcd., mm.
−78.5	59.7	59.4	−45.2	408.7	405.2
−72.0	90.1	90.8	−39.7	527.7	528.1
−68.4	113.0	113.6	−35.0	655.6	655.7
−66.8	125.5	125.2	−31.6	759.6	762.8
−63.0	154.3	156.6	−28.0	886.0	881.2
−58.0	206.0	207.8	−23.7	1064.	1067.
−52.8	276.0	275.2	−20.3	1214.	1226.
−50.2	315.1	315.1	−16.3	1405.	1431.

By means of the Clausius–Clapeyron equation and the equations for the vapor pressures of trifluorochlorosilane and difluorodichlorosilane the heats of vaporization have been calculated as 4420 cal. and 5080 cal., respectively. From these values Trouton's constant for trifluorochlorosilane, 21.8, and for difluorodichlorosilane, 21.1, were calculated.

By placing p equal to 760 in the equations for the vapor pressures of the two substances, the boiling point of trifluorochlorosilane is found to be −70.0° and that of difluorodichlorosilane −31.7°. These values are believed to be accurate to within ±0.2°.

Melting Point.—The melting point of trifluorochlorosilane was determined as −138° and that of difluorodichlorosilane as −144°. These melting points, which are probably accurate to ±2°, were determined as follows. A small sample of the substance, sealed in a thin-walled melting point tube and attached to the bulb of a pentane thermometer, was immersed in a cryoscopic liquid (50–60 cc.) contained in a double-walled tube (not evacuated), which was in turn immersed in an unsilvered Dewar tube containing liquid air. To prevent frosting of the inner tube and to facilitate observation, a slow stream of well-dried air was circulated through the upper part of the inner tube. The non-inflammable cryoscopic liquid, which was kept stirred during these measurements, was one recommended by Kanolt.[6] The pentane thermometer was checked at the freezing point of pure carbon bisulfide and the boiling point of oxygen.

Hydrolysis.—When trifluorochlorosilane and difluorodichlorosilane are passed into water, hydrochloric, hydrofluoric, silicic and fluosilicic acids

[6] Kanolt, U. S. Bur. Standards, Sci. Paper, No. S520, **20**, 619 (1924–1926).

are formed. As in the case of the other silicon halides, these compounds are also readily hydrolyzed by the moisture of the air. When trifluorochlorosilane is hydrolyzed with an excess of water at ordinary temperatures, the following reactions take place

$$SiF_3Cl + 4H_2O \longrightarrow HCl + 3HF + H_4SiO_4 \quad (1)$$
$$H_4SiO_4 + 6HF \longrightarrow H_2SiF_6 + 4H_2O \quad (2)$$

The first reaction is very rapid and the speed of the second will depend upon the conditions under which the hydrolysis takes place, such as concentration and temperature. The hydrolysis of difluorodichlorosilane is analogous to that of trifluorochlorosilane. It will be noted that the hydrolysis of these two compounds cannot be satisfactorily accounted for by the mechanism usually given for silicon tetrafluoride.

Analysis.—The method used for the analysis of trifluorochlorosilane and difluorodichlorosilane was quite similar to that used in the analysis of hexafluorodisilane and previously described in detail.[2] The combined chlorine and fluorine in the hydrolyzed sample was determined by titration with standard sodium hydroxide, the silicon was calculated from the weight of silica collected, and the chlorine was determined as silver chloride; the fluorine in the sample was determined as the difference between the combined chlorine and fluorine and the chlorine alone. The results obtained are shown in the tables.

	Si, %	(F + Cl), %	Cl, %	F, %
	TRIFLUOROCHLOROSILANE			
	22.87	76.68	29.29	47.39
	23.04	76.58	29.31	47.27
Calcd.	23.28	76.72	29.42	47.29
	DIFLUORODICHLOROSILANE			
	20.13	79.37	51.50	27.77
	20.35	79.04	51.13	27.91
Calcd.	20.49	79.51	51.77	27.74

Summary

1. The reaction of chlorine with hexafluorodisilane, Si_2F_6, has yielded two new fluorochlorides of silicon, SiF_3Cl and SiF_2Cl_2. The formulas have been verified by molecular weight determinations and analysis of the compounds.

2. Trifluorochlorosilane boils at $-70.0°$ and melts at $-138°$; difluorodichlorosilane boils at $-31.7°$ and melts at $-144°$. The existence of a third substitution product, $SiFCl_3$, is indicated, but an insufficient quantity to establish its identity has been obtained.

3. The vapor pressure of liquid SiF_3Cl has been measured from -86 to $-58°$; that of SiF_2Cl_2 from -78 to $-16°$. Empirical equations representing these data are given, together with calculated values for the heats of vaporization and Trouton's constant.

4. The hydrolysis of these substances, which served as the basis for the elementary analysis, is discussed. The resemblance of these compounds to the analogous compounds of carbon, as is to be expected, is for the most part merely a matter of similarity in formula.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

THE THERMAL DECOMPOSITION OF METHANE[1]

BY LOUIS S. KASSEL[2]

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Introduction

The thermal decomposition of methane has been repeatedly studied, but none of the results obtained has been of much value from the standpoint of reaction kinetics. The only previous work which need be considered here is that of Holliday and his co-workers.[3] It was found that the earlier stages of the reaction, at 900–1200°, were homogeneous in silica vessels; the reaction is retarded very greatly by the hydrogen produced, and the final slow stages of the decomposition are at least partly heterogeneous. It is a practical impossibility to attain equilibrium without a catalyst; the "false equilibrium" which is reached from the methane side is characterized by a "constant," $(CH_4)^2/(H_2)^3$; the temperature coefficient of this constant corresponds to a heat term of 72,000 cal. Holliday worked only at temperatures where the first few per cent. of decomposition occurred too rapidly for measurement in static systems; nevertheless, Holliday and Gooderham decided that the initial reaction was the bimolecular process

$$2CH_4 = C_2H_2 + 3H_2 - 91{,}000 \text{ cal.} \quad (1)$$

They gave two reasons for this proposal; the first of these was the rather surprising statement that "homogeneous, unimolecular reactions are rare, and a bimolecular process is much more probable than one of higher order";[4]

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) A portion of this work was presented at the New Orleans meeting of the American Chemical Society, March, 1932.

[2] Associate Physical Chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] Holliday and Exell, *J. Chem. Soc.*, 1066 (1929); Holliday and Gooderham, *ibid.*, 1594 (1931).

[4] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Company, 1932, lists 20 reactions which are probably unimolecular, seven which may be bimolecular, excluding the large group of bimolecular reactions which involve free atoms; of these seven, four involve the participation of two different substances, and hence could not be expected to be unimolecular. From the available statistical data, therefore, the odds are 20 to 3 that the initial step in the decomposition of a gaseous substance will be unimolecular.

and second, the slightly greater percentage decomposition obtained at higher pressures during the earlier stages of the decomposition.[5] It is easy to see that (1) is at best a very unlikely first step. At 912° and 500 mm. pressure, the initial rate of decomposition estimated from the curves given by Holliday and Gooderham is 1.5 mm./sec.; the corresponding second order rate constant is 6×10^{-5} mm.$^{-1}$ sec.$^{-1}$, or 4.8×10^{3} cc. mole^{-1} sec.$^{-1}$. It is safe to assume that the rate constant of (1) will not exceed $10^{14}e^{-E/RT}$ cc. mole^{-1} sec.$^{-1}$, where E is its energy of activation; the minimum value possible for E is the negative of the heat of reaction; at 912° this would not differ significantly from the 91,000 cal., which is correct at room temperature. The maximum rate to be expected at 912° for a reaction with an energy of activation of 91,000 cal. is 3×10^{-2} cc. mole^{-1} sec.$^{-1}$, or about 10^{-5} the observed value. To give a sufficiently rapid bimolecular reaction, an energy of activation not greater than 61,000 cal. would be needed. This might conceivably have been possible for

$$2CH_4 = C_2H_4 + 2H_2 \quad (2)$$

or

$$2CH_4 = C_2H_6 + H_2 \quad (3)$$

but it will be shown clearly in what follows that these reactions do not occur to an appreciable extent.

The experiments to be reported here were designed to unravel as completely as possible the complex kinetic behavior of methane decomposition in static systems. They constitute part of a larger program in progress at this station, the goal of which is the more efficient utilization of natural gas. A subsequent paper by Storch,[6] to which reference will be made later, reports on another phase of this investigation.

Experimental Method

Two electric furnaces were used in this work; the first of these was wound with platinum wire on an alundum core which contained the reaction vessel, a long clear quartz tube of 1 or 2 cm. diameter. The temperature was regulated by a Leeds–Northrup controlling potentiometer used in conjunction with a platinum–platinum-rhodium thermocouple in contact with the reaction vessel. The second furnace was wound with nichrome ribbon on a large alundum core, 10 cm. in diameter; it could hold a reaction vessel of 500 cc. capacity. In both furnaces there were temperature gradients along the axis; for the longer tubes used in the platinum-wound furnace, the extreme temperature differences may have reached 10°; hence, the temperature of the thermocouple is not strictly the average temperature of the reaction vessel, and the temperatures measured in different series are not quite comparable.

In almost all of the work the reaction was followed by measurement of the pressure change. Under the experimental conditions adopted, the only products of importance are carbon and hydrogen, as will be clearly shown later; traces of oily material condense in the capillary leading to the manometer, chiefly in the region which is at approximately

[5] In the experiments being reported here, this relation was not confirmed.

[6] Storch, THIS JOURNAL, in press.

100°, but their quantity is negligibly small. Hence the pressure increase is a direct measure of the amount of reaction. In view of the small volume of the reaction vessel used in part of the work, and of the high temperature of the reaction zone, a small outside volume was essential. In some of the earliest experiments this was achieved by using a capillary manometer; later a click gage, built with the smallest possible bulb, was used; the clicking pressure was then read with a cathetometer on a wide-bore manometer filled with either mercury or α-bromonaphthalene; the results obtained in this way were far more satisfactory. When a larger reaction vessel was used, the click gage was unnecessary. In all cases, a correction for the outside volume was made in the usual manner.

Throughout the work the loss of hydrogen by diffusion through the quartz was a source of difficulty. The order of magnitude of this loss is about 1% per hour, depending upon the surface–volume ratio of the vessel, the wall thickness, possibly the extent of devitrification; between 700 and 1050° the rate about triples. Over a considerable range of pressure, at least from 1 to 50 cm., the rate of diffusion is proportional to the hydrogen pressure. In some of the experiments a double-jacketed reaction vessel was used, the hydrogen which diffused through the inner wall being caught in the outer annular space, and its pressure read on a McLeod gage; since only a few per cent. of this hydrogen remained within the hot zone, the loss by secondary diffusion was entirely negligible. This method failed at such pressures that the primary diffusion was about ten times the reaction rate, it being no longer possible to attain accuracy in the pressure measurements sufficient to permit calculation by difference of the small pressure change due to reaction. Since knowledge of the rate in this region is of considerable importance to a complete understanding of the reaction mechanism, experiments were tried also with sillimanite tubes. These proved slightly less permeable than quartz, possibly because of their greater thickness; the difference was not sufficient to compensate for the practical impossibility of constructing a double-jacketed reaction vessel.

The occurrence of an induction period, as will be described later, suggested that appreciable quantities of ethane or ethylene (*ca.* 5 mm.) might be present during the middle stage of the reaction. An attempt to isolate these substances was therefore made. A large bulb immersed in liquid nitrogen was connected by a stopcock to the reaction vessel; methane was admitted to the former, allowed to decompose for a few minutes, and then frozen out in the cold bulb; the products of about 25 runs were collected, the methane removed by cautious pumping until a pressure of about 0.5 mm. was reached, and the residue warmed to room temperature. The quantity of gas obtained was far too small for analysis, corresponding to a pressure in the reaction vessel of about 0.1 mm. per run.

The methane used was prepared from Pittsburgh natural gas by removing the ethane with active charcoal; the product analyzed 97% or more of methane, the remainder being almost entirely nitrogen; this material was further purified in the apparatus by liquefaction and repeated pumping until the vapor pressure at liquid nitrogen temperature had become constant; after about 75% of the resulting material had been used, the remainder was ordinarily discarded, but no difference in rate was found when this was not done. The purity of the final product probably exceeded 99.9%.

Experimental Results

The Induction Period.—Under some conditions an induction period was observed, the nature of which remains obscure. A typical pressure–time curve showing this induction period is reproduced in Figure 1. The difference between the measured initial pressure and that extrapolated from the straight line part of such curves varied from 1 or 2 mm. up to

1 cm. The general tendency was toward longer and more intense induction periods at low pressures and in bulbs free from carbon; in the packed bulb, where the surface–volume ratio was highest, no induction period was observed. In some other series of experiments, also, it was absent; within any single series it behaved in a fairly uniform way, but results could not be exactly reproduced. The possibility that the induction period might represent the accumulation of steady-state concentrations of higher hydrocarbons suggested the attempts to isolate ethane and ethylene, with the negative result already described.

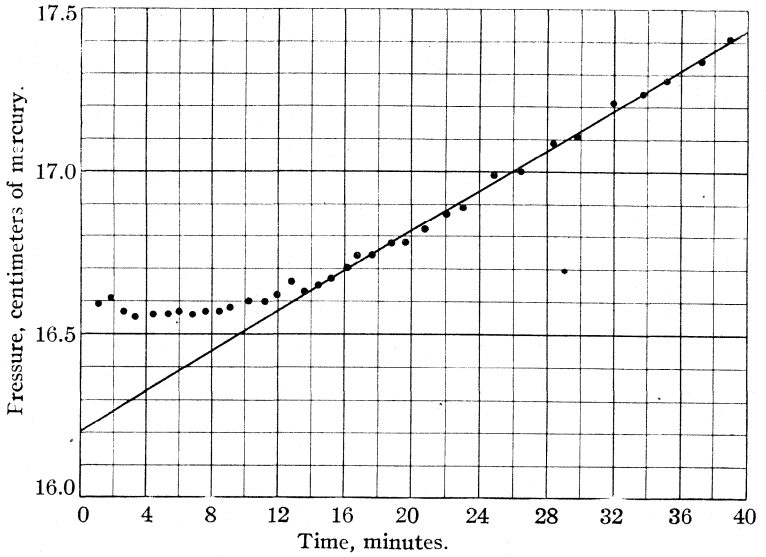

Fig. 1.—Run E29: typical induction period.

Homogeneity.—The homogeneity of the initial reactions at the lower temperatures of the present work could not be assumed to be proved by the experiments of Holliday and Gooderham; accordingly, measurements were made with a clear quartz flask of 415 cc. capacity, and with the same flask packed with short lengths of clear quartz tubing, the free volume then being 280 cc. For the empty flask the surface–volume ratio was 0.65 cm.$^{-1}$, and with the packing it was at least 13 cm.$^{-1}$. The results are shown in Table I. Due to an oversight, the somewhat high rate obtained in the single run made with the packed bulb free from carbon was not noticed in time to run a duplicate. Even if this high value is correct, only 3% of the rate in the empty, clean bulb would be due to surface reaction. In the carbon-coated bulb, the possible contribution of a wall reaction during the initial stages is less than 1%. Hydrogen disappeared in the packed bulb at the rate of 6% per hour. This was sufficiently small so that no appreciable error was caused in pressure readings during the

first fifteen minutes, which is the period used in the experiments of Table I. The justification for using first-order rate constants is contained in the next paragraph.

TABLE I

INITIAL RATE OF DECOMPOSITION IN PACKED AND UNPACKED BULBS, AT 800°

Run no.	State of bulb	Initial press., cm.	k, sec.$^{-1}$
F17	Empty, clean	24.5	4.36×10^{-5}
F18	Empty, carbon	15.1	5.71
F19	Empty, carbon	24.5	6.55
F20	Empty, clean	25.2	5.67
F21	Empty, carbon	24.5	5.14
F22	Empty, carbon	24.5	6.10
F23	Empty, carbon	25.4	6.14
F24	Packed, clean	26.6	8.47
F25	Packed, carbon	26.6	4.84
F26	Packed, carbon	25.1	5.13
F27	Packed, carbon	15.8	6.08
F28	Packed, carbon	38.5	5.45
Average	Packed, carbon		5.37
Average	Empty, carbon		5.93
Average	Packed, clean (1 run)		8.47
Average	Empty, clean		5.01
Average	Packed, all runs		6.00
Average	Empty, all runs		5.67

Order.—All of the results which provided any test of the order of the reaction during the first few per cent. of decomposition showed that it was of the first order. The most extensive study of this point is that recorded in Table II. These experiments were made in a long quartz tube, using a click gage and, at the lower pressures, an α-bromonaphthalene manometer. The constancy of the first-order rate constants is all that could be desired. The pronounced retardation by hydrogen makes it utterly impossible to calculate first-order rate constants during a single run; the variation of initial rate with initial pressure, however, is in any case the only trustworthy criterion of order.

The series of experiments reported in Table II is one of those in which no induction period was observed. When induction periods did occur, the first-

TABLE II

FIRST ORDER CONSTANTS BASED ON THE INITIAL RATES AT 735°

Run no.	Initial press., cm.	k, sec.$^{-1}$
B2	1.30	1.19×10^{-5}
B3	2.44	1.06
B4	2.60	1.40
B5	4.75	1.13
B6	11.18	1.21
B7	16.47	1.03
B8	29.64	1.14

TABLE III

TEMPERATURE DEPENDENCE OF THE FIRST ORDER CONSTANTS FOR THE INITIAL RATE

T, °C.	$k \times 10^6$ (sec.$^{-1}$) Obs.	Calcd.	Number of runs
976	1.31	1.2	3
1008	4.30	4.5	9
1061	32.5	32	2
1113	192	190	3

The calculated values are derived from the equation $\log k = 11.864 - 17{,}352/T$, or $k = 7.3 \times 10^{11} e^{-79385/RT}$.

order constants were calculated from the straight line part of the pressure–time curve. The constants so obtained were very consistent and showed absolutely no dependence upon the amount of carbon initially present.

Temperature Coefficient of the Initial Reaction.—The temperature coefficient of the initial reaction may be determined from the data of Table III. The absolute rates of this table are low for two reasons: first, they have not been corrected for the outside volume, and, second, they are based on rather too great an extent of reaction, so that the hydrogen retardation has reduced them; the possible error in the energy of activation may be estimated as 6000 cal. The rate constant for the initial period of the reaction may be rounded off and written

$$k = 1.0 \times 10^{12} e^{-79385/RT} \text{ sec.}^{-1}$$

with an uncertainty in absolute value of a factor of about 2. It may be noted that this equation for the initial rate is apparently capable of extrapolation even to 1500°. This is shown by Table IV, which is based on rates estimated from curves given by Holliday and Gooderham, and computed from percentage conversions given by Rudder and Biedermann.[7] The results of these latter workers scatter rather badly; only those experiments have been considered in which the percentage conversions are comparatively low; in many cases the longer contact time gave the smaller

TABLE IV

COMPARISON OF INITIAL RATES FOUND BY HOLLIDAY AND GOODERHAM AND BY RUDDER AND BIEDERMANN WITH VALUES EXTRAPOLATED FROM THE DATA OF TABLE III

T, °C.	Observer	($k_{obs.}$ sec.$^{-1}$)	($k_{calcd.}$ sec.$^{-1}$)
1173	R + B	0.0009 to 0.014	0.0016
1185	H + G	.0030	.0023
1273	R + B	0.018 to .057	.023
1286	H + G	.08	.03
1473	R + B	0.14 to .25	1.7
1573	R + B	1.0 to 4.5	9.3
1673	R + B	10 to 26	43
1773	R + B	50	160

Rudder and Biedermann's conversions at 1473 °K. are all far too low and must be disregarded.

[7] Rudder and Biedermann, *Bull. soc. chim.*, **47**, 704 (1930).

conversion, and hence the variation in k represents experimental error and not any perturbation due to hydrogen retardation. The rate at 1500° is about 10^6 times the highest rate measured in the present experiments; if the extrapolated rate at that temperature is wrong, even by a factor of 4, this could be explained by an error in the temperature coefficient of only 8000 cal. The comparisons of Table IV, in spite of their approximate character, furnish evidence that the initial rate determining steps remain the same over the entire temperature range from 700 to 1500°.

Dependence of the Rate on Hydrogen Concentration.—As has already been stated, it was a matter of considerable difficulty to get accurate measurements when the hydrogen pressure was large because the rate became very small and at the same time the rate of loss of hydrogen increased. Table V contains the data for one of the few successful experiments made. The constancy of the values in the columns headed K and K' is to be used in a later section as evidence for the essential correctness of the mechanism there proposed. Other runs also give constant values for K' and, after sufficient hydrogen has accumulated, for K also. With an initial methane pressure of about 25 cm., K' is rather less, being perhaps as low as 0.02; the significance of this will be considered later.

TABLE V

HYDROGEN DEPENDENCE OF THE RATE AT 760°, RUN NO. C 1

CH_4, cm.	H_2, cm.	$-(dCH_4/dt)$, cm./min.	K	K'
8.05	0.85	0.0450		0.045
7.39	2.16	.0348		.044
6.59	3.75	.0374	0.045	.091
6.06	4.81	.0133	.040	.058
5.72	5.47	.0130	.065	.084
5.38	6.11	.00668	.053	.063
5.44	6.72	.00513	.061	.069
4.73	7.24	.00343	.058	.064
4.41	7.75	.00285	.068	.073
4.07	8.21	.00178	.060	.063
3.81	8.48	.00113	.047	.050
3.51	8.51	.000435	.022	.023
2.83	8.87	.00124	.11	.11
2.28	8.92	.000248	.034	.035

The values in the columns headed K and K' are given by

$$K = \frac{[H_2]^3}{[CH_4]^2}\left(-\frac{d[CH_4]}{dt}\right)$$

$$K' = \frac{[H_2]^3 + 8[CH_4]}{[CH_4]^2}\left(-\frac{d[CH_4]}{dt}\right)$$

Discussion and Conclusions

There appears to be no possibility, and no necessity, of considering any primary process except the unimolecular dissociation of methane. This might conceivably take place in two ways

$$CH_4 = CH_3 + H - 125{,}000 \text{ cal.} \quad (2)$$
$$CH_4 = CH_2 + H_2 - 47{,}000 \text{ cal.} \quad (3)$$

Comparison of the heats of these reactions, which unfortunately are but crude estimates, with the experimental heat of activation provides good reason for favoring (3). At the start of the reaction, CH_2 will of necessity react with CH_4; it will not dissociate further, since it is physically stable; it will not recombine with H_2, which is present at too low a concentration, and for a similar reason it will not polymerize to ethylene. The product of the reaction between CH_2 and CH_4 might *a priori* have been predicted as either ethane or ethylene; the lamp bulb experiments of Storch[6] show that under suitable conditions 95% of the decomposed methane can be recovered as ethane; we therefore write as the next step

$$CH_2 + CH_4 = C_2H_6 + 36{,}000 \text{ cal.} \quad (4)$$

It may be well to point out that this reaction could perfectly well be bimolecular as written; it is only in the case of quite simple molecules that a bimolecular association reaction is subject to difficulties.[8] The next step is one to which no uncertainty attaches. Long ago, Bone and Coward[9] showed that at 675° ethane dissociates rapidly, the first products being ethylene and hydrogen; hence we write

$$C_2H_6 = C_2H_4 + H_2 - 30{,}000 \text{ cal.} \quad (5)$$

There is abundant evidence from later work that (5) is a first order reaction. The pyrolysis of ethylene at temperatures of 700° and higher yields a complex group of products, including hydrogen, methane, ethane, small amounts of acetylene and varying quantities of heavier hydrocarbons. At the low partial pressure of ethylene encountered in the present experiments, the polymerization reactions will no longer be of importance. There are then these possibilities

$$C_2H_4 = C_2H_2 + H_2 - 48{,}000 \text{ cal.} \quad (6)$$
$$C_2H_4 = 2CH_2 - 53{,}000 \text{ cal.} \quad (7)$$
$$CH_4 + C_2H_4 = C_3H_8 + 17{,}000 \text{ cal.} \quad (8)$$

The process (8) is somewhat analogous to (4); it may take place to some extent but under the conditions prevailing in these experiments it is probably not of major importance; (7) can be made to account for the products obtained in ethylene pyrolysis only with the help of such postulated reactions as

$$CH_2 = CH + H \quad (9)$$
$$CH_2 = C + H_2 \quad (10)$$

it being supposed then that CH polymerizes to acetylene, and that CH_2 and C_2H_4 are hydrogenated to methane and ethane, respectively. This picture is found repeatedly in the literature; it suffers from the serious difficulty that the hydrogen atoms in CH_2 are probably bound much more

[8] Kassel, THIS JOURNAL, **53**, 2143 (1931).

[9] Bone and Coward, *J. Chem. Soc.*, **93**, 1197 (1908).

firmly than those in methane,[10] and that as a consequence CH_2 would decompose far more slowly than methane; it would then be impossible to obtain the high yields of methane which have been repeatedly observed. Any CH_2 formed by (7) during the initial pyrolysis of ethylene would probably give propylene

$$CH_2 + C_2H_4 = C_3H_6 \qquad (11)$$

This substance was actually found in significant quantities by Frey and Smith[11] as an early product of the pyrolysis of ethylene at 575°; it was accompanied, however, by comparable quantities of methane, ethane and hydrogen. These latter products can most naturally be accounted for by (6), followed by the reversed reactions (5), (4) and (3). It will be considered here that (6) is the only mode of decomposition of the ethylene; (7) may quite possibly occur also, but to consider both would complicate the scheme unwarrantedly. It will be supposed also that the acetylene decomposes simply to carbon and hydrogen

$$C_2H_2 = 2C + H_2 \qquad (12)$$

This reaction may be wholly or in part heterogeneous. In support of (12) there may be noted the fact that at 1000° and above, where polymerization has become unimportant, the chief products of acetylene pyrolysis are carbon, hydrogen and methane. At the low partial pressures of acetylene in the present experiments, polymerization would never have much chance to occur. The methane is presumably formed by the reversed reactions (6), (5), (4) and (3).

This scheme of reactions, which has been formulated almost entirely independently of the observed kinetics of methane composition, is surprisingly successful in accounting for these kinetics. The reactions and the rate constants which will be used for them are as follows (k is the constant for a reaction as written, r for the reverse reaction)

(k_1, r_1)	$CH_4 = CH_2 + H_2 - 47{,}000$ cal.	(3)
(k_2, r_2)	$CH_2 + CH_4 = C_2H_6 + 36{,}000$ cal.	(4)
(k_3, r_3)	$C_2H_6 = C_2H_4 + H_2 - 30{,}000$ cal.	(5)
(k_4, r_4)	$C_2H_4 = C_2H_2 + H_2 - 48{,}000$ cal.	(6)
(k_5, r_5)	$C_2H_2 = 2C + H_2$	(12)

The consequences of this scheme may be deduced by the usual steady-state method; the concentrations of CH_2, C_2H_6, C_2H_4 and C_2H_2 are all small compared to those of H_2 and CH_4, and hence their rates of change may be set equal to zero. The four resulting equations may be solved to give these four concentrations; the rate of decomposition of the methane is

$$-(d[CH_4]/dt) = 2(k_5[C_2H_2] - r_5[H_2])$$

$$= 2\,\frac{k_1k_2k_3k_4k_5[CH_4]^2 - r_1r_2r_3r_4r_5[H_2]^4}{r_1r_2r_3r_4[H_2]^3 + r_1r_2r_3k_5[H_2]^2 + r_1(r_2 + k_3)k_4k_5[H_2] + k_2k_3k_4k_5[CH_4]}$$

[10] The best value available is $CH_2 = C$ (gaseous) $+ H_2 - 124{,}000$ cal., as compared with $CH_4 = CH_2 + H_2 - 47{,}000$ cal.

[11] Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928).

It is evident that, at equilibrium

$$\frac{k_1k_2k_3k_4k_5}{r_1r_2r_3r_4r_5} = \frac{[H_2]^4}{[CH_4]^2}$$

The best available free energy equation for the formation of methane is probably

$$\Delta F = -15{,}313 + 10.54T \ln T - 4.36 \times 10^{-3}T^2 - 0.11 \times 10^{-6}T^3 - 48.56T$$

This is based on the equation given by Storch,[12] except that the entropy of methane is taken as 44.35, the value obtained spectroscopically by Giauque, Blue and Overstreet.[13] Calculation of the equilibrium constant from this equation gives $k_1k_2k_3k_4k_5/r_1r_2r_3r_4r_5 = 1.06 \times 10^8$ mm.^{2} at 760°; hence, for the greatest hydrogen concentrations of Table V, the correction for the resynthesis of acetylene drops out, amounting to only 1 part in 10^3; hence, r_5 may be put equal to zero. This was to be expected, since the greatest hydrogen pressures for which the rate was measurable are still far from equilibrium; it could scarcely be taken for granted, however. The ratio $k_1k_2k_3k_4k_5/r_1r_2r_3r_4r_5$ turned out to be the square of the usual equilibrium constant; if it had been the square root instead, the value of r_5 could not have been neglected.

When the concentration of hydrogen is small enough, the rate given by this mechanism is simply

$$-(d[CH_4]/dt) = 2k_1[CH_4]$$

This accounts for the first-order constants of the early stages. When the hydrogen concentration is large enough, the first term in the denominator will become far larger than any of the others, and the rate will be

$$-(d[CH_4]/dt) = 2k_1k_2k_3k_4k_5[CH_4]^2/r_1r_2r_3r_4[H_2]^3$$

The constancy of the values of K in Table V shows that this relatively simple equation is valid over a considerable range; when it fails at the beginning of the reaction, K' remains constant. The implication of the constancy of K', if this could be accepted at its face value, would be that for the entire range of concentrations the terms in $[H_2]$ and $[H_2]^2$ in the denominator remain unimportant. Actually, the accuracy available is far from sufficient to prove this and the variation of K' values from one experiment to another is of a sort that could be at least partially accounted for by the omission of these terms. To obtain any reliable values for the various coefficients would require much improved accuracy of the experimental rates.

From K of Table V, which for the late stages of the reaction equals $2k_1k_2k_3k_4k_5/r_1r_2r_3r_4$, we see that $k_1k_2k_3k_4k_5/r_1r_2r_3r_4$ is 0.03 cm.^{2} min.$^{-1}$ or 3 mm.^{2} min.$^{-1}$ at 760°. From spectroscopic free energy equations which will be published shortly, we find

[12] Storch, THIS JOURNAL, **53**, 1266, 4469 (1931).

[13] Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

$$K_p = \frac{[H_2]^3[C_2H_2]}{[CH_4]^2} = 0.11 \text{ mm.}^2 = k_1k_2k_3k_4/r_1r_2r_3r_4$$

Together these results require $k_5 = 27$ min.$^{-1}$ at 760° in a vessel with surface volume ratio of about 2 cm.$^{-1}$. The experiments presented here provide no evidence as to the homogeneity of the acetylene decomposition, but, judging by the work of Holliday and Gooderham, it is at least partially a wall reaction. The value for k_5 is in any case an approximate one, as it is based on a rather crude estimate for K_p. As nearly as can be told from work at atmospheric pressure, however, it is of the right order of magnitude. From the value of k_5 and the initial rate recorded in Table V, it may easily be computed that the partial pressure of acetylene in the beginning of the reaction was 0.07 mm.; this appears to be a reasonable value.

The rate constants k_3 and r_3 are known at lower temperatures, the best measurements being those of Marek and McCluer[14] and Pease;[15] the extrapolated value of k_3 at 760° is 0.44 sec.$^{-1}$; the partial pressure of ethane during the first part of Run No. C 1 was therefore about 0.007 mm.

We can draw some conclusions also about the reactions involving CH_2, though here we are on more uncertain ground. From the heat of reaction and activation energy of (3), the heat of activation for the reverse of (3)

$$CH_2 + H_2 = CH_4 + 47{,}000 \text{ cal.} \qquad (13)$$

is determined to be 32,000 cal. The heat of activation of (5) is 73,000 cal.; that of

$$C_2H_6 = CH_2 + CH_4 - 36{,}000 \text{ cal.} \qquad (14)$$

must be greater than 73,000 cal., since the rate of this reaction must be less than that of (5). If we estimate 80,000 cal., we can then calculate that the activation energy for (4) is 44,000 cal. The rate constant for (4) will be approximately $10^{14}e^{-44000/RT}$ or, at 760°, 5×10^4 cc. mole^{-1} sec.$^{-1}$. In conjunction with the initial rate of Table V, this leads to a steady-state concentration of CH_2, at the beginning of the reaction, of 0.07 mm. The bimolecular rate constant for

$$2CH_2 = C_2H_4 + 53{,}000 \text{ cal.} \qquad (15)$$

may be estimated as $10^{12}e^{-E/RT}$; the smaller value of the constant coefficient is reasonable in view of the simplicity of the molecule being formed. The value necessary for the energy of activation, to keep (15) from being more than a slight side reaction, is 24,000 cal. This would mean an activation energy for (7) of at least 77,000 cal.; this seems to be an acceptable value.

In the experiments made by Storch with the lamp-bulb immersed in liquid nitrogen, the chief reaction products are ethane and hydrogen; any

[14] Marek and McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931).

[15] Pease, THIS JOURNAL, **54**, 1876 (1932).

hydrogen retardation which occurs is then directly assignable to the single reaction (13). It is unfortunate that due to experimental troubles which do not concern us the rate measurements under these conditions are extremely uncertain. It is clear, however, that at 1700° the rate constant for (13) is not greater than that for (4). Since the activation energy is 12,000 cal. less for (13), the associated constant factor must be but one-twentieth as large, or only 5×10^{12} cc. mole^{-1} sec.$^{-1}$; since methane is about as simple a molecule as can be formed by a bimolecular association process, this smaller value is reasonable.

It appears, from the evidence available, that CH_2 is a comparatively inert substance, the activation heats for its addition reactions with methane, hydrogen and itself being 44,000 cal., 32,000 cal. and 24,000 cal. On the basis of these results an attempt will be made in this Laboratory to prepare the radical at lower temperatures and study it more fully.

For calculation of the maintenance of the rate of the unimolecular reaction (3) at low pressures, we have available experimental values for the vibrational frequencies. Dennison[16] gave for the four different frequencies of the nine modes of vibration 4217 cm.$^{-1}$, 1520 cm.$^{-1}$ (double), 3014 cm.$^{-1}$ (triple) and 1304 cm.$^{-1}$ (triple). Villars[17] has suggested that 2915 cm.$^{-1}$ in place of 4217 cm.$^{-1}$ will bring the assignment into agreement with Raman shifts without impairing the agreement with infra-red data. The change is in any case of little effect here, as the frequency remains so high as to be but rarely excited. At 1000°K. about 85% of the internal energy is due to the frequencies 1520 cm.$^{-1}$ and 1304 cm.$^{-1}$. Since it is not known how to use non-commensurable frequencies in calculating the behavior of unimolecular reactions, a natural procedure is to use a model of five oscillators all with the same frequency, which is so chosen that the energy content of the model at 1000°K. is equal to that of a methane molecule as calculated from the correct frequencies; when this is done, it is found that at 1 cm. pressure the rate should have fallen to perhaps a third of its high-pressure value. This result is not very satisfactory and the calculation was repeated with nine oscillators in the model, the total energy content being kept the same. The rate at 1 cm. pressure then came out 88% of the high-pressure value. It may therefore be concluded that there is probably no difficulty in accounting for the observed maintenance of the rate of this reaction.

It may be worth while to mention another procedure, in a way more rigorous, which might have been adopted for the calculations. By combination of the known frequencies it would be possible to determine the energies and quantum weights of all the activated states of methane. Reaction rates could be assigned to these levels in any way whatever, subject

[16] Dennison, *Astrophys. J.*, **62**, 84 (1925).

[17] Villars, paper presented at the New Orleans meeting, American Chemical Society, March, 1932; *cf.* Dickinson, Dillon and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

to the single easily applied condition that the correct activation energy was obtained. If no assignment could be found which satisfied this condition and gave satisfactory maintenance of the rate, it would be necessary to abandon the mechanism which has been suggested. It seems likely, however, that there would prove to be an ample margin of safety.

It is difficult to know what should be said about the induction period. The view that it represents the formation of steady state concentrations of the intermediate products became untenable when these concentrations were shown to be less than 0.1 mm. It can scarcely be caused by adsorption on the walls of the initial amounts of hydrogen produced, since in that case it would have become much more prominent in the packed vessel; actually, it was not observed at all. For a reaction of this character, it is almost unthinkable that any impurity could be responsible for an induction period. It would appear probable that the explanation lies in some peculiarity of the experimental arrangements, and that there is really no induction period at all.

Summary

The thermal decomposition of methane has been studied in quartz bulbs at 700–850°. The initial reaction is homogeneous and kinetically first order. The primary process is probably the unimolecular reaction $CH_4 = CH_2 + H_2$, with a rate constant $5 \times 10^{11} e^{-79385/RT}$; the observed rate constant is twice this, since the next step in the reaction is considered to be $CH_2 + CH_4 = C_2H_6$. The rate of methane decomposition is very greatly retarded by hydrogen; when this is present in sufficient quantity the reaction rate becomes proportional to $[CH_4]^2/[H_2]^3$. This result, together with the more complex hydrogen dependence of the intermediate stages, is fully accounted for by supposing that the ethane dehydrogenates in successive steps to ethylene, acetylene and finally carbon, and that all the reactions involved in the mechanism are reversible.

PITTSBURGH, PENNSYLVANIA

NOTE

The Strength of Semicarbazide—and a Correction

BY NORRIS F. HALL

Bartlett[1] gives a value of 3.68 at 25° and $\mu = 0.079$ for the uncorrected acid dissociation constant (pK_A) of semicarbazide cation. This prompts me to call attention to the value of 3.65 for the same constant, obtained here[2] by Dr. Marshall R. Sprinkle by a similar method at 26° and at ionic strengths between 0.05 and 0.046. These two independent determinations seem to settle the question.

[1] Bartlett, THIS JOURNAL, **54**, 2857 (1932).

[2] Hall, *ibid.*, **52**, 5124 (1930).

I must also note a regrettable error in my own recalculation[2] of Wood's value, which should read 3.07 at 25° instead of 3.67. This calculation is based on the temperature coefficients determined in this Laboratory.[3]

[3] Hall and Sprinkle, THIS JOURNAL, **54**, 3469 (1932).

DEPARTMENT OF CHEMISTRY
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[CONTRIBUTION FROM THE COAL RESEARCH INSTITUTE OF PRAGUE]

ANALYSIS OF SMALL QUANTITIES OF VOLATILE MATERIAL BY DETERMINATION OF THE VAPOR PRESSURE AND MOLECULAR WEIGHT DURING DISTILLATION

BY B. G. ŠIMEK AND R. KASSLER

RECEIVED FEBRUARY 25, 1932 PUBLISHED OCTOBER 5, 1932

The distillation analysis of liquid petroleum products is of importance as a criterion of their technical properties. Conclusions as to the adaptability of a motor to changes of load, the determination of the necessary preheating of the main air, of the cooling water temperature, etc., may be drawn from the behavior of a benzine during distillation.[1]

The A. S. T. M. method[2] specifies the use of 100 cc. of liquid in accordance with the original method of Engler–Ubbelohde.[3] In the course of our catalytic work on a laboratory scale, however, it often became necessary to analyze such reaction products, available in very small quantity. Yields of liquid products of 12–14 cc. usually result from 100 liters of water gas in a gasoline synthesis with cobalt catalysts by the Fischer-Tropsch method.[4] Small amounts of hydrocarbons are often produced in high pressure hydrogenations, and their behavior during distillation is of interest.

The distillation analysis of small quantities of material has been the subject of numerous researches, so a survey of the subject is unnecessary. The procedures of Gawalowski,[5] Gross and Wright,[6] and those of Pregl[7] are microdistillation methods. In all of them the apparatus has been designed for the handling of small amounts of material. Berl and Althoff[8] have designed such an apparatus, using a packed tower and a dephlegmator at a definite temperature; this apparatus works satisfactorily with 8–10 cc.

[1] Wa. Ostwald, *Glückauf*, **61**, 550 (1925).

[2] A. S. T. M. Ser. design, D. 86-27; Bureau of Mines, *Tech. Papers* 323, b. p. 49.

[3] Ubbelohde, *Mitt. a. d. Materialprüf.-Amt. Berlin*, **25**, 261 (1907).

[4] F. Fischer and H. Tropsch, *Ber.*, **59**, 830 (1926); literature by Fischer, *Brennstoff-Chemie*, **11**, 489 (1930).

[5] Gawalowski, *Z. anal. Chem.*, **49**, 744 (1910).

[6] P. Gross and A. H. Wright, *J. Ind. Eng. Chem.*, **13**, 701 (1921).

[7] F. Pregl, "Die quantitative organische Mikroanalyse," Julius Springer, Berlin, 1930, p. 220.

[8] E. Berl and F. W. Althoff, *Die Chem. Fabrik*, **3**, 220 (1930).

of liquid. Stock and his collaborators[9] have worked with a closed system under high vacuum, distilling fractions of a volatile liquid or condensed gas into a cooled buret, and ascertaining the weight and homogeneity from the volume and the vapor pressure. Stock[10] has also carried out determinations of vapor density by means of adjustments in the vacuum apparatus. The distillation analysis of gaseous hydrocarbon mixtures by Tropsch and Dittrich[11] is a further improvement of Stock's principle. In this process the hydrocarbon condensate is again evaporated and the gases are led through a series of vessels at successively lower temperatures. In the Podbielniak[12] process of fractional vacuum distillation, the temperature of the distillation flask and the dephlegmation column are regulated so that a higher pressure (usually 1 atm.) is maintained in these than in the receiver, where the vapor pressure of the condensate is measured. Wawrziniok and Lindner[13] have devised a method for determining the saturation pressure of fuels, which depends on the temperature, and pointed out the relationship between saturation pressure and the behavior of the fuel in the engine, particularly as related to the preheating temperature. C. Conrad[14] has carried out distillation analyses of liquid fuels on the basis of weight, with greater precision than in the process of Engler for gasolines or that of Krämer–Spilker for benzols.

We have tried to devise a simple method for ascertaining the behavior during distillation of liquid mixtures which are available only in small amounts. With this in mind we have chosen a method involving the determination of the vapor pressure, in which the behavior of the material during an Engler distillation may be calculated from the isobarometric temperature–distillate mass diagram. The mean molecular weight of various fractions may also be determined by this procedure. It is thus possible not only to observe the behavior during distillation, but also to determine the mean molecular weight of individual fractions.

Apparatus and Procedure

We have made use of Hüttig's tension eudiometer,[15] an apparatus much used in inorganic chemistry, and will describe it briefly.

The apparatus is shown in Fig. 1. The sample to be analyzed is weighed into the bulb A, which is connected to the rest of the apparatus through the

[9] A. Stock, *Ber.*, **47**, 154 (1914); **50**, 989 (1917); **51**, 983 (1918); **53**, 751 (1920); **54**, 142 (1921).

[10] Stock and Massenez, *ibid.*, **45**, 3561 (1912); Stock, *ibid.*, **50**, 1003 (1917); Stock and Zeidler, *ibid.*, **54**, 534 (1921).

[11] H. Tropsch and E. Dittrich, *Brennstoff-Chemie*, **6**, 169 (1925).

[12] W. J. Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931).

[13] Wawrziniok and Lindner, *Automobiltech. Z.*, **34**, 653, 724 (1931).

[14] Conrad, Lecture at the 44th General Meeting of the V. D. Ch., Vienna, 1931.

[15] G. F. Hüttig, *Z. anorg. allgem. Chem.*, **114**, 162 (1920).

stopcock F and a ground joint. The large bulb B has a volume of about 1.5 liters and is carefully calibrated before it is sealed into the system; by means of it, the volume of all the apparatus may be ascertained. The large volume of vapor which it contains even at a pressure of 20 mm. also serves to render negligible the usual errors of weighing and operation. C is a mercury manometer while the stopcocks D and E serve to admit air and connect the system to the vacuum pump. Mercury cut-offs have been avoided, for simplification. Contamination from stopcock grease has been minimized by applying it only to the outer one-third of grindings.[16] Sirupy phosphoric acid also has been used as a lubricant.

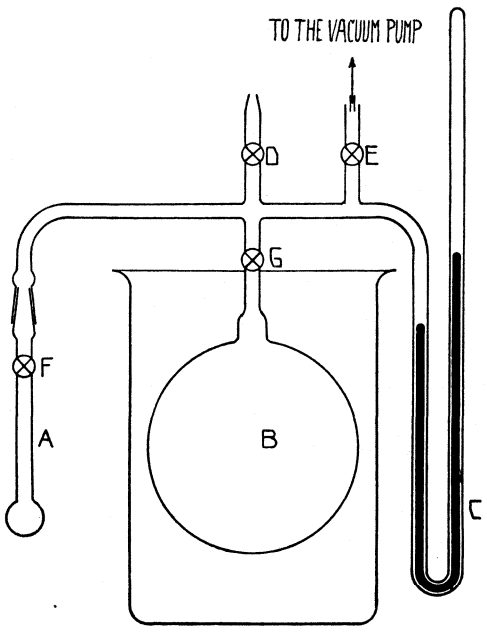


Fig. 1.

In carrying out an experiment, F is closed, the sample in A is cooled with liquid air and the rest of the apparatus is evacuated. Stopcock E is now closed, F is opened and closed and the system pumped out. This step is repeated, resulting finally in complete evacuation of the system with little or no loss of material from A. The part A is now weighed.

The vapor pressure determinations were carried out at a constant pressure of 20 mm., so the temperature varied from −22 to 18°. Constant temperatures were produced by the use of liquid air in an aluminum block provided with a drilled hole for the bulb A of the apparatus. The block is placed in a Dewar vessel. As soon as the constant pressure, 20 mm., has been established (five to ten minutes), F is closed and A is detached and weighed. A is then again connected and the temperature raised until a pressure of 20 mm. is again established. The test portion of material usually amounted to 0.8 g. in the case of benzines, corresponding to 6–7 points on the temperature–distillate mass diagram. The method can be applied to small quantities of any substance by choosing a suitable constant pressure or adjusting the size of the flask B. In case the boiling point of the substance requires a temperature above that of the room, a lower pressure should be chosen.

[16] Stähler, "Handbuch der Arbeitsmethoden i. d. anorg. Chem.," 1925, Vol. II, p. 887.

The determination of the mean molecular weight follows from the gas law, $pv = nRT$, in which n is the weight of gas divided by its molecular weight; the other quantities are all known by observation.

The work of Rogers and Brown[17] indicates that hydrocarbon mixtures such as gasoline do not follow Raoult's law strictly, but deviate from it by 5–15%, depending on the composition. Our molecular weights, therefore, are not truly exact; they are, however, quite satisfactory as applied technically to hydrocarbon mixtures.

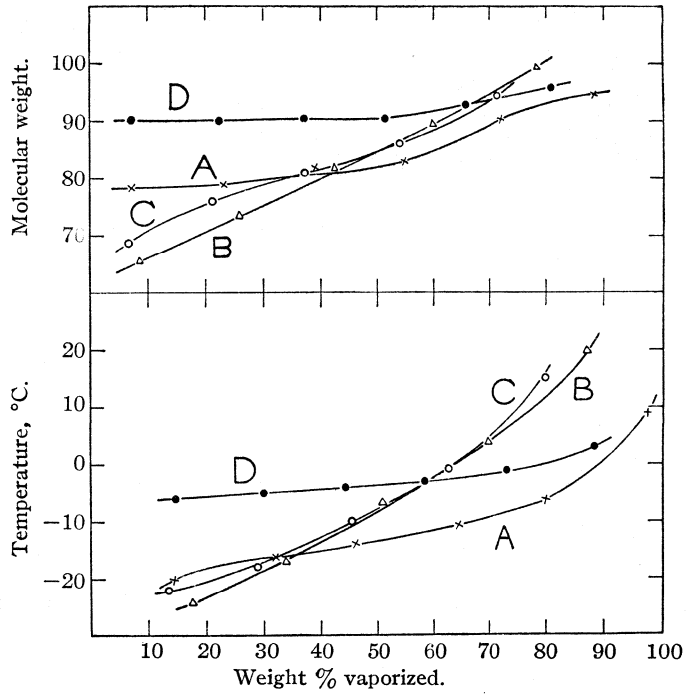


Fig. 2.

Experiments

In order to test the apparatus we made an experiment with chemically pure benzene and found a value, 77.73, which compares favorably with the theoretical value, 78. This result indicates that the apparatus and procedure are satisfactory for practical purposes.

Vapor pressure measurements have been carried out on four gasolines: a surgical gasoline (A), a light motor gasoline (B), a synthetic material (C) and normal gasoline (Kahlbaum) (D). The results are shown in Fig. 2, in which the percentage by weight is plotted on the abscissa and the temperature and mean molecular weight on the ordinate. It should be noted

[17] M. C. Rogers and G. G. Brown, *Ind. Eng. Chem.*, **22**, 258 (1930).

that in the graphical presentation of the molecular weight, the middle points of the distances representing the separate fractions have been joined by a curve which agrees with the mean values of the molecular weights.

Measurements also have been carried out on three kinds of benzene: Motor benzol (E), a commercial benzol (F) and so-called pure benzene (G). The results are given in Fig. 3.

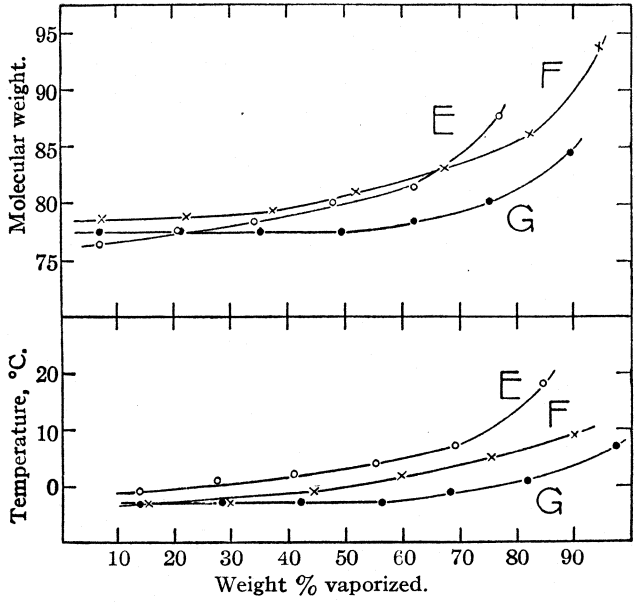


Fig. 3.

In addition, Dynalcol (H), a motor fuel used in Czechoslovakia, consisting of 30% gasoline, 20% benzene and 50% ethyl alcohol, as well as a mixture of 80% of acetone and 20% methyl alcohol (I) have been investigated, the results being shown in Fig. 4. This last mixture was chosen to demonstrate that our method is practicable for characterizing mixtures the components of which have no great difference in boiling point or specific gravity but a great difference in molecular weight.

On the assumption that there are no excessive differences between the specific gravity of the mixture being examined and of its components, we may calculate in a simple manner from the vapor pressure measurements the behavior of the material in a regular Engler distillation, and it will be shown subsequently that this behavior of various kinds of gasoline and benzene may be calculated accurately enough for technical purposes.

On the basis of the relationships formulated by Young and Kraffts, Gary[18] has prepared a nomogram for use in ascertaining the normal boiling

[18] W. W. Gary, *Petroleum World Oil Age*, **26**, 115–152 (1929).

point from vacuum distillation. In our work the calculations were based on the following relationships. Using the approximation formula of Nernst for a pressure of 20 mm. corresponding to our isobarometric process,

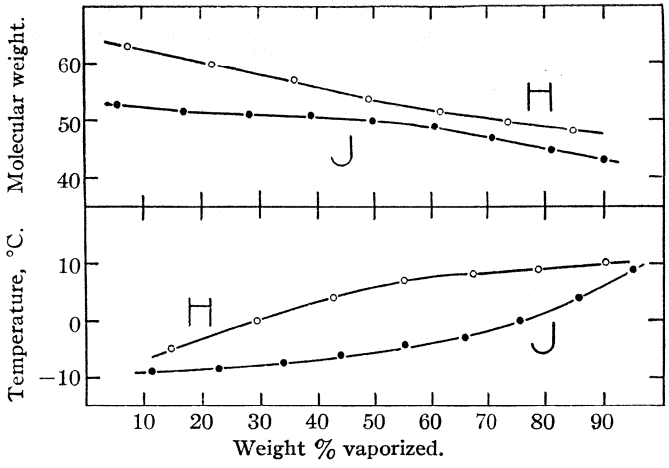


Fig. 4.

and for one atmosphere, according to the A. S. T. M. method, there are available the equations

$$\log \frac{20}{760} = -\frac{\lambda_0}{4.571T_1} + 1.75 \log T_1 + j'$$

$$\log 1 = -\frac{\lambda_0}{4.571T_2} + 1.75 \log T_2 + j'$$

in which λ_0 is the heat of evaporation, T_1 is the absolute temperature for the measurements at 20 mm., T_2 is the absolute temperature for the same numerical values of the mass of distillate in the A. S. T. M. method at 760 mm. (assuming that the specific gravities differ only by amounts comparable to the other experimental errors) and j' is the appropriate chemical constant.

By subtracting one equation from the other we obtain

$$\log \frac{760}{20} = 1.58 = \frac{\lambda_0}{4.571}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + 1.75 \log \frac{T_2}{T_1}$$

The value of $1.75 \log (T_2/T_1)$ is 0.20 for gasolines and benzenes, which may be confirmed by comparing the vapor pressure measurements with the results of the A. S. T. M. method.[19] We may therefore take this expression as a constant in the calculation and thus obtain the relation as obtained

$$1.38 = \frac{\lambda_0}{4.571}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\lambda_0 = 4.571T_1(1.75 \log T_1 + j' + 1.58)$$

from the Nernst formula. Substituting the numerical value of the chemi-

[19] The deviations from this value amount at most to ±0.01.

cal constant j', which amounts to 3 for benzene, and the mean value of 1.75 log T_1, which is 4.25, we obtain a simple relation for λ_0, namely

$$\lambda_0 = 4.571T_1(4.25 + 3 + 1.58) = 4.571 \times 8.83 \times T_1$$

We have taken 1.75 log T_1 as equal to 4.25 for the reason that the measurements are made in the temperature range -22 to $+18°$, so that 1.75 log T_1 lies between 4.20 and 4.31, the mean of which is 4.25.

$$1.38 = 8.83T_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \text{ and}$$

$$T_2 = 1.18T_1$$

We have not used this formula as a basis for our calculations; it shows clearly, however, that there is a direct proportionality between T_1 and T_2. By comparing the results of our experiments, we derived the empirical formula $T_2 = 1.306T_1$, which we have used in our calculations.

TABLE I

CALCULATED AND OBSERVED VALUES

Vol., % of distillate	Temperature, °C. Calcd.	Found	Vol., % of distillate	Temperature, °C. Calcd.	Found
	Surgical Gasoline (A)			Motor Benzol (E)	
25	60	60	25	83.1	84.3
50	65.9	66	50	87.4	87.2
75	73.7	75	75	97	95.5
	Motor Gasoline (B)		85	107	106
25	56.7	59.5		Commercial Benzol (F)	
50	73.7	75	25	80.3	83
75	94	95	50	83.5	84.5
	Synthetic Gasoline (C)		75	90	88
25	57.4	55.5	90	95.3	98
50	72.1	68			
75	95.3	91			
85	110.3	108			

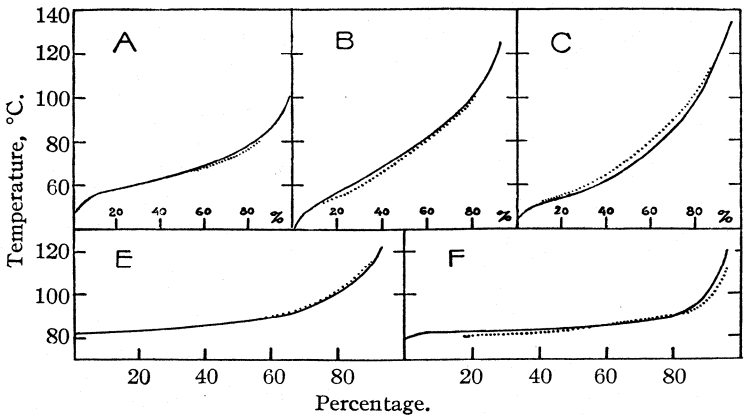


Fig. 5.——— Experimental, ····· Calculated.

The values calculated in this way from the vapor pressure measurements, as well as those found in the normal distillation of gasoline according to the A. S. T. M. method and for benzenes by the method of Krämer–Spilker, are given in Table I and are shown in Fig. 5.

Comparison shows that the differences in specific gravity of the components of a mixture make possible a direct calculation from the vapor pressure measurements of the temperature in the A. S. T. M. method corresponding to the numerical volume percentages of the distillate, with an accuracy sufficient for technical purposes.

Summary

A method has been described for ascertaining the behavior of small quantities of material during distillation. In this method temperatures are measured in a tension eudiometer at 20 mm. From these measurements it is possible to calculate the behavior of a substance in a regular A. S. T. M. distillation or in one carried out by the Krämer–Spilker method. The mean molecular weight of the distillate fractions may be determined simultaneously in the tension eudiometer, which is a further valuable attribute in the characterization of liquid mixtures.

PRAGUE, CZECHOSLOVAKIA

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

PREPARATION OF CERTAIN REDUCTION PRODUCTS OF BENZOIN

BY DONALD A. BALLARD AND WILLIAM M. DEHN

RECEIVED MARCH 14, 1932 PUBLISHED OCTOBER 5, 1932

Theoretically benzoin can yield thirteen reduction products; all of these except the optically active phenylbenzylcarbinols are known. Isostilbene has not been prepared by the reduction of benzoin; we have prepared didesyl and isodidesyl by reduction of benzoin. All of the other compounds have been prepared from benzoin; however, most of them have usually been prepared either from one another or from other compounds.

Since benzoin is easily and cheaply prepared,[1] it seemed desirable to prepare from it certain of these reduction products. Superior yields and simple methods of preparation of stilbene, desoxybenzoin and β-desoxybenzoinpinacone were developed.

Stilbene.[2]—In a one-liter beaker or large evaporating dish are placed in order, 50 g. of mercuric chloride, 500 cc. of water and 200 g. of zinc dust, the last having been freed

[1] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 33.

[2] Hitherto stilbene has best been prepared by the Grignard reaction, involving the intermediate formation of benzylmagnesium bromide, phenylbenzylcarbinol and the acetate of the carbinol [Hell, *Ber.*, **37**, 453 (1904)]. The above-described method gives 50% yields in two to three hours by one operation. Variations of conditions and materials gave no larger yields, because, perhaps, only the *d*- or the *l*-form of benzoin is reduced.

from lumps by sifting through a thirty-mesh screen. The mixture is stirred until all the mercuric chloride dissolves. The zinc is then allowed to settle, supernatant liquid is decanted and the solid is washed with water. The amalgamated zinc dust is placed in a 2–3 liter battery jar equipped with a mechanical stirrer and surrounded by ice; 100 g. of benzoin and 500 cc. of alcohol are added. While stirring and maintaining a temperature below 15°, 400 cc. of concentrated hydrochloric acid is added through a dropping funnel at such a rate that the addition is complete in one to two hours. Stirring is continued for another hour to ensure further reaction of the acid. The jar is filled with cold water and the contents are filtered. The precipitate is transferred to a large beaker, the stilbene is extracted with 500 cc. of hot alcohol, and the mixture is filtered through a hot water funnel to remove zinc dust. After cooling with ice the stilbene is filtered off and washed with a small quantity of alcohol, and the filtrate and washings are used for a second extraction of the zinc dust. Two extractions should remove all the stilbene, which amounts to 42–47 g. or about 50% of the theoretical.

Evaporation of the alcohol filtrate yields an oil which contains phenylbenzylcarbinol, desoxybenzoin and a small mass of tarry substance. If this oil is boiled with acetic anhydride for about one hour and distilled, the phenylbenzylcarbinol present will be converted into stilbene which can be freed from the desoxybenzoin by recrystallization from alcohol.

Desoxybenzoin.—In a 1-liter flask are placed 100 g. of powdered tin, 15 g. of mercuric chloride and 100 cc. of water. This mixture is permitted to stand with occasional shaking until the tin acquires a shiny coating of mercury. The solution is decanted and the tin is washed with water and drained. In the flask containing the tin are then placed 100 g. of benzoin, 250 cc. of alcohol and 200 cc. of concentrated hydrochloric acid. The flask is attached to a reflux condenser and the contents are boiled for sixteen hours. The flask is then removed, filled to the neck with water and cooled until the oil which has formed has solidified. The desoxybenzoin and tin are filtered off, dissolved in a small quantity of hot alcohol and filtered hot to remove the tin, which is washed with a little hot alcohol. While stirring, the filtrate and washings are cooled with ice and the precipitated desoxybenzoin is filtered and washed with a small volume of 50% alcohol. At this point, 65 g. or 70% of the theoretical amount melting at 52–58° is obtained. The remainder of the yield is obtained by evaporation of the alcohol and distillation of the oil up to 325°. This will give an additional 17 g., which can be recrystallized from alcohol, making a total yield[3] of 88%.

β-Desoxybenzoin Pinacone.—In a 500-cc. round-bottomed flask are placed 100 g. of benzoin, 47 g. of potassium iodide and 10 g. of red phosphorus. The flask is attached to a reflux condenser and the contents are heated to melting, when 26 cc. of concentrated hydrochloric acid is added gradually[4] through the top of the condenser. After the acid has been added, the contents are boiled gently for twenty hours. The flask is then filled with water and heated to boiling, after which the contents are poured into a beaker and stirred occasionally while cooling to break up the oil into small globules before it solidifies. When cold the solid is filtered off and dissolved in a small quantity of hot benzene, and filtered to separate the red phosphorus. The filtrate is transferred to a

[3] Other methods of preparation employed zinc. See THIS JOURNAL, **51**, 2164 (1929). If benzoin is reduced by zinc and sodium hydroxide, there are obtained desoxybenzoin, isodidesyl melting at 160°, didesyl melting at 248–250° and an unknown compound characterized by fine needles and melting at 208°. When 50 g. each of benzoin zinc dust and sodium hydroxide were heated for twenty-three hours with 300 cc. of alcohol and 100 cc. of water, 5 g. of isodidesyl was obtained.

[4] The hydrochloric acid is added slowly to minimize the escape of hydriodic acid through the condenser.

large beaker and the benzene is evaporated on the water-bath, leaving a mixture of desoxybenzoin and desoxybenzoin pinacone. To this mixture 500 cc. of 80% alcohol is added and the beaker is heated on the steam-bath for one hour, while breaking up the lumps[5] that are formed. After filtering through a hot water funnel and washing with a little alcohol, 30 g. of β-desoxybenzoin pinacone melting at 160–165° is obtained. The filtrate contains desoxybenzoin which can be recovered. One recrystallization from boiling alcohol yields β-desoxybenzoin pinacone[6] melting at 172°.

Summary

Four methods of reduction of benzoin were studied and superior methods of preparation of stilbene, desoxybenzoin and β-desoxybenzoin pinacone developed.

[5] Since desoxybenzoin is very soluble in alcohol and β-desoxybenzoin pinacone so very insoluble, a good separation can be made by this method provided the lumps are broken up to allow the alcohol to penetrate.

[6] β-Desoxybenzoin pinacone was first made by Wislicenus and Blank [*Ann.*, **248**, 7 (1888)] together with the α-form and other products by the reduction of benzoin with zinc dust and acetic acid. Since then it has only been made by the prolonged action of light on an alcoholic solution of desoxybenzoin, Cohen, *Rec. trav. chim.*, **38**, 110 (1919).

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

ELECTRON SHARING ABILITY OF ORGANIC RADICALS. VI. ALPHA-SUBSTITUTED PYRROLINES AND PYRROLIDINES

BY D. F. STARR, HELEN BULBROOK AND R. M. HIXON

RECEIVED MARCH 23, 1932 PUBLISHED OCTOBER 5, 1932

The preceding paper by Craig and Hixon extended the studies[1] of this Laboratory on the electron sharing ability of organic radicals to the nitrogen heterocyclics. The data available have been increased in this paper by the preparation and measurement of a series of α-substituted pyrrolines and pyrrolidines.

The α-substituted pyrrolines were synthesized by the reaction of Cloke[2] as modified by Craig and Hixon.[3] In using this reaction, it was found that the yields of the pyrrolines were markedly increased by avoiding the large excess of Grignard reagent recommended by Cloke. The yields obtained by using equimolar quantities of Grignard reagent and γ-chlorobutyronitrile are reported in Table I in comparison with yields by the original procedure as used by Craig.

The α-substituted pyrrolidines were prepared by the catalytic reduction of the corresponding α-substituted pyrrolines.

[1] I, Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927); II, Allison and Hixon, *ibid.*, **50**, 168 (1928); III, Johns, Peterson and Hixon, *J. Phys. Chem.*, **34**, 2218 (1930); IV, Johns and Hixon, *ibid.*, **34**, 2226 (1930); V, Craig and Hixon, THIS JOURNAL, **53**, 4367 (1931).

[2] Cloke, *ibid.*, **51**, 1174 (1929).

[3] Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931).

TABLE I

Compound	Yield, %	Original yield, %
α-Benzylpyrroline	41	13
α-Phenylpyrroline	66	55
α-(*p*-Tolyl)-pyrroline	69	59

Preparation of Compounds

Trimethylene chlorobromide was prepared as described by Cloke.[4]

γ-Chlorobutyronitrile was prepared according to the directions found in "Organic Syntheses."[5]

α-Phenylpyrroline was prepared as reported by Craig,[3] except that an equimolecular ratio of γ-chlorobutyronitrile and Grignard reagent was used. In calculating the amount of γ-chlorobutyronitrile required, the yield of phenylmagnesium bromide obtained was assumed to be within 5% of that reported by Gilman, Zoellner and Dickey.[6] The boiling range was 120–130° (18 mm.) as reported by Craig. The melting point of the picrate checked that obtained by Gabriel and Colman at 198°. The compound was titrated electrometrically because the colorimetric end-point obtained with sodium alizarin sulfonate was indefinite.

Anal. Calcd. for $C_{10}H_{11}N$: neutralization equivalent, 145.1. Found: Fraction II, 145.8; Fraction III, 145.9.

α-Benzylpyrroline was prepared in much better yields than those reported by Craig.[3] The reaction was carried out with the same modifications that were mentioned above in the preparation of α-phenylpyrroline. The compound boiled at 148–152° (34–36 mm.) or 110–114° (11–13 mm.). The chloroaurate melted at 125° as reported by Craig. The picrate prepared from an alcohol and ether mixture and recrystallized three times from alcohol and twice from an alcohol and ether mixture maintained a constant melting point at 111–112°. This compound was further identified by reduction to α-benzylpyrrolidine.

Anal. Calcd. for $C_{11}H_{13}N$: neutralization equivalent, 159.1. Found: Fraction I, 158.5; Fraction II, 159.3; Fraction III, 159.1.

α-Ethylpyrroline was prepared by the general method already mentioned and the separation of the compound was carried out according to Craig's directions. The compound boiled at 126° and the picrate melted at 87° as reported.

Anal. Calcd. for $C_6H_{11}N$: neutralization equivalent, 97.1. Found: Fraction I, 96.7; Fraction II, 96.7; Fraction III, 96.8.

α-(*p*-Tolyl)-pyrroline was prepared using the general method for the preparation of pyrrolines. The separation of the compound was carried out as in the preparation of α-phenylpyrroline; the compound is a solid melting at 60–61° and boiling at 125–132° (6–8 mm.) or 136–140° (16–18 mm.). A picrate was prepared from alcohol and recrystallized twice from a mixture of alcohol and water. It melted at 185–186°.

Anal. Calcd. for $C_{11}H_{13}N$: N, 8.80; neutralization equivalent, 159.1. Found: N, 8.65, 8.66; neutralization equivalent, 159.8, 159.9. Calcd. for $C_{11}H_{13}N \cdot HAuCl_4$: Au, 39.51. Found: Au, 39.77, 39.80.

The compound was further identified by reduction to α-(*p*-tolyl)-pyrrolidine.

α-Cyclohexylpyrroline was prepared by following the general procedure. The separation was similar to that for α-phenylpyrroline. The compound boils at 114–116°

[4] Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53**, 2791 (1931).

[5] "Organic Syntheses," Vol. VIII, p. 52.

[6] Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1576 (1929).

(22–24 mm.) or 77–79° (4–6 mm.). A picrate was prepared in a mixture of alcohol and ether and recrystallized from alcohol. The melting point was 117°. It was difficult to obtain the base completely dry. The compound was reduced to α-cyclohexylpyrrolidine.

Anal. Calcd. for $C_{10}H_{17}N$: N, 9.26; neutralization equivalent, 151.2. Found: N, 9.36, 9.09; neutralization equivalent, Fraction II, 152.9; Fraction III, 151.9.

α-Benzylpyrrolidine was prepared from α-benzylpyrroline by the catalytic reduction method according to Craig.[3] Adams and Shriner's platinum-oxide platinum black catalyst was used, with absolute alcohol acidified with hydrochloric acid as a solvent. The reduction was complete after two to three hours of shaking under 90 lb. of hydrogen pressure.

The compound boils at 129–131° (17–19 mm.) or 150–153° (44–46 mm.). The picrate was prepared and recrystallized twice in alcohol; m. p. 136–137°.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.85; H, 9.33; neutralization equivalent, 161.1. Found: C, 81.78, 81.30; H, 9.22, 9.40; neutralization equivalent, Fraction I, 160.8; Fraction II, 161.0; Fraction III, 161.0.

α-(*p*-Tolyl)-pyrrolidine was obtained from the corresponding pyrroline using the procedure mentioned for α-benzylpyrrolidine. The boiling points found were 128–130° (8–10 mm.) and 141–144° (23–25 mm.). A picrate was prepared and recrystallized in a 75% solution of alcohol. The melting point was 173°.

In 1901 Katzenellenbogen[7] reported α-(*p*-tolyl)-pyrrolidine by the reduction of *p*-tolylpyridazine. The identity of the compound is questioned in the handbooks since the only evidence offered is the analysis of the picrate. The melting point of the picrate was reported as 150°, which does not check the picrate listed above.

The method of synthesis and analysis are sufficient evidence as to the identity of the compound.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.85; H, 9.33; neutralization equivalent, 161.1. Found: C, 81.50, 82.00; H, 9.29, 9.38; neutralization equivalent, Fraction I, 160.2; Fraction II, 161.7; Fraction III, 160.2.

α-Cyclohexylpyrrolidine was obtained by the addition of two hydrogen atoms to a molecule of α-cyclohexylpyrroline. The pyrroline contains but one double bond and in this case there is no doubt as to the position taken by the hydrogen atoms. The method of reduction is the same as that used previously and the reaction is perfectly definite. The theoretical amount of hydrogen being absorbed in two to three hours, gives practically a quantitative yield. The boiling point was 214–221°. When distilled under reduced pressure the boiling point was 84–87° (7–9 mm.) or 120–126° (39–41 mm.). The most satisfactory derivative prepared was the chloroaurate, which was recrystallized twice from benzene. The melting point is 105–106°. The compound is a strong base which forms a solid carbonate if allowed to stand in contact with the atmosphere.

Wibaut and DeJong[8] have reported being able to obtain α-cyclohexylpyrrolidine by catalytic reduction of α-phenylpyrrole although Craig[3] found that the catalytic reduction of α-phenylpyrroline gave an indefinite mixture containing some α-phenylpyrrolidine. Wibaut and DeJong identified the compound by analyzing the picrate for nitrogen. The boiling point given above, 214–221°, checks their value, 220–230°, but the melting point of the picrate given as 153° could not be confirmed.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.4; H, 12.53; neutralization equivalent, 153.2. Found: C, 78.8, 79.0; H, 12.31, 12.08; neutralization equivalent, Fraction II, 156.1;

[7] Katzenellenbogen, *Ber.*, **34**, 3828 (1901).

[8] Wibaut and DeJong, *Rec. trav. chim.*, **49**, 237 (1930).

Fraction III, 154.0. (The compound was difficult to obtain dry. Even though distilled from chips of sodium only the last fraction was completely dry.)

Measurement of Dissociation Constants.—The method used was that described by Carothers, Bickford and Hurwitz.[9] The technique in measuring was that described by Craig[1] except for the α-(*p*-tolyl)-pyrroline which was a solid and could not be sealed in ampules for weighing. It was weighed in a watch glass as rapidly as possible.

The criteria of purity were constant boiling point, three fractions were collected within a range of 2°. Neutralization equivalents of each fraction were determined. In the case of α-cyclohexylpyrroline and α-cyclohexylpyrrolidine, where the first two fractions were not completely dry, the solutions were made up according to the amount of base titrated. The P_H of these solutions checked the P_H of the solutions made up from fractions that were completely dried. In all cases dissociation constants were

TABLE II

DISSOCIATION CONSTANTS OF α-SUBSTITUTED PYRROLINES AND PYRROLIDINES (25°)

Compound		E. m. f.	P_H	$-\text{Log } K_B$
α-Ethylpyrroline	Fraction I	0.7133	7.91	6.09
	Fraction II	.7133	7.91	6.09
	Fraction III	.7138	7.92	6.08
α-Benzylpyrroline[a]	Fraction I	0.6648[a]	7.08[a]	6.92[a]
	Fraction II	.6651	7.08	6.92
	Fraction III	.6693	7.16	6.84
α-(*p*-Tolyl)-pyrroline	Fraction I	0.6941	7.59	6.41
	Fraction II			
	Fraction III	.6942	7.59	6.41
α-Phenylpyrroline	Fraction I	0.6519	6.88	7.12
	Fraction II	.6428	6.73	7.27
	Fraction III	.6440	6.75	7.25
α-Cyclohexylpyrroline	Fraction I	0.7160	7.95	6.05
	Fraction II	.7159	7.95	6.05
	Fraction III	.7160	7.95	6.05
α-(*p*-Tolyl)-pyrrolidine	Fraction I	0.8381	10.02	3.98
	Fraction II	.8375	10.00	4.00
	Fraction III	.8343	9.95	4.05
α-(Benzyl)-pyrrolidine	Fraction I	0.8594	10.37	3.63
	Fraction II	.8583	10.34	3.66
	Fraction III	.8589	10.36	3.64
α-Cyclohexylpyrrolidine	Fraction I	0.8859	10.81	3.19
	Fraction II	.8838	10.78	3.22
	Fraction III	.8849	10.80	3.20

[a] The values given represent the precision obtainable, but the voltage drifts and the values are probably too low. See discussion.

[9] Carothers, Bickford and Hurwitz, THIS JOURNAL, 49, 2908 (1927).

measured on three fractions. The results are reported in tabular form (Table II) and are shown graphically in Fig. 1.

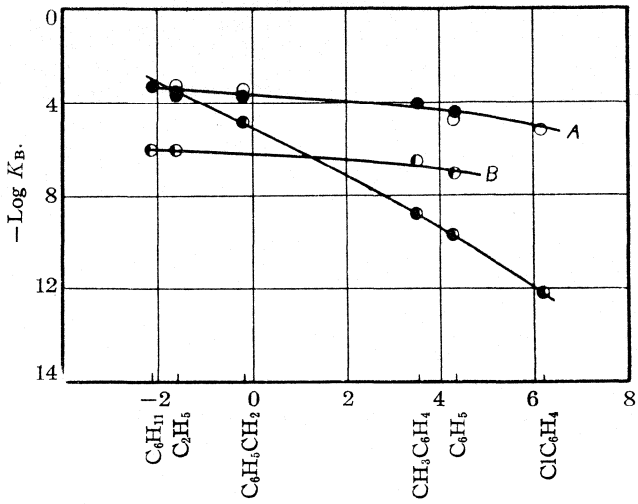


Fig. 1.—Relative magnitudes of the basic dissociation constants of substituted amines of the series RNH_2 ◐; of the series RCH_2NH_2 ○; of the α-substituted pyrrolidines ●; and of the α-substituted pyrrolines ◐. The drop from curve A for the α-substituted pyrrolidines to curve B for the α-substituted pyrrolines represents the influence of the introduction of one double bond in the pyrrolidine ring.

Discussion of Results

A satisfactory dissociation constant could not be obtained for α-benzylpyrroline. The value always drifted and was lower than the value which would be predicted on the basis of the curve for the pyrroline series. A solution of the base containing one-half equivalent of hydrochloric acid became colored after standing for eight hours. The voltage of the solution continued to drop from day to day, and after a month's time a total drop of 150 millivolts had been observed. The solutions became dark orange in color and deposited sediment at the bottom even though the solutions were less than 0.01 molar in concentration. In comparison, a solution of α-ethylpyrroline and one-half equivalent of hydrochloric acid showed no sign of turbidity and only a slight yellow color after twice the period of time. The drop in voltage was only 9 millivolts, which lowered the value for $-\log K_B$ by 0.16. These observations indicate that even though the α-ethylpyrroline is not stable indefinitely, it is stable enough to give a reliable dissociation constant by the half-neutralization method. The α-benzylpyrroline is relatively unstable and the method would probably

give results lower than the true values. Lipp and Widnmann[10] report that α-substituted pyrrolines react with water to give γ-aminopropyl substituted ketones. This would offer a possible explanation of the change observed.

The drift in e. m. f. of a half-neutralized benzylpyrroline solution is shown in Fig. 2, where the voltage of the solution is plotted against time, Similar values for the α-ethylpyrroline are also represented for comparison.

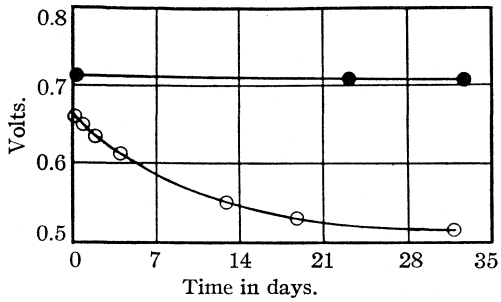
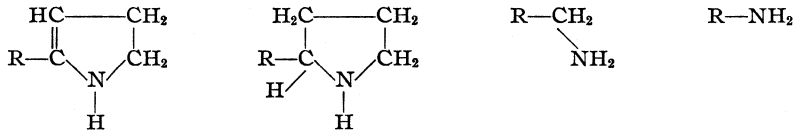


Fig. 2.—Comparison of the stability of an α-benzylpyrroline solution ⊙ with the stability of an α-ethylpyrroline solution ● as measured by the change in e. m. f. of half-neutralized solutions.

It was hoped that the α-benzylpyrroline might be more stable in the presence of an equivalent of hydrochloric acid. The solutions did not color and the voltage seemed to be more constant over periods of time, but the necessary precision was not obtained and the results were therefore discarded. The properties of this compound should be more thoroughly investigated before a value for the dissociation constant is accepted.

The available dissociation constants of the four series of compounds



are compared graphically in Fig. 1 using the same magnitudes for the electron sharing ability of the various radicals R used in the previous publications. The results substantiate the working hypothesis actuating these studies; if the criteria for measuring chemical affinity are observed, the polar properties of any group may be expressed as a mathematical function of the electron sharing ability of the attached radical.

Summary

The general method for the preparation of α-substituted pyrrolines has been modified to improve yields.

α-(p-Tolyl)-pyrroline, α-cyclohexylpyrroline and α-benzylpyrrolidine have been described for the first time.

Dissociation constants of a few α-substituted pyrrolines and pyrrolidines have been measured.

AMES, IOWA

[10] Lipp and Widnmann, *Ann.*, **409**, 79 (1915).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATES OF THE HYDROLYSIS TO BETAINES OF SOME QUATERNARY BASES OF ALPHA-AMINONITRILES. A STUDY OF QUATERNARY AMMONIUM BASES

BY T. D. STEWART AND KARL KORPI

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Introduction

A. Klages and S. Margolinsky[1] reported the preparation of betaines through the reaction

$$R_3N^+—CH_2—CN + OH^- + H_2O \longrightarrow R_3N^+—CH_2—COO^- + NH_3 \quad (1)$$

The hydrolysis takes place rapidly in dilute alkali, without appreciable side reactions, so a study of the kinetics of the reaction has been undertaken in an attempt to determine, first, the nature of the rate-determining step, and, second, what connection, if any, exists between this reaction and quaternary ammonium base decomposition.

Since these are quaternary ammonium compounds it would not have been surprising to find an appreciable decomposition typical of such compounds

$$R_3N^+—CH_2—CN + OH^- \longrightarrow R_3N + HO—CH_2—CN \quad (2)$$
$$HO—CH_2—CN + OH^- \longrightarrow CH_2O + CN^- + H_2O$$

The only evidence we have observed of the formation of a tertiary amine is in the case of the acetone derivative, $[(CH_3)_3N—C(CH_3)_2CN]^+OH^-$, which yields easily detectable amounts of trimethylamine during the betaine formation.[2] The question arises as to whether this lack of quaternary decomposition is due to a fundamental stability of these quaternary ammonium hydroxides, or to the existence of the faster reaction of betaine formation. In the latter case the same factors which affect quaternary ion decomposition might also affect betaine formation, and point to a common initial step in the reaction mechanisms.

According to Stewart and Aston[3] the position and intensity of charge on a quaternary ammonium ion affect the ease of activation of the bonds concerned in its decomposition and hence affect the rate of the reaction. A decrease in the intensity of the charge by means of solvation, conjugation with neighboring atoms, or association with negative ions would hinder the reaction. The fact that in water solution only strongly basic negative ions bring about quaternary decomposition indicates that the point of attack is a hydrogen atom, presumably upon either the α or β position to the nitrogen. The cyanide group might well have contributed to the ease of quaternary decomposition through its influence upon the

[1] Klages and Margolinsky, *Ber.*, **36**, 4189 (1903).

[2] The betaines yield trimethylamine with concentrated hot sodium hydroxide, but do not decompose detectably under the conditions of this nitrile hydrolysis.

[3] Stewart and Aston, THIS JOURNAL, **49**, 1718 (1927).

reactivity of the hydrogen atom adjacent to it. We shall then presume that the initial step in the present case is the same as that in quaternary ammonium ion decomposition, namely, loss of hydrogen ion, but that the following reaction involves the cyanide instead of the ammonium radical

$$R_3N^+—CH_2—CN + OH^- \longrightarrow R_3N^+—CH{=}C{=}N^- + H_2O \xrightarrow{H_2O} R_3N^+—CH_2—CO_2^- + NH_3 \quad (3)$$

Without this alternative reaction the hypothetical intermediate would have rapidly undergone quaternary decomposition. A second path for the reaction, likewise fostered by the positive charge, would be the direct addition of the hydroxyl ion to the cyanide triple bond

$$R_3N—CH_2—C{\equiv}N + OH^- \longrightarrow R_3N^+—CH_2—\underset{\displaystyle OH}{\underset{|}{C}}{=}N^- \xrightarrow{H_2O} R_3N^+—CH_2—C\begin{matrix}\nearrow O \\ \searrow O^-\end{matrix} + NH_3$$

According to either of the above mechanisms, the rate determining step might involve either (1) quaternary and hydroxide ions each to the first power or (2) an activation step of the quaternary ion alone. Neither of these assumptions seems justified from a simple analysis of the reaction kinetics. Other ions, particularly negative ions, could be expected to exert a strong influence upon the reaction rate.

The Specific Reaction Rate Law.—In each of the experiments made the total ionic strength of the solutions was high, and for purposes of comparison the effect of changing ionic strength, as such, has been disregarded. The reactants are considered to be completely ionized, so that uncorrected formula concentrations by volume of the ions have been used. The remarkable insensitivity of our rate law to changes in concentration, temperature and the presence of inert salts demands this simple treatment as a first approximation.

The quaternary nitrile ion will be represented by A, hydroxide ion by B and ammonia by x. Assuming the concentration of the water constant, the general rate expression for the hydrolysis reaction represented by equation (1) may be written

$$\frac{dx}{dt} = K(A - x)^n(B - x)^m \quad \text{(I)}$$

in which $(A - x)$ and $(B - x)$ are the concentrations of the reactants at any time, derived from the corresponding initial concentrations, (A) and (B). By keeping B in large excess it may be considered constant, and the best value of n may then be obtained by plotting $(1/A - x)^{n-1}$ against the corresponding values of t, using various values of n until a straight line may be drawn through the points. The value of m could similarly be obtained when A is in large and constant excess.

The Reaction in Excess Hydroxide Ion and Varying Iodide Ion.[4]—Table I gives the initial and final conditions of a number of experiments;

TABLE I

EXPERIMENTAL CONDITIONS FOR THE HYDROLYSIS IN EXCESS HYDROXIDE ION B, AND VARYING IODIDE ION, OF DIETHYLMETHYLAMMONIUM ACETONITRILE ION, A. TEMP., 35°

Expt.	Concn. of A Initial	Concn. of A Final	Concn. of B Initial	Concn. of B Final	Other concentrations Na^+	Other concentrations I^-	Other concentrations K^+	Elapsed time, min.
28	0.0990	0.0099	0.5000	0.4110	0.5000	0.0990	....	74.5
34	.1019	.0125	.5000	.4106	.5000	0.5084	0.4065	103.8
33	.1029	.0130	.5000	.4110	.5000	1.000	.898	128.0
37	.1024	.0034	.6000	.5010	.600	0.4024	.300	102.0
31	.1003	.0065	.950	.8562	.950	.980	.880	57.6

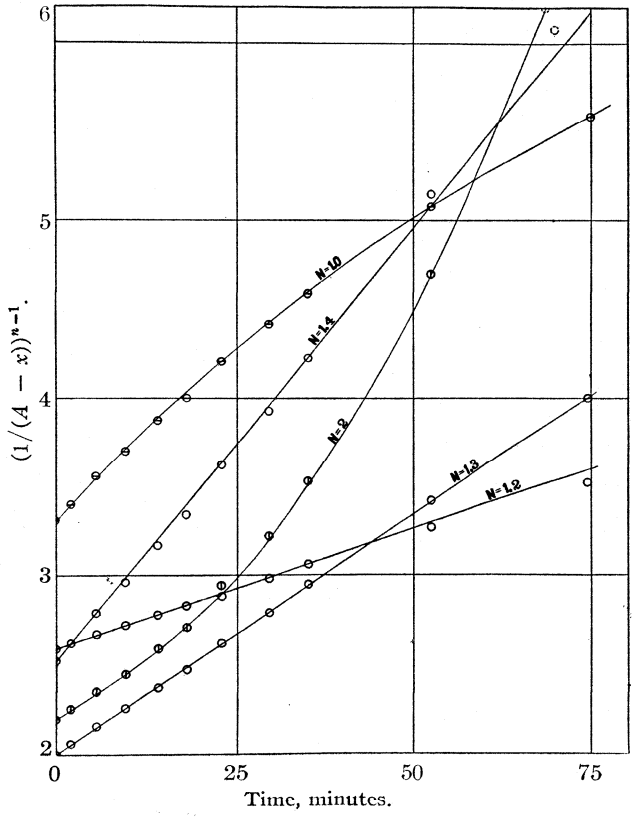


Fig. 1.—Plot of $(1/(A - x))^{n-1}$ against time in minutes for Expt. 28.

[4] Only a few experiments are included here. In others the analytical work was not as accurate or the reaction was not carried near enough to completion. In every case the results were consistent with these subsequent experiments.

Figs. 1 and 2 give the corresponding plots of $(1/(A - x))^{n-1}$. All concentrations are in moles per liter of solution.

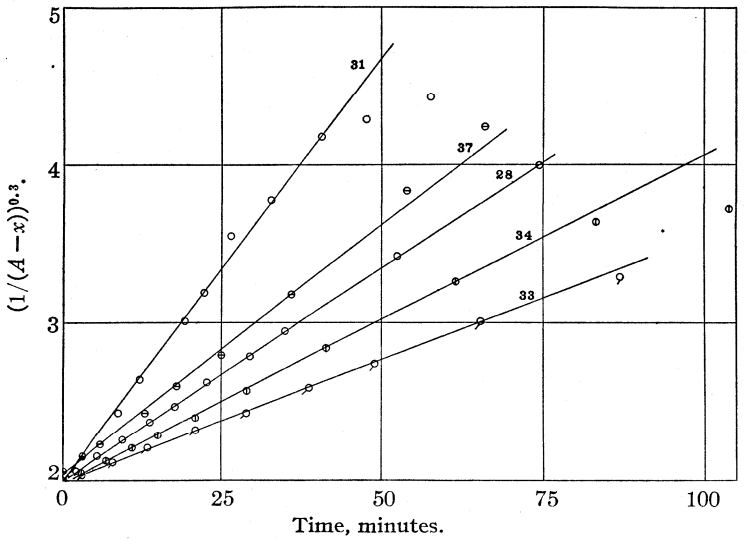


Fig. 2.—Plot of $(1/(A - x))^{n-1}$ when $n = 1.3$, against time.

It is seen from the plots that with a five to ten-fold excess of hydroxide ion, the rate of betaine formation is proportional to neither a first nor second power of the ammonium nitrile ion concentration, but is between the two. When n is about 1.3, a very good straight line is obtained in the plots for 80% or better of the total reaction during which the concentration of A changes five-fold. This power law ($n = 1.2$ to 1.4) holds over the following variations of the experimental conditions: (1) addition of betaine or ammonia, or both; (2) addition of potassium iodide, potassium chloride, potassium perchlorate, lithium chloride, potassium sulfate, potassium nitrite and potassium carbonate, from 0.1 M to 5 M; (3) variation of temperature over a range of 100°; (4) variation of proportional excess of hydroxide ion; (5) removal of ions other than A and B; (6) use of homologs varying the substituents on the nitrogen and substituting methyl for hydrogen on the carbon.

This fractional power naturally suggests a combination of first and second order reactions, but all attempts to approximate these extremes throughout application of the above variables have failed. Analytical difficulties have not permitted measurements at concentrations of the nitrile below 0.01 molal, in which range some other exponent or rate law may serve.

No attempt will be made in this paper to give physical significance to this fractional exponent. Its use gives a means of comparing one experiment with another and of ascertaining the effect upon the specific reaction

rate of changing conditions. Taking the value 1.3 for n in all experiments where hydroxyl ion is in excess, we may use the slope of the plot of $(1/(A - x))^{n-1}$ against time as the specific reaction rate when the concentration of A is the sole variable, and compare the effect of changing salt and hydroxyl-ion concentrations. The results are given in Table II.

TABLE II

RATES OF THE REACTIONS TAKEN FROM TABLE I AND FIG. 2 WHEN $n = 1.3$; TEMPERATURE, 35°

Expt.	Concentration A (Initial)	Concentration B (Average)	$Na^+ + K^+$	I^-	Slope (K_s)	$\frac{K_s}{B}$
28	0.0990	0.455	0.5000	0.0990	0.0269	0.0591
34	.1019	.455	.9064	.5084	.0202	.0444
33	.1020	.455	1.398	1.000	.0157	.0345
37	.1024	.550	0.900	0.4024	.0315	.0573
31	.1003	.903	1.830	.980	.0540	.0598

It is seen that the specific reaction rate decreases with increasing iodide (Expt. 28, 34, 33) and is not proportional to the first power of the hydroxide-ion concentrations (Expt. 33, 31). It would thus appear that the exponent m in Equation I is also greater than unity.

The Effect of the Products Formed upon the Reaction.—Ammonia alone produces too slow a reaction to be readily measured. Ammonia (0.0926 N) in strong base (0.500 N) gave for the same fractional exponent for $(A - x)$, the same slope (K_s) throughout as for a comparative reaction without ammonia present. Similarly the presence of 0.102 N ammonia together with 0.102 N betaine in one of two parallel experiments caused no perceptible difference in the rate.

The Reaction in Excess Quaternary Ammonium Ion.—Under these conditions the concentration of A (Equation I) is constant and that of B variable. Plotting $(1/(B - x))^{m-1}$ against time as before no straight line corresponding to values of m between one and two could be found. The closest approach to a straight line was given by a value of 1.6 for m, which agrees closely with the value of 1.84 taken from Expts. 31 and 33, Table II. In the latter case a correction for the effect of the difference in the iodide ion concentrations would lower the value of m. It is believed that the salt effect in these experiments takes the form of a ratio of the reacting ion to the sum of all ions of the same sign (a mole fraction) and this ratio changes markedly in these experiments during the progress of the reaction. In the case of excess hydroxide ion this ratio is nearly constant. An analysis of these and other data from this standpoint will be presented in another paper.

The Reaction in Equal Concentrations of the Reactants. The Effect of Temperature.—When (A) and (B) (Equation I) are equal the values of $(1/(A - x))^{n+m-1}$ plotted against time should lie on a straight line for the

correct values of m and n. This is true for 80% of the reaction when $m + n$ is taken as 2.4 (Fig. 3), and regardless of the presence or absence of sodium and iodide ions. Solutions made up from the quaternary iodide salt and silver oxide conformed to the same rate law (same exponent) as those made up of the quaternary iodide and sodium hydroxide. The reaction was slower in the presence of the iodide. A series of solutions about 0.1 M each in the quaternary iodide and sodium hydroxide was subjected to temperatures from 25 to 115°. There was no apparent change in the best value of $m + n$ (2.4). When the logarithm of the slope taken from each plot was plotted (Fig. 4) against the reciprocal of the temperature, a straight line was obtained, indicating that the heat of activation was constant over this range of temperature.

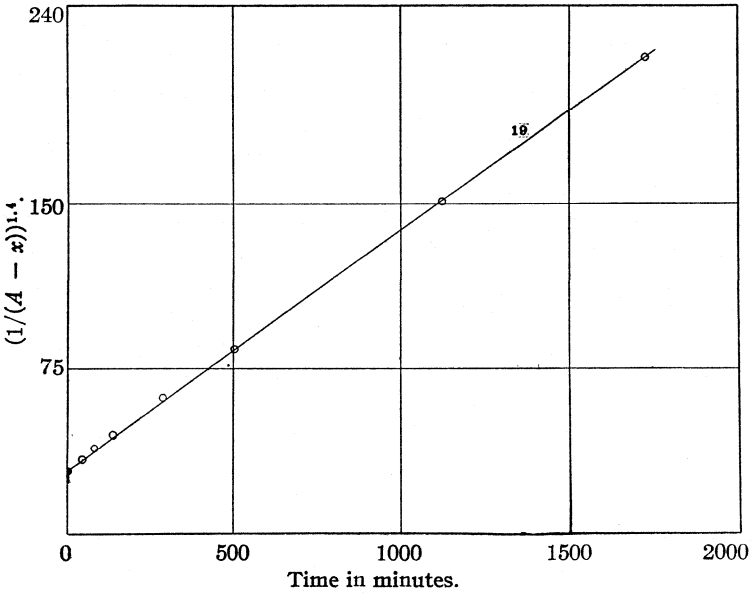


Fig. 3.—The reaction when (A) and (B) are equal (Expt. 19), plotting $(1/(A - x))^{n+m-1}$ against time, with $n + m$ equal to 2.4.

Table III summarizes the data. The final times and concentrations are given, but in the actual plotting to obtain the slopes (K_s) these last points received little weight because of the error in assuming $(A - x)$ equal to $(B - x)$ at all times. Actually even these points fell very close to the ruled line, with most of the points directly on the line. Reproducibility is indicated by the Experiments 23 and 24. A numerical average of the two concentrations was used.

The heat of activation, as calculated from the plot by the usual formula, is 13,000 calories.

TABLE III

RATES OF THE REACTION OF DIETHYLMETHYLAMMONIUMACETONITRILE ION WITH HYDROXIDE ION IN EQUAL AMOUNT, AT VARIOUS TEMPERATURES, ASSUMING $m + n = 2.4$

Expt.	Concentration A (Initial)	A (Final)	B (Initial)	Na^+	I^-	Time, min.	Temp., °C.	K_s
18	0.0910	0.0258	0.0895	0.0985	0.1000	2670	25	0.0575
19	.0918	.0225	.0898	.0985	.1000	1728	35	.110
20	.0911	.0158	.0891	.0985	.1005	1612	45	.212
21	.0822	.0109	.0815	.0985	.0992	345	75	1.34
22	.0903	.0080	.0882	.0985	.1006	1751	60	0.528
23	.0798	.0119	.0781	.0985	.1002	180	90	2.67
24	.0845	.0104	.0828	.0985	.1002	201	90	2.65
25	.0825	.0082	.0805	.0985	.1005	198	100	4.63
26	.0666	.0065	.0645	.0985	.1006	135	115	11.3

Whereas no physical interpretation can be given this heat of activation, it is apparent that this exponential rate law represents some very simple process rather than a summation of several rate-determining steps, as otherwise either the law itself would probably fail to hold with change of temperature or the apparent heat of activation would have changed.

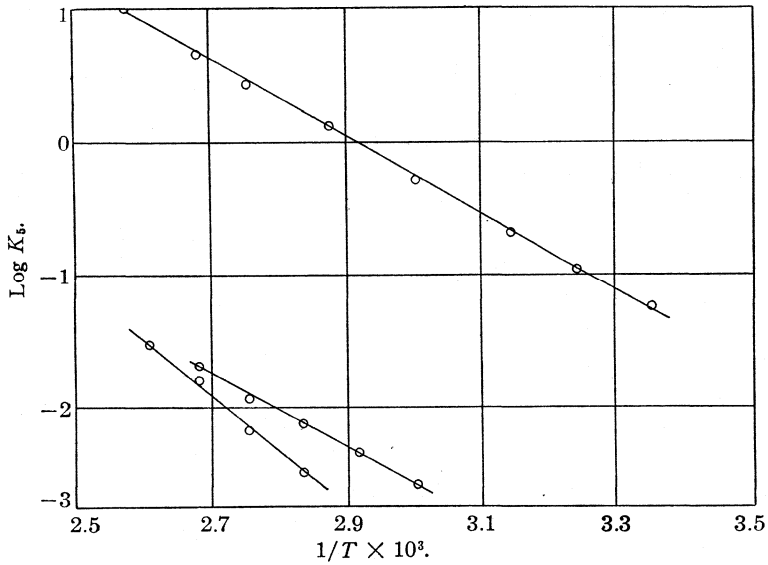


Fig. 4.—The change in reaction rate with the temperature. Upper curve, acetonitrile derivative; middle curve, propionitrile derivative; lower curve, isobutyronitrile derivative.

If the best value of n is 1.3 and the best value of m about 1.8 when B is in excess, but the best value of $m + n$ when the hydroxyl-ion concentration is equal to that of the quaternary ion is 2.4, the values of both m and n cannot be constant, except under the restricted conditions of one

experiment. Therefore this fractional power has no real physical significance but is simply a close approximation to, but not an equivalent of, the real rate law.

The Effect of the Removal of All Negative Ions except Hydroxide Ion.—Two experiments were made at 17.3° in which the solutions were prepared by adding silver oxide in slight excess to an aqueous solution of the iodide, and filtering off the silver iodide. In each case some silver was left in solution, partially due to ammonia formed. In one experiment excess potassium hydroxide was added to this solution. Table IV describes the conditions and results.

TABLE IV

RATES OF HYDROLYSIS OF DIETHYLMETHYLAMMONIUMACETONITRILE HYDROXIDE IN THE ABSENCE OF IODIDE ION

Temp., 17.3°; K_s taken from plots of $(1/(A - x))^{1.4}$ and $(1/(A - x))^{0.3}$ against time in Experiments 11 and 14, respectively.

Expt.	Concentration A (Initial)	A (Final)	B (Initial)	Ag^+	K^+	Time, min.	K_s
11	0.2011	0.0270	0.2175	0.016	...	6157	0.0342
14	.1842	.0289	.5605	.036	0.340	210	.0060

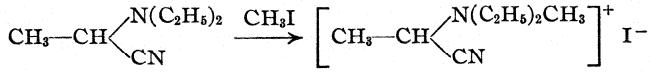
In the absence of iodide ion just as good plots were obtained as in its presence, using the same fractional power law, showing that the nature of the exponent is not affected by other electrolytes. Since the temperature is different[5] and the temperature coefficient in the absence of iodide ion has not been determined, the effect of iodide ion upon the rate has not been calculated. The salt effect is being studied in more detail. A rough comparison of these experiments with Experiments 19 and 28 indicates that the effect of a given concentration of iodide ion (0.1 M) depends upon the hydroxide-ion concentration, being relatively less when the latter is in excess. These two experiments may be used to determine the rate law with respect to hydroxide ion in the absence of iodide ion. The reaction rate in each case was taken graphically at the point where the concentration of the positive ion was 0.05 M and those of hydroxide ion were 0.0639 M and 0.4230 M, respectively. The specific rates were 1.96×10^{-5} and 4×10^{-4}, respectively, in corresponding units. Assuming the same exponent for A in the two cases, the exponent m for hydroxide ion is 1.6, in good agreement with the exponent found in the presence of high concentrations of iodide ion.

The conclusion is drawn that the fractional exponent is due to some property of the reacting system, and that the actual reaction rate, but not the rate law, is affected by other electrolytes present.

The Effect of the Substitution of Methyl Groups for Hydrogens in Trialkylammoniumacetonitrile Ion.—The theory presented in the

[5] Other experiments at the same temperature were made earlier, but the analyses were not as accurate.

introduction involved the hydrogens near the ammonium radical. Therefore the effect on the rate and on the form of the rate law of substitution of these hydrogens by carbon groups was studied. One methyl was introduced by means of starting with the acetaldehyde derivative.



This quaternary compound reacted so slowly that the temperature range used was from 60 to 120°. Table V gives the experimental conditions and results.

TABLE V

RATES OF THE REACTION OF α-DIETHYLMETHYLAMMONIUMPROPIONITRILE ION (A') WITH HYDROXIDE ION (B)

$n = 1.3$. K_s corrected to B = 0.95 M, assuming $m = 1.8$

Expt.	Concentrations A' (Initial)	A' (Final)	B (Average)	Na^+	I^-	Time, min.	Temp., °C.	K_s (corr.)
5A	0.0925	0.0070	0.866	0.913	0.100	641	70	0.00450
6A	.0869	.0118	.869	.913	.100	282	80	.00749
7A	.0417	.0098	.883	.913	.050	155	80	.0106
8A	.0872	.0160	.871	.913	.100	146	90	.0115
9A	.0716	.0043	.952	1.000	.100	151	100	.0198
10A	.0901	.0054	.953	1.000	.099	1687	60	.00260

In the plots of $(1/A' - x)^{0.3}$ against time, the eight or ten points fell on the ruled line well within experimental error, except in Experiment 10A, in which the excessive time required probably allowed a reaction with the glass bombs. In this case only the first six points were used, involving about 75% of the total reaction. In Fig. 4, K_s is plotted against $1/T_{Abs.}$ as before. The calculated activation energy is 12,650 calories, or the same within experimental error as for the unsubstituted derivative.

An experiment was made in which the concentrations of reactants were equal, and, as before, the value of $m + n$ of 2.4 gave a straight line plot.

The amino nitrile from acetone yielded diethylmethylammonium-isobutyronitile ion. Table VI describes the experiments and results using this substance.

TABLE VI

EXPERIMENTS WITH THE ISOBUTYRONITRILE DERIVATIVE, A", WITH K_s TAKEN FROM PLOTS WITH $n = 1.4$

Expt.	Concentrations A" (Initial)	A" (Final)	B (Average)	Na^+	I^-	Time, min.	Temp., °C.	K_s
1B	0.0387	0.0113	0.983	1.000	0.0453	164	100	0.0158
2B	.0354	.0062	.984	1.000	.0395	1245	80	.00320
3B	.0403	.0100	.983	1.000	.0453	447	90	.00672
4B	.0381	.0131	.984	1.000	.0453	75	110	.0306

Each of these experiments as reported involved five or six samples, the last one of which in each case plotted off the ruled line. Subsequent

samples gave points which deviated widely. Consequently no clear distinction could be drawn between an exponent of 1.3 and 1.4. The latter seemed to yield the better results, and since there was abundant evidence of tertiary amine in the samples taken at higher temperatures, it was concluded that the discrepancy lay in a simultaneous decomposition of the quaternary type, which forbade utilizing much of the possible reaction. Whether this reaction follows the betaine formation or is independent of it is not known, as the amount of the tertiary amine formed was small.

It is interesting to observe that the quaternary amine decomposition is found only in this case, in which both methylene hydrogens are substituted, and that the formal heat of activation (Fig. 4) is much higher (20,500 calories). The fact that the quaternary amine decomposition was greater at the higher temperatures means that the temperature coefficient of that reaction is even greater, and that the two reactions do not have the same rate determining step as postulated in the introduction. It is hoped that some derivatives may be found that yield the two reactions at some reasonable temperature at more nearly the same rate, in order that the rate laws, salt effects and temperature coefficients of both reactions may be compared.

There was no evidence of ethylene formation during any of these experiments, indicating that at the temperatures employed this type of quaternary ion decomposition was very slow compared to the other possible reactions.

The three derivatives then differ in rate and formal activation energy as follows

		E	K_s at 120°
1	$[R_3N—CH_2—CN]^+$	13,200	14.1
2	$[R_3N—CH(CH_3)—CN]^+$	12,600	0.327
3	$[R_3N—C(CH_3)_2—CN]^+$	20,500	0.144

The comparison in rate (K_s) above was made with the quaternary ion equal in concentration to the hydroxide ion, each 0.0992 M, with iodide and sodium ions also 0.0992 M and $m + n$ equal to 2.4. It is also interesting to observe that von Peskoff and Meyer[6] found the activation energy for the alkaline hydrolysis of simple alkyl nitriles to be 19,400 calories, with the kinetics of the reaction a simple second order. From this it would follow that the third compound above corresponds in mechanism closely to simple nitriles, that in the others the rate and activation energy are markedly influenced by the ammonium ion present, and that the transmission of this effect depends upon the presence of hydrogens on the carbon adjacent to the nitrogen.

Cryoscopic Study of the Salt Solutions.—To ascertain that the structures of the compounds used involved no anomalies, the freezing points

[6] Von Peskoff and Meyer, *Z. physik. Chem.*, **82**, 167 (1913).

of aqueous solutions at concentrations varying from 0.2 *M* to 0.01 *M* were determined, and the apparent degree of ionization calculated, assuming a molecular freezing point lowering of 1.86° for 1000 grams of solvent. Above 0.1 *M* the iodides were between 60 and 70% ionized, and the apparent dissociation increased rapidly upon dilution until at 0.01 *M* it was over 95%.

Experimental Part

Preparation of Materials.—Diethylaminoacetonitrile was prepared by the method of Knoevenagel and Mercklin[7] from a saturated sodium formaldehyde bisulfite solution, anhydrous diethylamine and a saturated solution of potassium cyanide. The oil which separates was dried with anhydrous potassium carbonate and treated with methyl iodide to form the *methiodide*. The reaction is rapid; the crystals were recrystallized from propyl iodide, yield about 80%.

Diethylaminopropionitrile and Diethylaminoisobutyronitile (b. p. 730 at 12 mm.) are best made from the cyanhydrins of acetaldehyde and acetone, respectively, and anhydrous diethylamine. In the first case the reaction is rapid, with evolution of heat, and drying with anhydrous sodium sulfate suffices. In the second case the reaction requires several hours at 40 to 50° with lime as a dehydrating agent. In both cases addition of methyl iodide was carried out in bombs at 80° until a solid mass of crystals formed, which were recrystallized from propyl alcohol. Analyses made for both nitrogen and iodine indicated 100% purity.

Procedure.—The solutions for measurement were prepared by dissolving weighed quantities of the salt in a known volume of water and diluting with known base to the desired concentrations. Where the iodide ion was removed, the known salt solutions were treated with the required amount of silver oxide and the silver iodide was filtered off. This left only the two reacting ions in solution.

For the faster reactions the solutions that were to be mixed (the base and the salt solutions) were brought to the temperature of the bath beforehand. The base solution was then poured into the reaction bottle and thoroughly mixed to ensure homogeneity. The bottle was then stoppered. Ten-cc. samples were taken from this at intervals and run into a slight excess of acid which stopped the reaction.

Bombs made from test-tubes were used for the slower reactions and for those at higher temperatures. Various kinds of glass were tried to see whether the surface affected the reaction in any way. It was found necessary to use Pyrex glass at the higher temperatures to reduce the action of the alkali on the glass.

When bombs were used, the stock solutions were mixed without preheating and a 10-cc. sample was placed in each bomb. After sealing, the bombs were placed in a wire basket and completely immersed in the bath. By trial it was found to require about eight minutes for the samples to reach temperature equilibrium. When a bomb was taken out, it was agitated violently in a freezing bath to reduce the reaction to a negligible rate. Time was taken at this point. The bomb was opened and excess acid was run into it to reduce the chance of losing ammonia. The sample was poured into a beaker for titration and the bomb was rinsed with distilled water.

Analytical Method.—The method of Rouchese[8] was used. The acidified sample taken from the reaction mixture was first neutralized to methyl red. Ten cc. of 20% formaldehyde solution, neutral (to methyl red), was then added, and the mixture titrated with standard sodium hydroxide to phenolphthalein. Small amounts of methyl

[7] Knoevenagel and Mercklin, *Ber.*, **37**, 4087 (1904).

[8] A. Rouchese, *J. pharm. chim.*, [6] **25**, 611; *Chem. Abstracts* **1**, 2355 (1907).

red do not obscure the end-point, which can be found to 0.05 cc. of 0.1 *N* alkali in volumes of less than 50 cc. The equivalents of alkali used are equal to the equivalents of ammonia present.

Summary

The alkaline hydrolysis of quaternary ammonium substituted acetonitrile to the betaine cannot be expressed as a simple second order reaction between positive and negative ions. In excess hydroxide ion the rate is proportional to the 1.3 power of the ammonium ion and to the 1.6 to 1.8 power of the hydroxide ion. When in equal concentrations the sum of the necessary exponents is about 2.4. These facts are unchanged by changes in salt concentration, temperature and in the homolog used, and should furnish a useful system for the study of electrolyte solutions.

The effect upon nitrile hydrolysis of the presence of the ammonium group has been studied, together with the effect of alkyl substitutions.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF THE PUNJAB]

STUDIES IN CHEMOTHERAPY: ATTEMPTS TO FIND ANTIMALARIALS. II. PYRRYL INDOLES

BY JOTI SARUP AGGARWAL, AMANAT ULLAH QURESHI AND JNANENDRA NATH RAY

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The most prolific method for the synthesis of indoles has been the well-known Fischer reaction[1] but the exact mechanism of this excellent reaction is still uncertain. However, the application of this method to the aliphatic and aromatic ketones has resulted in the synthesis of a large class of indoles mostly substituted in the α-position. This explanatory piece of research was undertaken with a view to ascertain whether pyrryl methyl ketones would respond to the Fischer reaction and yield α-pyrryl indoles (III) and also to decide if possible between the rival theories of the reaction. These α-pyrryl indoles are likely antimalarials because of their analogy to harmine; moreover, the pyrrole nucleus might endow a certain amount of local anesthetic property to the compounds because of the partial resemblance to the tropine structure.[2]

The only heterocyclic ketone which hitherto has been found to give the Fischer reaction is 2-thionyl methyl ketone.[3] Tetrahydroquinolone,[4] also has been converted into an indole.

[1] Fischer, *Ber.*, **16**, 2245 (1883).

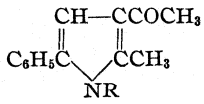
[2] Blicke and Blake, THIS JOURNAL, **53**, 1015 (1931).

[3] Brunck, *Ann.*, **272**, 201–208 (1893).

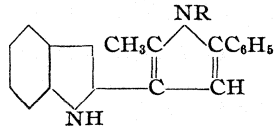
[4] Clemo and Perkin, *J. Chem. Soc.*, **125**, 1612 (1924).

The pyrryl methyl ketones used in this investigation were prepared from α,α-diacetyl-β-benzoylethane (I)[5]

I



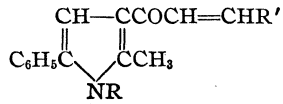
II



III

5-Phenyl-3-aceto-2-methylpyrrole (II, R = H) although it furnished a phenylhydrazone in the usual manner was not converted into an indole. Aniline, *o*-, *m*-, and *p*-toluidine, *o*-, *m*-, and *p*-nitraniline, phenetidine, anisidine and naphthylamines and a variety of other amines were condensed with the substance (I) to give the N-arylated pyrryl methyl ketones analogous to (II). Of these, the phenylhydrazones of the substances (II, R = C_6H_5, *m*-$C_6H_4CH_3$, *p*-$C_6H_4CH_3$, *p*-$C_6H_4OCH_3$) were only converted to the corresponding indoles, III, when heated with zinc chloride. Reddelien's mechanism of the Fischer indole transformation[6] does not furnish an explanation of the non-formation of an indole from the phenylhydrazone of the substance (II, R = H).

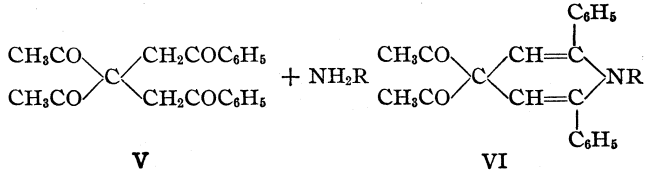
The pyrryl methyl ketones now described condense with aldehydes to give condensation products of the type (IV)



IV

With salicylaldehyde, the corresponding chalcones are formed but these are not converted into a pyrryllium chloride with hydrogen chloride which simply forms an addition compound at the exocyclic double bond. These hydrochlorides are curiously fairly stable to boiling water, being reconverted into the unsaturated ketone only on prolonged heating of an aqueous alcoholic solution.

During the preparation of α,α-diaceto-β-benzoylethane by the method of March,[5] we isolated varying amounts of a solid of m. p. 125°. This substance is now identified as the interesting tetraketone (V), formed



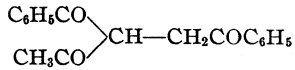
V VI

no doubt by diacylation of acetylacetone. If this is the correct view of the constitution of the substance, then it should be possible to prepare it from

[5] March, *Compt. rend.*, **133**, 46 (1901).

[6] Reddelien, *Ann.*, **388**, 179 (1912).

acetylacetone by taking appropriate amounts of sodium and bromoacetophenone. This has been done and the substance (V) has been prepared in good yield. This substance (V) can only react with an amine to give a dihydropyridine (VI). With aniline, the substance VI (R = C_6H_5) has been prepared which after oxidation with sodium hypobromite furnishes bromoform



VII

α,β-Dibenzoyl-α-acetoethane (VII) furnished pyrryl ketones analogous to II, but their phenylhydrazones could not be converted to an indole in any single instance. Some of the compounds are being tested with respect to their antimalarial properties, and have been found to be antipyretic.

Experimental

α,α-Diacetyl-β-benzoylethane (I) is best prepared by the following modification of March's[5] process.

To acetylacetone (10 g.) in absolute alcohol (50 cc.) was gradually introduced sodium ethoxide solution prepared from sodium (2.3 g.) and alcohol (20 cc.) and then bromoacetophenone (20 g.) at 5–10°. After an hour, the mixture was warmed gently until it showed neutral reaction. The cooled product poured into much ice-cold water deposited an oil, which was separated, dissolved in alcohol (*ca.* 25 cc.) and allowed to stand on ice, when a substance separated of m. p. 125° after recrystallization from alcohol; yield 2.3 g., found: C, 75.2, H, 5.8. $C_{21}H_{20}O_4$ requires: C, 75.0; H, 6.0. This substance was the tetraketone (V). The alcoholic filtrate when treated with alcoholic copper acetate solution gave after standing for some time the copper salt of the substance I. The quickly dried copper salt decomposed by dilute sulfuric acid was extracted with ether and obtained as pale yellow needles, m. p. 58°, yield 12–15 g. Ferric chloride colors its alcoholic solution an intense red. The substance is soluble in concentrated alkali carbonate solution with a yellow color.

The substance when condensed with a primary aromatic amine furnishes the pyrryl methyl ketones of the type II. A typical experiment is described below.

The substance I (2.2 g.) and aniline (1.0 g.) were well ground and heated for two hours at 80°. The cooled product, well washed with water and dilute hydrochloric acid, was crystallized twice from alcohol, when the substance II (R = C_6H_5), m. p. 101° was obtained (yield 2.0 g.). (Found: N, 5.10. $C_{19}H_{17}ON$ requires N, 5.09.) The substance is soluble in benzene, chloroform, ether, methyl alcohol and acetone. It develops a yellow color with strong sulfuric acid. It is insoluble in cold hydrochloric acid but dissolves slightly on warming. The phenylhydrazone prepared in the usual way had m. p. 162° (darkening at 114°) after crystallization from hot acetic acid. (Found: N, 11.55; $C_{25}H_{23}N_3$ requires N, 11.50.)

The following pyrryl methyl ketones analogous to II were similarly prepared.

The Transformation of the Phenylhydrazone to the Indole III (R = C_6H_5).—The phenylhydrazone (2.0 g.) well ground with zinc chloride (freshly fused, 8 g.), was heated at 162° for one and one-half hours. The hard brownish mass obtained after cooling, well washed with water and dilute hydrochloric acid, was crystallized from hot acetic acid in brownish-red needles, m. p. 221°. (Found: N, 8.03; $C_{25}H_{20}N_2$ requires N, 8.01).

The substance is soluble in chloroform, ether and benzene. Its solution in concentrated sulfuric acid gives an intense carmine coloration; the color is discharged with

TABLE I

	Reactants	M. p. of product, °C.	N analysis, % Found	Calcd.	Phenylhydrazone of product, m. p., °C.	Nitrogen analyses of phenylhydrazone Found	Calcd.
1	I + *o*-Toluidine	95	4.89	4.84	126 (dec.)	11.19	11.08
2	I + *m*-Toluidine	142	4.85	4.84	156 (*ex* hot alc.)	11.10	11.08
3	I + *p*-Toluidine	150	4.9	4.84	167–168	11.03	11.08
4	I + Ammonium acetate	178	*Cf.* March, *loc. cit.*		188	14.5	14.53
5	I + *o*-Anisidine	152	4.62	4.59	174 (*ex* hot HAc)	10.7	10.63
6	I + *p*-Anisidine	124	4.62	4.59	185	10.68	10.63
7	I + *o*-Phenetidine	100	4.44	4.38	...	...	...
8	I + α-Naphthylamine	128	4.40	4.30	...	...	...
9	I + β-Naphthylamine	140	4.31	4.30	152 (dec.)	10.18	10.12
10	I + *o*-Nitraniline	170	8.82	8.75	182	13.7	13.65
11	I + *m*-Nitraniline	136	8.77	8.75	158	13.7	13.65
12	I + *p*-Nitraniline	115	8.82	8.75	...	...	...

a drop of water and a yellowish substance is precipitated. The solution in concentrated sulfuric acid gives a transient emerald-green color with isatin and also with alloxan and with benzil on warming a yellowish-brown coloration results, indicating the presence of an indole nucleus. A solution of the substance in nitric acid gives a red color which on dilution with water gives a red precipitate suspended in a yellow solution. It does not develop any color with nitrous acid.

The following indoles analogous to III were prepared from the phenylhydrazones of the substances described in Table I in a similar way.

TABLE II

	Substance	M. p. of the indole, °C.	Analyses Found	Calcd.	Formula
A	2 of Table I	220–221	N, 7.70	N, 7.73	$C_{26}H_{22}N_2$
B	3 of Table I	224	C, 86.31	C, 86.19	
			H, 6.06	H, 6.08	$C_{26}H_{22}N_2$
			N, 7.66	N, 7.73	
C	6 of Table I	228	N, 7.65	N, 7.60	$C_{26}H_{22}ON_2$

Condensation of 1-*p*-Tolyl-2-methyl-3-aceto-5-phenylpyrrole II (R = *p*-$C_6H_4CH_3$) with Piperonal.—The pyrrole (2.9 g.) and piperonal (1.5 g.) dissolved in alcohol were treated with a potassium hydroxide solution (0.3 g.) in water (1 cc.) and boiled on the steam-bath for one and one-half hours. The product poured in water deposited a viscous oil which solidified after standing for two hours. It crystallized from alcohol in bright yellow needles, m. p. 132° (found: N, 3.55; $C_{28}H_{23}O_3N$ requires N, 3.32). The substance gives with strong sulfuric acid a transient blue color which changes to red, and on dilution with water a reddish-brown mass separates, probably a sulfate. Similarly the substance II (R = C_6H_5) gives a piperonylidene derivative, m. p. 164° (found: N, 3.39; $C_{27}H_{21}O_3N$ requires N, 3.44), the salicylidene derivative, m. p. 192° (found: N, 3.77; $C_{26}H_{21}O_2N$ requires N, 3.69). The latter substance gives a deep red colored solution in strong sulfuric acid which deposits an orangish precipitate on dilution with water, probably a benzopyrryllium sulfate. When hydrogen chloride is passed into an ice-cold solution of the substance in acetic acid, a deposit of scarlet needles, m. p. 135° (with dec.) is obtained. Found: N, 3.55; $C_{26}H_{22}O_2NCl$ requires N, 3.37. The substance is stable to boiling water but when its aqueous alcoholic solution is boiled and water added, the salicylidine derivative of m. p. 192° is recovered.

α-Acetyl-α,β-dibenzoylethane was prepared from benzoylacetone (8.2 g.), ω-bromoacetophenone (10 g.) and sodium ethoxide from sodium (1.2 g.) in alcohol first at 0–5°, then by warming till neutral, and was crystallized from alcohol, m. p. 85° (yield 8 g.). The substance is soluble in alcohol, ether, chloroform and benzene. When the above substance (4.4 g.) in absolute alcohol (15 cc.) was treated with bromoacetophenone (4 g.) and sodium (0.5 g.) in alcohol (7 cc.) first at 0° and then warmed, dibenzoyldiacetylpropane m. p. 125° (colorless plates from alcohol) was produced. (Found: C, 75.2; H, 5.8. $C_{21}H_{20}O_4$ requires C, 75.0; H, 6.0.)

α-Acetyl-α,β-dibenzoylethane furnished with aniline the pyrrole (formula analogous to II), m. p. 134° (from alcohol), (found: N, 4.27; $C_{24}H_{19}ON$ requires N, 4.15), phenylhydrazone m. p. 174° (found: N, 9.76; $C_{30}H_{25}N_3$ requires N, 9.83) but this was not converted to an indole. The foregoing substance gave with *o*-, *m*- and *p*-toluidines the pyrroles m. p. 150° (found: N, 4.08; $C_{25}H_{21}ON$ requires N, 3.98); m. p. 156° (found: N, 4.08), m. p. 142° (found: N, 4.01), respectively. α,γ-Dibenzoyl-β,β-diacetylpropane (4.4 g.) when heated with aniline (2 g.) at 100° for four hours and the product crystallized fractionally from hot dilute alcohol gave the substance VI (R = C_6H_5), m. p. 130° (found: C, 82.7; H, 6.0; N, 3.66. $C_{27}H_{23}O_2N$ requires C, 82.44; H, 5.85; N 3.56). The substance is easily soluble in most solvents but is insoluble in hydrochloric acid. When treated with sodium hypobromite solution and gently warmed, bromoform is produced but the corresponding dihydropyridine-carboxylic acid could not be isolated.

We are indebted to Mr. G. S. Ahluwalia, M.Sc., for his assistance in the investigation.

Summary

1. By the Fischer indole reaction some pyrryl methyl ketones have been converted into the corresponding indoles. The reaction is not a general one in this series.

2. The rival theories of the indole transformation do not furnish an explanation of the non-formation of the indoles in some cases.

3. A tetraketone, *e. g.*, β,β-diaceto-α,α′-dibenzoylpropane has been prepared and converted into a pyridine derivative.

4. Some of the compounds are studied with respect to their pharmacological (antimalarial) properties. Preliminary trials indicate that they have antipyretic properties and are toxic to paramecium.

LAHORE, INDIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

THE OIL OF THE BITTERSWEET SEED[1]

BY CHARLES BARKENBUS AND CHARLES F. KREWSON

RECEIVED MAY 14, 1932 PUBLISHED OCTOBER 5, 1932

The bittersweet (*Celastrus scandens*) is a hardy vine growing over a wide area east of the Rocky Mountains and is well known for its fruit, which is widely used in the fall for its decorative value. The fruit consists of clusters of small berries which when ripe break open and expose the brilliant scarlet pulp. Imbedded in the pulp are from four to six seeds which are about the size of a grape seed.

A review of the literature indicated that very little work of a chemical nature had been done on this plant and practically none on the seed. Extracts of the bark have been used in medicine[2] for the treatment of chronic liver infections and it is said to be an emetic and a diaphoretic. The superficial analyses of the bark which have been made[3] showed the presence of the usual constituents that are found in all plants and that no glucoside or alkaloid was present. A study by Keller[4] of the red coloring matter of the pulp seemed to show that this material was a connecting link between carotin and xanthin. Only one reference could be found concerning the seed. Wells and Reeder[5] made an alcoholic and an ether extract of the seeds which they said contained palmitic acid, palmitin and olein. At best, our knowledge of the chemical nature of this plant is meager, and since about two pounds of the seed became available[6] it was thought worth while to subject the oil to a complete chemical analysis. The seeds contained a high percentage of oil and the oil itself was found to be an exceptional mixture for a vegetable oil.

The berries that supplied the seed for this investigation came from the Kentucky river region within a radius of twenty miles of Lexington, Kentucky. They had been gradually collected over a period of four years and were free from pulp. The seeds showed no deterioration and appeared to be the same as some freshly separated. Because of their oily nature the seeds had to be ground in a food chopper and the oily mash was extracted with ether at once.

[1] From a thesis presented by Charles F. Krewson to the Faculty of the Graduate School of the University of Kentucky in partial fulfilment of the requirements for the degree of Master of Science, June, 1932.

[2] Wood and La Wall, "United States Dispensatory," Lippincott, Phila., 1926, 21st ed., p. 1247.

[3] Bernhard, *Am. J. Pharm.*, **54**, 1 (1882); Hoch, *ibid.*, **63**, 523 (1891); Dillingham, *Am. Naturalist*, **51**, 391 (1907).

[4] Keller, *Am. J. Pharm.*, **68**, 183 (1896).

[5] Wells and Reeder, *Chem. News*, **96**, 199 (1907).

[6] We are indebted to Dr. F. E. Tuttle of this department for furnishing us the seed.

Experimental Part

Quantitative extractions were made as shown in Table I.

TABLE I

QUANTITATIVE EXTRACTIONS

	%
Petroleum ether (50–60°)	36.06
Ether	46.72
Ethyl alcohol (95%)	53.22

The seed contains an average percentage of oil and the large difference between the petroleum ether and the ether extracts is noteworthy. The large amount of esters of the lower fatty acids, which was shown to be present later, would account for this difference.

The approximate analysis was run by the official methods, the results being listed in Table II.

TABLE II

APPROXIMATE ANALYSIS OF THE EXTRACTED MEAL OF BITTERSWEET SEED

	%		%
Moisture	3.05	Free invert sugar	0.49
Ash	2.88	Sugar by inversion	1.60
Protein (N × 6.25)	18.94	Pentosans	5.87
Crude fiber	9.14	Starch (diastase)	0.68

The seed is very low in starch and rather high in crude fiber.

The Physical and Chemical Examination of the Oil.—The oil was obtained by extracting 950 g. of the ground seeds with absolute ether. The ether was evaporated and the last traces were removed in a vacuum. Three hundred and ninety-seven grams of a clear medium yellow oil having a slight agreeable odor and a bland taste was obtained. The physical and chemical properties are given in Table III.

TABLE III

PHYSICAL AND CHEMICAL CONSTANTS OF BITTERSWEET SEED OIL

d^{20}	0.9772	Acetyl value	147.5
n^{20}	1.4815	Unsaponifiable matter, %	2.96
Iodine No. (Hanus)	121.5	Soluble acids (% butyric acid)	18.98
Thiocyanogen Iodine No.	69.96	Insoluble acids, %	70.94
Saponification value	297.07	Unsaturated acids (corr.), %	57.13
Reichert–Meissl No.	70.86	Insol. saturated acids (corr.), %	9.83
Acid value	3.98	Hexabromide No. of insoluble acids	17.66

The results point to the fact that this oil is different in composition from most vegetable oils. The Reichert–Meissl number is higher than any other we have been able to find recorded in the literature. This would indicate a high per cent. of volatile acids as esters, which is further substantiated by the very high saponification value and the high value for soluble acids. The acetyl value is of very little significance under

these conditions. The saturated and unsaturated acids of the water insoluble mixture were separated by the lead salt–ether method using the usual precautions and corrections.[7] The results are probably not as accurate as they would be on an ordinary oil due to the high percentage of the soluble acids.

Unsaturated Acids.—Using the iodine number, the thiocyanogen–iodine number, and the percentage of unsaturated acids in the oil one can calculate the percentage of each unsaturated acid present.[8] Using this method the results in Table IV were obtained.

TABLE IV

PERCENTAGE OF UNSATURATED ACIDS IN THE OIL

Acid	Acids, %	Glycerol esters, %
Oleic	0.23	0.25
Linolic	36.79	38.46
Linolenic	20.11	21.03

The percentage of glycerol linolenate calculated from the hexabromide number[9] is 4.82%. The large difference between the two methods is probably accounted for by the presence of most of the linolenic acid in the beta form which does not form an insoluble hexabromide. The percentage of oleic acid is so small that it can be safely said that it is absent.

Insoluble Saturated Acids.—The saturated acids, separated by the lead salt–ether method, were esterified and 29.7 g. of methyl esters was obtained. These were fractionally distilled under diminished pressure as shown in Table V.

TABLE V

FRACTIONAL DISTILLATION OF THE METHYL ESTERS OF THE INSOLUBLE SATURATED ACIDS

Pressure 4.2 mm.

Fraction	Temp., °C.	Wt., g.
1	156 –157	3.3
2	157 –157.5	9.6
3	157.5–159	4.3
4	159 –160.5	4.2
5	160.5–163	1.4
6	163 –172	3.0
7	172 –180	2.7
Residue		0.5

The iodine number and the saponification value of each fraction were determined and, using the method of Baughman and Jamieson,[10] the percentage of the various acids present was calculated. The results are given in Table VI.

[7] Baughman, Brauns and Jamieson, THIS JOURNAL, **42**, 2398 (1920).

[8] Kaufmann and Keller, *Z. angew. Chem.*, **42**, 73 (1929).

[9] Steele and Washburn, *J. Ind. Eng. Chem.*, **12**, 52 (1920).

[10] Baughman and Jamieson, THIS JOURNAL, **42**, 155 (1920).

TABLE VI

ANALYSES OF THE METHYL ESTERS OF THE INSOLUBLE SATURATED ACIDS

Fract.	Iodine number	Saponification value	Esters of unsaturated acids, %	Mean mol. wt. of esters of saturated acids	Palmitic acid %	Palmitic acid g.	Stearic acid %	Stearic acid g.
1	2.49	204.8	1.23	273.8	92.49	3.05	1.14	0.04
2	4.58	204.5	2.26	273.9	91.47	8.78	1.19	0.11
3	7.87	204.1	3.90	274.0	89.92	3.87	1.19	0.05
4	8.76	203.7	4.38	274.6	89.26	3.75	1.39	0.06
5	10.67	199.2	5.28	281.7	53.43	0.75	36.56	0.51
6	18.15	192.9	9.00	290.5	24.26	0.73	62.34	1.87
7	21.24	191.4	11.00	292.9	16.52	0.53	68.21	2.18

The results show that palmitic and stearic acids are the only acids present in the saturated acid mixture. The acids were obtained from fraction 1 and recrystallized several times from alcohol. The main fraction had a constant melting point of 62–62.5° and a molecular weight by titration of 255.79. Fraction 7 was treated in the same way and an acid melting constantly at 69.2° was obtained. This acid had a molecular weight by titration of 283.1. These results indicate the presence of palmitic acid and stearic acid. The residue was examined in the same way for arachidic acid but no acid with a melting point higher than 69° could be isolated.

Table VII shows the percentage of the two acids in the saturated acids in the oil, and in the oil as glycerides.

TABLE VII

INSOLUBLE SATURATED ACIDS

Acid	Acids in the saturated acids, %	Acids in the oil, %	Glycerides in the oil, %
Palmitic	81.65	8.03	8.42
Stearic	18.35	1.80	1.88

Volatile Acids.—168.5 g. of oil was dissolved in ether and shaken out several times with a dilute solution of sodium carbonate in order to extract the free acids present. This solution will be referred to later under free acids. The ether solution of the oil was evaporated, the remaining oil saponified, made acid with sulfuric acid and steam distilled. The distillate, which was collected in a dilute sodium carbonate solution, was extracted with ether to remove traces of non-acidic material and then concentrated to a volume of 690 cc. This solution was made acid with sulfuric acid, extracted with ether, and then distilled, the distillate being saved. By this means the soluble acids were separated into ether-soluble and water-soluble fractions.

The ether-soluble fraction, which amounted to only 5 g., was dissolved in water, made alkaline with ammonium hydroxide, and silver nitrate added. A small amount of a white solid precipitated and was crystallized. This was analyzed for silver but the material appeared to be a mixture and because of the small amount of the material it could not be further purified. Apparently there is a trace of higher fatty acids present.

The main precipitate came out on concentrating and this with another fraction obtained by further evaporation was analyzed for silver. Fraction 1. Found: Ag,

47.80. Fraction 2. Found: Ag, 49.08. Calcd. for silver caproate: Ag, 48.38. The ether-soluble part of the volatile acids must consist chiefly of caproic acid.

The water solution of the water-soluble fraction of the acids, which amounted to one liter, was made alkaline with ammonium hydroxide and silver nitrate added. No precipitate formed but on concentrating on a water-bath large amounts of free silver kept coming out, which indicated a fairly large amount of formic acid. At a volume of 300 cc., the hot solution was filtered from the silver and on cooling fine white needles crystallized out. Three other fractions of these crystals were obtained by further concentrating the solution. The precipitates were analyzed for silver. The four fractions gave Ag, 64.12, 64.54, 64.54, 64.38%. The percentage of silver in silver acetate is 64.63. This part of the volatile acid mixture must consist of formic and acetic acids.

In conclusion, the volatile acids of the oil which are present as esters consist chiefly of formic and acetic acids with a small amount of caproic acid and a trace of still higher acids. This combination of acids explains the high Reichert–Meissl number and the other abnormal constants.

The Free Acids of the Oil.—The alkaline extract of the ether solution of the oil was treated in the same manner as was the volatile acid solution. The ether-soluble part gave only a trace of material. The water-soluble fraction precipitated silver during the concentration and when a very small amount of solution was left a trace of white needles precipitated. The amount was too small to analyze but was probably silver acetate. The results show that formic acid is the main acid present in the free state in the oil while traces of other acids are also present.

Summary

The oil from the seed of the bittersweet has been analyzed and found to contain an exceptionally large amount of esters of the lower fatty acids. These consist chiefly of esters of formic and acetic acids but a small amount of an ester of caproic acid is also present. The composition of the oil is given in the table.

COMPOSITION OF THE OIL FROM THE BITTERSWEET SEED

Glycerides of	
Linolic acid, %	38.46
Linolenic acid, %	21.03
Palmitic acid, %	8.42
Stearic acid, %	1.88
Soluble acids, calculated as acetic, though about equal amounts of formic and a small amount of caproic are also part of the soluble acids. (It is not known whether these acids occur as glycerides or not.)	15.67
Unsaponifiable material, %	2.96

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHTS OF PHYCOCYAN AND OF PHYCOERYTHRIN. III

BY THE SVEDBERG AND INGA-BRITTA ERIKSSON

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In two previous papers[1,2] reports have been given of the determination of the molecular weights and the sedimentation constants of phycocyan from *Ceramium rubrum, Porphyra tenera* and *Aphanizomenon flos aquae* and of phycoerythrin from *Ceramium rubrum* and *Porphyra tenera.* In the present paper some new data concerning these interesting proteins will be communicated.

For some of the sedimentation velocity measurements a new high-speed ultracentrifuge giving a centrifugal force 200,000 times gravity at the center of the cell has been used. By the aid of this powerful machinery it was found possible to analyze *r*-phycocyan in the P_H region 5.5–6.7 where the sedimentation constant as measured at lower speed changes rapidly with the P_H and to show that *r*-phycocyan in this region actually consists of a mixture of normal molecules and half-molecules (see Figs. 8 and 9).

The new ultracentrifuge is constructed on the same general principles as the previous one which gave a centrifugal force 100,000 times gravity at a speed of 42,000 r. p. m. with an effective radius of 52 mm.[3] In order to attain a doubling of the centrifugal force, both the effective radius and the speed have been increased. The first rotor used in the present work was cylindrical, like the one described previously, and had a diameter of 180 mm. and a thickness of 60 mm.[3] It was provided with two holes for cells, 34 mm. in diameter with their centers 65 mm. from the center of the rotor. In order to lessen the strain in the rotor at high speed, part of the material between the cell holes was removed by drilling a number of extra holes through the rotor and closing them with steel plates (to prevent false light from reaching the photographic plate). This rotor exploded at a speed of 50,000 r. p. m. during a sedimentation velocity determination on phycoerythrin, although it had already been run at 55,000 r. p. m. several times. A new rotor of the same diameter, but only 54 mm. in thickness and with cell holes only 30 mm. in diameter, was then made. This rotor was tested at a speed of 63,000 r. p. m. corresponding to a centrifugal force 285,000 times gravity at the center of the cell and has since then been run regularly at speeds up to 55,000 r. p. m., which gives 218,000 times gravity. It was found rather difficult to construct cells which

[1] Svedberg and Lewis, THIS JOURNAL, **50**, 525 (1928).

[2] Svedberg and Katsurai, *ibid.*, **51**, 3573 (1929).

[3] Svedberg and Lysholm, *Nova Acta Reg. Soc. Scient. Upsaliensis*, vol. ex. ord., ed. 1927: Svedberg and Nichols, THIS JOURNAL, **49**, 2920 (1927).

would withstand these enormous centrifugal forces but this trouble has been overcome. The limit of the centrifugal force attainable is set by the breaking limit of the material of the rotor.

It is possible to lessen the strain in the rotor still more by machining away more of the material between the cell holes so as to give the rotor an

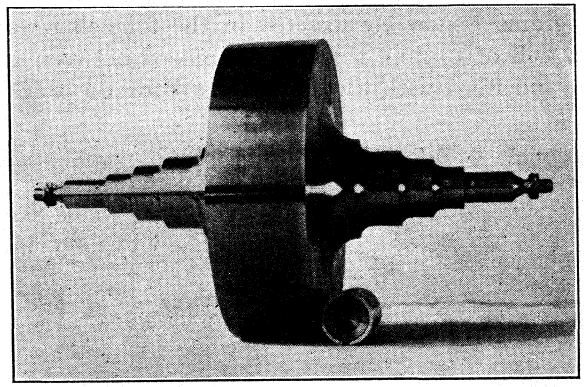


Fig. 1.

oval shape with a circular disk left for screening off false light. A rotor of this shape with an effective radius of 50 mm. has been run in the old ultracentrifuge with very good results at speeds up to 55,000 r. p. m., corresponding to a centrifugal force 170,000 times gravity. An oval rotor is now being made for the new ultracentrifuge and it is hoped that it will be possible to run it regularly at speeds up to 65,000 r. p. m. which will give a centrifugal force 300,000 times gravity at the center of the cell.

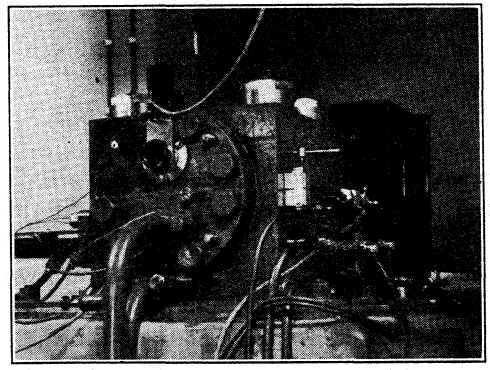


Fig. 2.

Figure 1 shows the rotor and Fig. 2 the centrifuge used for the sedimentation analysis of *r*-phycocyan. In Fig. 3 a general view of the apparatus is given. A detailed description of the new ultracentrifuge will be published elsewhere.

For converting the microphotometric records of the sedimentation pictures into diagrams giving the relation between concentration and distance from the center of rotation, a slightly different method has been adopted both for the sedimentation equilibrium and the sedimentation

velocity measurements. Previously a concentration scale was photographed onto the plate carrying the sedimentation pictures by means of filling the cell in turn with a series of different concentrations of the solution studied, speeding up the centrifuge and taking pictures with the same times of exposure as for the sedimentation pictures. This procedure is rather tedious. The intensity scale necessary for evaluating the sedimentation diagrams is now constructed in the following way. A plane parallel quartz cell of 10 mm. thickness is placed between the lamp and the centrifuge and filled with the solvent used for the solution which is

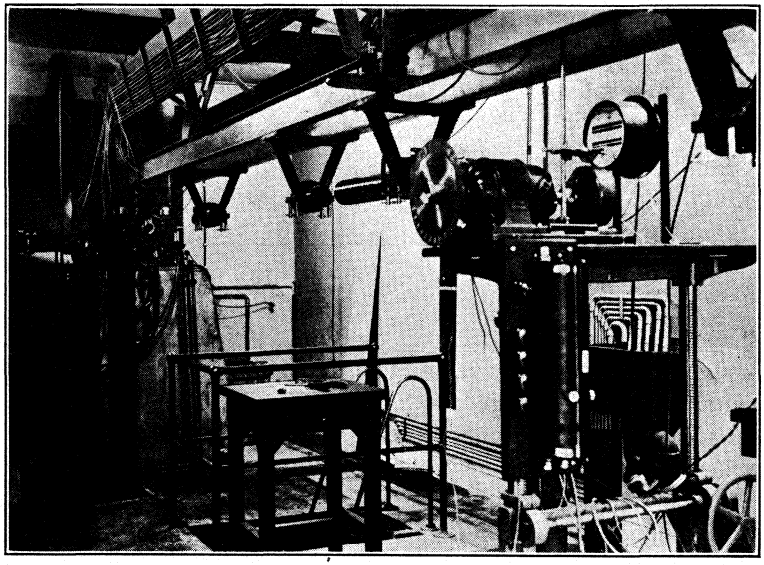


Fig. 3.

being centrifuged. In the case of a sedimentation velocity determination the following procedure is used. At the end of the run when a layer of pure solvent has been formed at the top of the column of solution the cell outside the centrifuge is filled in turn with a series of different concentrations of a suitable arbitrary solution, say, potassium chromate, and pictures are taken on the plate which carries the sedimentation pictures. A curve giving the relation between concentration of the arbitrary solution and blackening is then constructed, as well as a curve giving the relation between distance from the center of rotation and blackening in the sedimentation picture. It is easily seen that for pairs of points in the two curves corresponding to equal blackenings the ratio of the concentrations must be equal. The relative concentrations in the sedimentation picture corresponding to the different distances from the center of rotation can

therefore be found from the first curve. The only assumption which has been made is that the light absorption constant in both the arbitrary solution and the solution centrifuged is proportional to the concentration. This condition is fulfilled for the solutions studied so far.

In the case of a sedimentation equilibrium measurement where pure solvent is not formed at the top of the column of solution, the cell rotating in the centrifuge has to be filled with pure solvent when the pictures of the arbitrary solution are taken.

The Sedimentation Constant of Native Phycocyan from Aphanizomenon Flos Aquae.—In the course of the ultracentifugal investigations on proteins carried out in this Laboratory, it has become evident that there exist cases where the so-called purified protein is more or less an artificial laboratory condensation product built up out of some low molecular native substance through the action of the chemicals used in the purification process, especially the ammonium sulfate. It therefore seemed of considerable importance to reëxamine phycocyan and phycoerythrin in a state as close to their native occurrence as possible.

The *Aphanizomenon* material was collected in Lake Valloxen near Upsala. It was freed from excess of water by centrifuging and kept at room temperature for three days to allow autolysis to set in. After that time the aqueous extract was filtered off and clarified in a Sharples centrifuge. Toluene was added as a preservative. Table I gives the determinations of the sedimentation constant.

TABLE I

AQUEOUS EXTRACT OF APHANIZOMENON CONTAINING *C*-PHYCOCYAN, SEDIMENTATION VELOCITY MEASUREMENTS

Centrifugal force 200,000 to 210,000 times gravity; thickness of column of soln., 1.20 cm.; source of light, mercury lamp; light filter, Wratten K3; aperture of lens F:25; plates, Ilford rapid process panchromatic; time of exposure 10 sec.; metol developer, 1 min.

Solution	$S_{20°} \times 10^{13}$
Extract diluted 10 times with 1% NaCl	11.6
Extract diluted 4 times with 1% NaCl	11.7
Extract diluted 4 times with 1% NaCl	11.2
Mean value	11.5

The sodium chloride was added in order to depress the Donnan effect. Previous experience with native lactalbumin[4] and native ovalbumin[5] has shown that sodium chloride probably does not affect the molecular state of native proteins. For the sedimentation constant of *c*-phycocyan purified by crystallization with ammonium sulfate, a value of 11.2×10^{-13} has been found.[2] These values are identical within the limits of experi-

[4] Sjögren and Svedberg, THIS JOURNAL, **52**, 3650 (1930).

[5] Unpublished determinations by Sjögren; *cf. Nature*, **128**, 999 (1931).

mental error, proving that *c*-phycocyan exists in the cell extract in the same molecular state as in the solutions of the purified protein.

The Sedimentation Constant of Native Phycoerythrin from Ceramium Rubrum.—The *Ceramium* material was collected near Havstensund on the west coast of Sweden. It was washed six times with sea water in order to remove contaminations, then divided into three parts and treated in the following way. (1) One part of the alga plus five parts of distilled water was kept at room temperature for three days; the extract was filtered off and examined in the ultracentrifuge without the addition of toluene. (2) The material was treated as above but with only four parts of distilled water to one part of alga and toluene was added to the extract after three days. (3) The washed material was kept in sea water for one day, after which time phycoerythrin began to appear in the water; the mass was squeezed out and left with five parts of sea water for three days, after which time the extract was filtered off and toluene was added. Table II gives the determinations of the sedimentation constant.

TABLE II

EXTRACT OF CERAMIUM CONTAINING *r*-PHYCOERYTHRIN, SEDIMENTATION VELOCITY MEASUREMENTS

Centrifugal force 100,000 times gravity; optical conditions similar to those of Table I

Solution	$S_{20^\circ} \times 10^{13}$
Extract 1 diluted 4 times with 1% NaCl	11.5
Extract 2 diluted 3 times with 1% NaCl ($P_H = 7$)	11.1
Extract 2 diluted 4 times with 1% NaCl	11.8
Extract 2 run through the Sharples centrifuge and then diluted 4 times with 1% NaCl	11.3
Extract 3 diluted 3 times with 1% NaCl	11.3
	Mean value 11.5

The sedimentation constants for the three extracts are identical within the limits of error and also identical with the value for purified *r*-phycoerythrin, *viz.*, 11.5×10^{-13}, as previously determined.[1,2] The amount of *r*-phycocyan present in Extracts 1 and 2 is too small compared with the amount of phycoerythrin to be noticeable in the sedimentation diagrams. In Extract 3 there was no phycocyan at all because when treating the alga with sea water all the phycocyan and some of the phycoerythrin remains in the cells and is not extracted. The run on Extract 1 compared with the runs on Extract 2 show that toluene has no effect on the molecular state of phycoerythrin. The run on Extract 3 shows that the salts of the sea water do not influence the sedimentation constants of this protein.

The Sedimentation Constant and Molecular Weight of Phycoerythrin from Polysiphonia Urceolata.—During his investigations on the occurrence of phycocyan and phycoerythrin in various algae, Kylin came across a new modification of phycoerythrin in a material of *Polysiphonia* collected

near Kristineberg on the west coast of Sweden. It is closely allied to the form of *r*-phycoerythrin which occurs in *Ceramium* and *Porphyra*;[6,7] the light-absorption curve[7] shows three maxima in the visible corresponding very closely to the maxima of normal phycoerythrin except that the maximum in the blue-green is the strongest one in this variety, while it is the weakest one in normal phycoerythrin.[8] The most marked difference in optical respect between the two forms is, however, the very slight fluorescence of the *Polysiphonia* phycoerythrin compared with that of the normal form. Professor Kylin has kindly put at our disposal the phycoerythrin material which he had extracted from *Polysiphonia urceolata* in the summer of 1930 and which had been purified by precipitating five times with ammonium sulfate. The ultracentrifugal measurements were carried out in the fall of 1931, the solution having been kept in the refrigerator at a temperature between 0 and 4° in the meantime. The sedimentation constant was measured at different P_H values and the molecular weight was determined near the isoelectric point by means of the sedimentation equilibrium method.

The material proved to be inhomogeneous with regard to molecular weight. Values ranging from 160,000 to 270,000 were found. The mean weight was 196,000, which shows that the main constituent of the material probably possesses the same molecular weight, 208,000, as the ordinary phycoerythrin. Because of the inhomogeneity of the material, much stress cannot be put on the values of the sedimentation constant obtained. Within the P_H range 4.4–8.0 the sedimentation velocity was found to be independent of P_H. Ten determinations gave for the sedimentation constant 12.4×10^{-13}, which value is about 10% higher than that found for the ordinary phycoerythrin. The discrepancy is probably due to the inhomogeneity of the material. At a P_H of 10.6, the protein was partly decomposed. The *Polysiphonia* phycoerythrin therefore resembles closely the ordinary phycoerythrin.

The Sedimentation Constant of Phycoerythrin from Bornetia Secundiflora, Griffithsia Furcellata and Sebdenia Monardiana.—During a stay at the Stazione Zoologica at Naples, Italy, one of us (T. S.) prepared extracts of some Mediterranean algae in order to see whether any phycoerythrin or phycocyan of abnormal behavior could be found there.[9] To judge

[6] Kylin, *Z. physiol. Chem.*, **76**, 396 (1912).

[7] Kylin, *ibid.*, **197**, 1 (1931).

[8] The light absorption curve was measured in this Laboratory by Dr. A. Tiselius and published by Kylin. The discrepancy between the values for the wave lengths of the absorption maxima of phycoerythrin and phycocyan as given by Svedberg and Katsurai[2] and those of Lemberg [*Ann. Chem.*, **461**, 46 (1928)] was found by Tiselius to be due to a change in the zero-point of the instrument used by Katsurai.

[9] For the kindness and help shown him on this occasion by the Director, Prof. R. Dohrn, as well as by the Staff of the station, sincere thanks are expressed.

from the color and fluorescence of the extracts three of the algae examined, *viz.*, *Bornetia secundiflora*, *Griffithsia furcellata* and *Sebdenia monardiana* seemed to be of special interest and the study of these extracts was therefore continued in Upsala.

The extracts were precipitated with 20 g. of ammonium sulfate per 100 cc., the precipitates were dissolved in water and the solutions reprecipitated with 25 g. of ammonium sulfate per 100 cc. These precipitates were then dissolved in water and dialyzed in the cold for a week against 0.001 *M* phosphate buffer of *P*H 6.8. Sedimentation velocity determinations were carried out within the *P*H range 5–9. No marked change of the sedimentation constant with *P*H was found in this region. Two determinations on *Bornetia* phycoerythrin gave 12.1×10^{-13}, four determinations on *Griffithsia* phycoerythrin 12.1×10^{-13} and three determinations on *Sebdenia* phycoerythrin (one of which was carried out on the crude extract) gave 11.3×10^{-13}. The value for the last kind of phycoerythrin is identical with the values obtained for phycoerythrin from *Ceramium* and from *Porphyra*. The values for the *Bornetia* and the *Griffithsia* phycoerythrin are slightly higher and identical with the value found for phycoerythrin from *Polysiphonia*. These higher values are probably due to inhomogeneity of the material.

The phycoerythrin modifications contained in *Bornetia*, *Griffithsia* and *Sebdenia* therefore resemble ordinary *r*-phycoerythrin both with regard to sedimentation constant and *P*H stability. To judge from the color, the phycoerythrin from *Bornetia* seems to be identical with the ordinary phycoerythrin from *Ceramium* and from *Porphyra*. *Griffithsia* phycoerythrin, however, is more purple-red in color and has a much weaker fluorescence. *Sebdenia* phycoerythrin is of a light red color and has a very strong yellow fluorescence. In order to have a quantitative comparison of their color, the light absorption bands in the visible spectrum for the phycoerythrin from *Bornetia*, *Griffithsia* and *Sebdenia* were determined by means of the König–Martens spectrophotometer.[10] The extinction coefficients as a function of wave length are given in the diagrams, Figs. 4, 5 and 6, which also contain

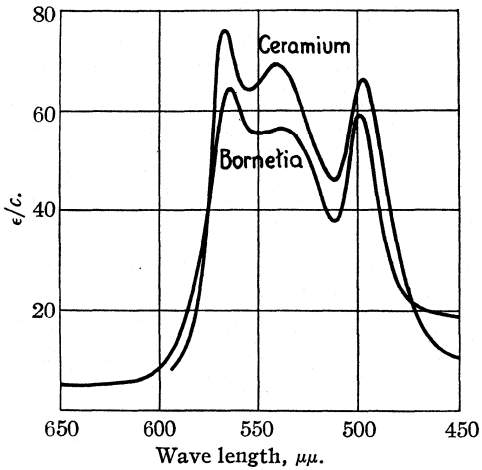


Fig. 4.

[10] We are indebted to Mr. S. Brohult for carrying out these measurements.

the curves for ordinary *Ceramium* phycoerythrin and for *Polysiphonia* phycoerythrin. It follows from the diagrams that the light absorption is very similar for ordinary phycoerythrin and *Bornetia* phycoerythrin on the one hand and for *Griffithsia* and *Polysiphonia* phycoerythrin on the other. *Sebdenia* phycoerythrin differs from all the others by having only two instead of three bands, the middle band being absent. This fact has already been noticed by Gaetano[11] in his extensive qualitative study of the light absorption of extracts from Mediterranean algae.

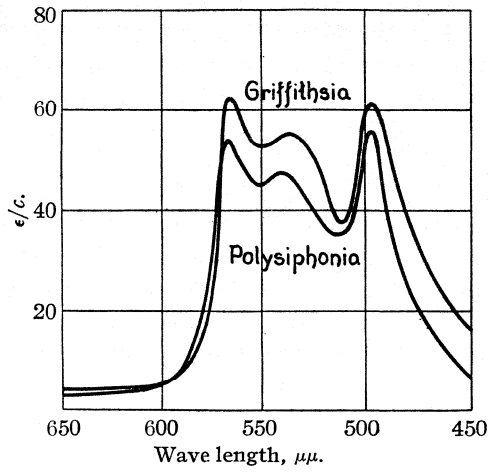


Fig. 5.

It seemed desirable also to get at least a semi-quantitative test of the difference in fluorescence between the phycoerythrin modifications. Dr. A. Tiselius of this Laboratory kindly undertook such an investigation, using an apparatus for Raman spectrum measurements. No definite difference in wave length of the fluorescence light was found for phycoerythrin from *Ceramium, Polysiphonia, Bornetia, Griffithsia* and *Sebdenia*. The intensity, however, was distinctly lower in the case of *Polysiphonia* and *Griffithsia*. No trace of the phycocyan fluorescence could be detected in the solutions obtained from *Polysiphonia, Bornetia, Griffithsia* and *Sebdenia*, although owing to the scarcity of the material at our disposal no attempt had been made to remove any phycocyan present. A comparison with the raw product of phycoerythrin from *Ceramium* showed that in this case phycocyan shows up distinctly in the fluorescence spectrum. It therefore appears that practically no phycocyan is present in *Polysiphonia, Bornetia, Griffithsia* and *Sebdenia*. The one which, to judge from the color of the solution, seemed most likely to contain traces of phycocyan was the *Griffithsia* solu-

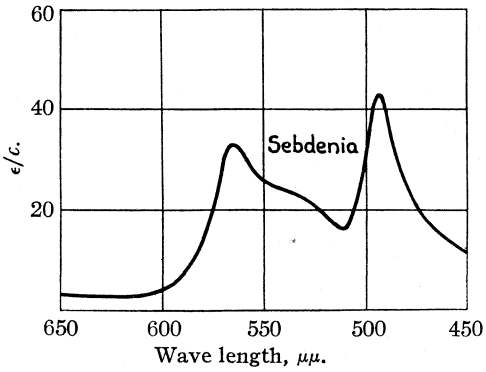


Fig. 6.

[11] Gaetano, *Publ. Staz. Zool. Napoli*, **7**, 88 (1926).

tion. It was therefore submitted to a still more severe test, electrophoretic analysis. Owing to the difference in isoelectric points phycoerythrin and phycocyan may easily be separated in a suitable moving boundary apparatus as shown by Tiselius.[12] The test, which was carried out by Dr. K. O. Pedersen of this Laboratory, proved that no phycocyan was present.

The Sedimentation Constant and Molecular Weight of *r*-Phycocyan from Ceramium Rubrum.—In a previous communication[2] it was shown that *r*-phycocyan from *Porphyra tenera* has a molecular weight of 206,000 at P_H 4.6 but only about half this weight, *viz.*, 107,000 at P_H 6.8. The sedimentation constant, which was found to be 11.1×10^{-13} at P_H 4.6, dropped to 5.98×10^{-13} at P_H 6.8. For *r*-phycocyan from *Ceramium rubrum*[1] a molecular weight of 106,000 had been found at P_H 6.8–7.9 with a sedimentation constant at P_H 6.8 of 5.59×10^{-13} (value reduced to 20°). In view of the fact that no determinations exist for *r*-phycocyan from *Ceramium* at P_H values where one would expect the higher molecular weight and higher sedimentation constant, it seemed desirable to carry out such determinations and at the same time make a complete study of the P_H stability curve for this interesting protein.

The *r*-phycocyan used in the present investigation was prepared in the following way. To 7500 g. of *Ceramium* which had been washed with sea water and superficially dried by pressing was added 2830 cc. of distilled water. After standing for twenty-four hours at room temperature, 10 cc. of toluene was added and after two more days the extract was filtered off. The 3650 cc. of liquid obtained was precipitated with 20 g. of ammonium sulfate per 100 cc. After standing for two days the precipitate was centrifuged off in a Sharples centrifuge and dissolved in 900 cc. of water. This solution was clarified by centrifuging and filtering. The separation of phycocyan from phycoerythrin was carried out as follows. To the solution were gradually added small amounts of saturated ammonium sulfate solution with intervals of three days according to the following scheme: 10 + 2.5 + 2.5 + 2.5 + 2.5 + 2.5 g. of salt per 100 cc. The precipitate was centrifuged off after every addition of ammonium sulfate and mixed with a small quantity of water. Most of the phycoerythrin and some phycocyan go into solution, while the bulk of the latter protein remains undissolved. Thus two fractions were obtained, *viz.*, the solutions on the one hand and the crystals on the other. The latter were brought into solution again and the two resultant solutions fractionated once more in the same way. If the process of dissolution is carefully controlled by observations in the microscope, it is possible to obtain pure phycocyan after the second series of fractionations. In order to dissolve the crystals completely a trace of Na_2HPO_4 had to be added. The P_H was then lowered by adding KH_2PO_4. The final phycocyan solution was

[12] Tiselius, *Nova Acta Reg. Soc. Scient. Upsaliensis*, [4] **7**, No. 4 (1930).

dialyzed for a week in the cold. The yield was 40 cc. of a 0.44% phycocyan solution.

TABLE III

r-PHYCOCYAN FROM CERAMIUM, SEDIMENTATION VELOCITY MEASUREMENTS

Centrifugal force about 100,000 times gravity; thickness of column of soln., 1.2 cm.; source of light, mercury lamp; light filter, nickel oxide glass (first and third run, Wratten K3); plates, Imperial process (first and third run, Ilford rapid process panchromatic); time of exposure, 20 sec.; metol hydroquinone developer, 1 min. (first and third runs, metol developer, 1 min.)

Solvent				P_H of soln.	Concn. of protein, %	$S_{20°} \times 10^{13}$
	M		*M*			
HCl	0.10	.....	..	1.0	0.04	8.0
HCl	.007	.....	..	1.3	.07	7.1
HCl	.03	KCl	0.02	1.5	.04	5.9
HCl	.03	KCl	.03	1.6	.09	5 9
HCl	.03	KCl	.03	1.6	.08	5.4
HCl	.02	KCl	.03	1.8	.10	5.9
HCl	.01	KCl	.04	2.0	.08	10.5
HCl	.007	KCl	.04	2.5	.07	11.4
HCl	.001	KCl	.04	3.0	.07	11.4
HAc[a]	.019	NaAc	.001	3.5	.07	10.6
HAc[a]	.016	NaAc	.004	4.0	.09	11.2
HAc[a]	.006	NaAc	.014	5.0	.10	11.7
HAc[a]	.006	NaAc	.014	5.0	.10	11.4
KH_2PO_4	.095	Na_2HPO_4	.005	5.5	.09	10.4
KH_2PO_4	.090	Na_2HPO_4	.010	5.8	.09	10.4
KH_2PO_4	.080	Na_2HPO_4	.020	6.2	.07	9.4
KH_2PO_4	.070	Na_2HPO_4	.030	6.5	.09	7.9
KH_2PO_4	.050	Na_2HPO_4	.050	6.8	.09	5.8
KH_2PO_4	.030	Na_2HPO_4	.070	7.1	.09	6.2
KH_2PO_4	.020	Na_2HPO_4	.080	7.3	.09	5.8
KH_2PO_4	.010	Na_2HPO_4	.090	7.7	.08	6.1
KH_2PO_4[a]	.005	Na_2HPO_4	.095	8.0	.09	5.7
.....	..	Na_2HPO_4	.10	8.6	.09	5.1
NaOH	.001	Na_2HPO_4	.009	9.1	.09	3.7

[a] 1% in NaCl.

The sedimentation constant was studied in the P_H range 1–10.5. In Table III and Fig. 7 the determinations are summarized. At a P_H higher than 9.1 the values of the sedimentation constant were erratic and uncertain owing to the decomposition of the molecule. These figures have therefore been omitted.

From Table III and Fig. 7 it follows that there are seven regions with regard

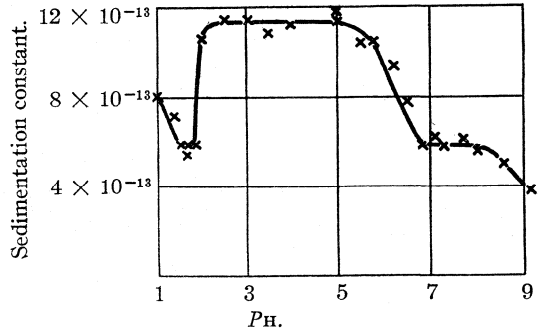


Fig. 7.

to the relation between sedimentation constant and P_H. The middle one is the widest. It extends from P_H 2.5 to 5.0 and contains the isoelectric point of *r*-phycocyan, which according to recent determinations by K. O. Pedersen is situated at P_H 4.85. The sedimentation is independent of P_H within this region and has a mean value of 11.3×10^{-13}, identical with the value previously found for *r*-phycocyan from *Porphyra* at P_H 4.6,[2] *viz.*, 11.1×10^{-13}. On both sides of this region the sedimentation falls off very rapidly with change in P_H and then reaches two new regions where it is again independent of P_H. The one at the alkaline side stretches from P_H 6.8 to 8.0. The sedimentation constant has the mean value 5.9×10^{-13}, identical with the values previously found[1] for *r*-phycocyan from *Ceramium* at P_H 6.8, *viz.*, 5.59×10^{-13}, and the value for *r*-phycocyan from *Porphyra* at P_H 6.8, *viz.*, 5.98×10^{-13}. The region with constant sedimentation at the acid side is very short. It extends only from P_H 1.5 to 1.8. The sedimentation constant has the mean value 5.8×10^{-13}, which is the same as the value in the alkaline region. When the P_H becomes still more alkaline and still more acid, the sedimentation begins again to change rapidly with P_H. At the alkaline side it decreases, at the acid side increases, with P_H.

Two sedimentation equilibrium measurements at P_H 5.0 gave for the molecular weight the mean value 209,000, which is identical with the value previously found[2] for *r*-phycocyan from *Porphyra* at P_H 4.6, *viz.*, 206,000. For phycocyan from *Ceramium* the molecular weight 106,000 has previously been found in the region P_H 6.8 to 7.9.[1]

An equilibrium run carried out on a phycocyan solution in the alkaline transition region, *viz.*, at P_H 6.2, showed a strong drift in the molecular weight values, an indication that *r*-phycocyan at this P_H contains a mixture of molecules of different weight. In order to determine the nature of these molecules, three sedimentation velocity runs were carried out at the same P_H in a very strong centrifugal field. In Fig. 8 are shown the sedimentation pictures from one of these runs and in Fig. 9 the microphotometric curve of exposure No. 8. It is quite evident that the solution contains two different and well-defined molecular species. In Table IV the results of these determinations are given.

TABLE IV

r-PHYCOCYAN, SEDIMENTATION VELOCITY MEASUREMENTS

Centrifugal force about 200,000 times gravity; thickness of column of soln., 1.2 cm.; concentration of protein soln., 0.09%; solvent, 0.080 *M* in KH_2PO_4 and 0.020 *M* in Na_2HPO_4; P_H of soln., 6.2; optical conditions as in Table IV.

Number of run	$S_{20°} \times 10^{13}$ From first boundary	From second boundary
1	5.9	11.5
2	5.5	11.5
3	6.7	11.6

The values of the sedimentation constant derived from the movement of the first boundary are identical with the value found for the half-molecules and the sedimentation constant calculated from the second boundary is the same as that characteristic of the undissociated phycocyan molecules.

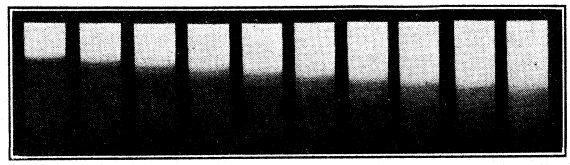


Fig. 8.

In the transition range between the region of non-dissociation and the alkaline region of complete dissociation into half-molecules, the *r*-phycocyan therefore consists of a mixture of these two kinds of molecules.

On the acid side of the region of normal, undissociated molecules the transition range is very narrow and therefore no attempt to analyze the solution in a very strong centrifugal field was made. In the acid region of sedimentation constant 5.8×10^{-13} no equilibrium measurements were performed because of the difficulty of preventing decomposition in the solution during the long time necessary for an equilibrium run. The fact, however, that a sedimentation constant around 5.8×10^{-13} corresponds to a molecular weight half that of normal phycocyan also in the case of serum globulin strongly supports the assumption that *r*-phycocyan is dissociated into half-molecules in the acid region P_H 1.5 to 1.8.

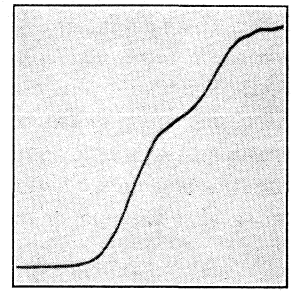


Fig. 9.

The expenses connected with this investigation, including the considerable cost of the construction of the new high-speed ultracentrifuge, have been defrayed by grants from the Nobel Fund of Chemistry, from the Rockefeller Foundation and from the Foundation "Therese och Johan Anderssons Minne."

Summary

1. The sedimentation constant of *c*-phycocyan has been determined in fresh extracts of *Aphanizomenon flos aquæ* and found identical with the value for *c*-phycocyan purified by means of crystallization with ammonium sulfate. *c*-Phycocyan therefore probably exists in the cells of the algae with the same molecular weight, 208,000, as in the purified laboratory product.

2. The sedimentation constant of *r*-phycoerythrin has been determined in fresh extracts of *Ceramium rubrum* and found to be identical with the

value for *r*-phycoerythrin purified with ammonium sulfate. Native *r*-phycoerythrin therefore probably is identical with the purified product with regard to molecular weight.

3. Phycoerythrin from *Polysiphonia urceolata* has been studied by means of the ultracentrifugal methods. The protein was not quite homogeneous but both the sedimentation constant, 12.4×10^{-13}, and the molecular weight, 196,000, were of the same order of magnitude as for normal *r*-phycoerythrin. The P_H stability range was also the same.

4. The sedimentation constant of the phycoerythrin modifications from three Mediterranean algae, *viz.*, *Bornetia secundiflora*, *Griffithsia furcellata* and *Sebdenia monardiana*, has been determined. *Sebdenia* phycoerythrin gave the same value for the sedimentation constant as *Ceramium* phycoerythrin, *viz.*, 11.3×10^{-13}. The constants for *Bornetia* and *Griffithsia* phycoerythrin were slightly higher, *viz.*, 12.1×10^{-13}. It is believed that this deviation is due to inhomogeneity of the solutions studied. The P_H stability range was the same as for normal phycoerythrin. With regard to light absorption, the *Bornetia* phycoerythrin was found to be identical with the *Ceramium* phycoerythrin, while *Griffithsia* phycoerythrin resembled closely the phycoerythrin from *Polysiphonia*. The light absorption of *Sebdenia* phycoerythrin differs considerably from that of the other modifications as already pointed out by Gaetano. A semi-quantitative study of the fluorescence of the phycoerythrin modifications did not reveal any marked difference in the wave length of the fluorescence light but showed that the intensity is considerably lower for the phycoerythrin from *Griffithsia*.

5. The behavior of *r*-phycocyan has been studied carefully within a wide P_H range. From P_H 2.5 to 5.0 the sedimentation constant is 11.3×10^{-13} and the molecular weight 209,000. On both the alkaline and the acid side of this normal region, which includes the isoelectric point (P_H 4.85), is a region where the sedimentation constant is $5.8\text{–}5.9 \times 10^{-13}$ and the molecular weight half the normal value. These two regions are connected to the normal region by transition regions where the *r*-phycocyan solution contains molecules of the normal and of half the normal weight at the same time. In solutions more acid than P_H 1.5 or more alkaline than P_H 8.0, the phycocyan molecule begins to decompose and form systems, inhomogeneous with regard to molecular weight.

UPSALA, SWEDEN

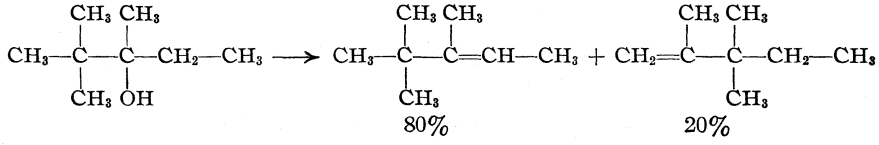
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE DEHYDRATION OF TERTIARY CARBINOLS CONTAINING A NEOPENTYL SYSTEM. I. METHYLETHYL-TERTIARY-BUTYL-CARBINOL AND DIMETHYL-TERTIARY-AMYLCARBINOL[1]

BY FRANK C. WHITMORE AND KENNETH C. LAUGHLIN

RECEIVED MAY 17, 1932 PUBLISHED OCTOBER 5, 1932

Methylethyl-*tert.*-butylcarbinol has been prepared previously by Clarke and Jones[2] and converted to an olefin by treating its iodide with alcoholic potassium hydroxide. This olefin was erroneously assumed to be *unsym.*-ethyl-*tert.*-butylethylene. The present study was undertaken to determine the nature of the olefinic products obtainable from this carbinol, especially in relation to the possible rearrangement of the neopentyl system. As will be recalled, primary and secondary alcohols having the hydroxyl attached to this system rearrange during dehydration or replacement of the hydroxyl by halogen.[3] In view of the extraordinary ease with which tertiary alcohols are dehydrated by heating with a trace of iodine, it seemed possible that an alcohol in which the hydroxyl is both tertiary and part of a neopentyl system might be dehydrated without rearrangement. At first this seemed to be the case since the dehydration product obtained from methylethyl-*tert.*-butylcarbinol was 2,2,3-trimethylpentene-3, the "normal" dehydration product. When the process was studied more minutely, however, it was found that the dehydration product also contained 20% of the rearranged olefin, 2,3,3-trimethylpentene-1. None of the olefin assumed by Clarke and Jones was found. The structure of the olefins was determined by ozonolysis and the preparation of semicarbazones of the methyl-*tert.*-butyl ketone and the methyl-*tert.*-amyl ketone thus formed.

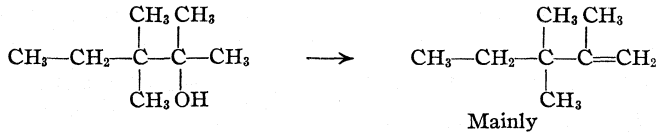


Dimethyl-*tert.*-amylcarbinol was prepared from methyl-*tert.*-amyl ketone and methylmagnesium chloride. Its dehydration with iodine gave mainly the "normal" dehydration product, 2,3,3-trimethylpentene-1, which was identified by ozonolysis. The small amount of by-product has not yet been identified.

[1] Presented by Kenneth C. Laughlin in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[2] Clarke and Jones, THIS JOURNAL, **34**, 170 (1912).

[3] See THIS JOURNAL, **54**, 3279 (1932).



Experimental

Methylethyl-*tert.*-butylcarbinol.—Methyl-*tert.*-butyl ketone, b. p. 103–106° (735 mm.), was prepared from acetone.[4] Ethylmagnesium bromide was prepared from 327 g. (3 moles) of ethyl bromide in 750 cc. of dry ether and an aliquot part was titrated; yield, 80%.

To 1.9 moles of ethylmagnesium bromide solution in a 3-liter flask equipped with a stirrer, was added 190 g. (1.9 moles) of the ketone in 600 cc. of dry ether at about four drops per second. A small amount of unsaturated gas was evolved. The mixture was heated for one hour on the steam-bath and then stirred for three hours more. The mixture was poured on ice and 50 g. of ammonium chloride. The ether layer was decanted and the water layer was treated with dilute sulfuric acid until it just turned clear (still alkaline to litmus). It was then extracted twice with 250-cc. portions of ether. The ether solutions were dried overnight with 75 g. of freshly calcined potassium carbonate. After filtering and removing the ether on the steam-bath, the residue was distilled through an 85 × 2 cm. total condensation column.

Fraction	B. p., °C.	Pressure, mm.	Amt.	n_D^{20}
A 1	25–45	240	27 cc.	1.3738
2	45–90	240–100	76 cc.	1.4316
3	76.2–75.8	41–39	147 g.	1.4353
4	Residue		15 cc.	

The yield was 60%.

Dehydration of the Carbinol and Distillation of the Products.—The methylethyl-*tert.*-butylcarbinol (147 g.) was refluxed with a crystal of iodine under a column connected with a device for separating the water distilled out. When no more water was formed, the product was dried with 25 g. of potassium carbonate. The yield of crude olefin was 111 g. or 86%. The distillation of 86 g. of this material through the 85 × 2 cm. column gave the following at 740 mm.

Fraction	B. p., °C.	Wt., g.	n_D^{20}
B 1	104–107	6	1.4170
2	107–108	4	1.4199
3	108–108.8	15	1.4219
4	108.8–109.2	42	1.4230
5	Residue	16	1.4262

Identification of 2,2,3-Trimethylpentene-3.—Fraction B 4 (42 g.) was ozonized[5] and the ozonide was decomposed with zinc dust and hot water. The oily layer of the distillate was combined with ether extracts of the water layer and dried, and distilled through a 40 × 0.8 cm. total condensation column at 741 mm.

Fraction	B. p., °C.	Amt., cc.	n_D^{20}
C 1	40–90	3	1.3831
2	90–98	6	1.3919
3	98–103	5	1.4945
4	103–106	7	1.3939
5	Residue		1.4120

[4] "Organic Syntheses," 1925, Vol. V, p. 87.

[5] See THIS JOURNAL, **54**, 3710 (1932).

The semicarbazone was prepared from 0.5 cc. of Fraction C 4 by adding 0.5 g. of semicarbazide and 0.7 g. of sodium acetate in 5 cc. of water, adding alcohol to form a clear solution, and warming on the steam-bath until cooling to 0° produced crystals. The crude semicarbazone melted at 150°. Recrystallization from petroleum ether raised the m. p. to 153–154°. The melting point was not lowered by a known sample of the semicarbazone of methyl-*tert.*-butyl ketone. The water layer of the distillate from the ozonide decomposition had a strong aldehyde odor but gave no test for formaldehyde (ferric chloride and resorcinol tests), thus indicating acetaldehyde. These results demonstrated the formation of the normal dehydration product of the carbinol, 2,2,3-trimethylpentene-3. The presence of so much lower boiling olefin indicated the necessity for a more exhaustive study of the olefinic products.

Isolation and Identification of the Rearranged Dehydration Product, 2,3,3-Trimethylpentene-1.—The pinacolone for this run was prepared in 20–50% yields by adding *tert.*-butylmagnesium chloride to an excess of acetyl chloride.[6] The other steps were the same, giving a 52% yield of methylethyl-*tert.*-butylcarbinol (163 g.). Dehydration of 122 g. of the carbinol with a trace of iodine was followed by refluxing with 1 g. of sodium for one hour. The yield of crude olefin with n^{20}_{D} 1.4222, was 95.5% (100 g.). This was carefully fractionated in a 90 × 1.2 cm. adiabatic, *partial condensation*, column packed with 5-mm. copper gauze cylinders.[7] The temperature was not recorded because the amount of vapor passing the thermometer was insufficient to give significant readings.

Fraction	Amt.	Reflux ratio	n^{20}_{D}
D 1	3.5 cc.	100:1	1.4185
2	3.5 cc.	100:1	1.4191
3	3.5 cc.	100:1	1.4192
4	3.5 cc.	100:1	1.4191
5	3.5 cc.	75:1	1.4198
6	3.5 cc.	60:1	1.4200
7	3.5 cc.	100:1	1.4203
8	5.5 cc.	300:1	1.4203
9	3.5 cc.	200:1	1.4207
10	3.5 cc.	150:1	1.4212
11	62 g.	Residue	1.4230

The residue was fractionated through the same column to give final values of n^{20}_{D} 1.4232 and b. p. 109° (740 mm.).

The lower fractions were redistilled through the same column, giving 7 cc. of material of refractive index, 1.4180. This was ozonized as usual. The water layer of the distillate from the zinc dust decomposition gave a strong test for formaldehyde (resorcinol). The oil layer was dried, distilled and converted to a semicarbazone, m. p. 134–136°. The semicarbazone of pure methyl-*tert.*-amyl ketone melted at 138–139° and a mixture of the two melted at 135–136°. This demonstrated the formation of the rearranged dehydration product, 2,3,3-trimethylpentene-1. Calculations based on the distillation data and on the refractive indices of the pure substances and the crude olefin mixture indicated that the normal and rearranged dehydration products were formed in the ratio of 4:1.

Preparation and Dehydration of Dimethyl-*tert.*-amylcarbinol.—Methyl-*tert.*-amyl ketone (60 g., b. p. 129–131° (731 mm.), n^{20}_{D} 1.4097), prepared by D. E. Badertscher of this Laboratory from acetyl chloride and tertiary amyl magnesium chloride,[8] was

[6] Whitmore and Badertscher, THIS JOURNAL, **54**, 825 (1932).

[7] See THIS JOURNAL, **54**, 3453 (1932).

[8] The tertiary amyl alcohol was kindly supplied by the Sharples Solvents Corporation of Philadelphia.

diluted with an equal volume of dry ether and added to a slight excess of methylmagnesium chloride in the usual way. The product was decomposed with ammonium chloride and worked up as usual. The 125 cc. of crude carbinol was distilled through a 38 × 1.5 cm. total condensation column. The yield was 65%.

Fraction	B. p., °C.	Pressure, mm.	Amt.	n_D^{20}
F 1	80	84	10 cc.	1.4118
2	80–82	58	9 cc.	1.4280
3	82–85	58	45 g.	1.4280
4	Residue		5 cc.	

The carbinol, 35 g. of Fraction F 3, was dehydrated with iodine as usual, dried and fractionated through the 40 × 0.8 cm. column at 742 mm.

Fraction	B. p., °C.	Amt.	n_D^{20}
G 1	104–106	0.5 cc.	1.4172
2	106–106.7	22 g.	1.4179
3	Residue	5 cc.	1.4200

Fraction G 2 represented a yield of 65%. This was ozonized and decomposed in the usual way. The oily layer was dried and distilled at 737 mm.

Fraction	B. p., °C.	Amt., cc.	n_D^{20}
H 1	to 115	4	1.4056
2	115–128	4	1.4062
3	128–132	4	1.4090
4	Residue	3.5	1.4252

Fraction H 3 corresponded to methyl-*tert.*-amyl ketone, b. p. 129–131° (731 mm.) and n_D^{20} 1.4097. The semicarbazone from this fraction melted at 135–136°. Its melting point was not lowered by a known sample of the semicarbazone of methyl-*tert.*-amyl ketone. These data show that the chief product of the dehydration of dimethyl-*tert.*-amylcarbinol is the normal dehydration product, 2,3,3-trimethylpentene-1. The other products are being studied.

The properties of the substances prepared in this research are as follows

	B. p., °C.		n_D^{20}
Methylethyl-*tert.*-butylcarbinol	76	(40 mm.)	1.4353
2,2,3-Trimethylpentene-3	109	(740 mm.)	1.4232
2,3,3-Trimethylpentene-1	106–106.7	(742 mm.)	1.4179
Dimethyl-*tert.*-amylcarbinol	82–85	(58 mm.)	1.4410

Summary

1. Two carbinols in which the hydroxyl is both tertiary and a part of a neopentyl system have been prepared and dehydrated.

2. The main product is the result of dehydration without rearrangement. One of the carbinols also gave 20% of the rearranged olefin.

3. The study of the dehydration of this type of carbinol is being continued.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

STERIC HINDRANCE IN CERTAIN MESITYLENIC KETONES

BY E. P. KOHLER AND R. BALTZLY

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Many reactions of organic compounds are affected to a remarkable degree by the extent to which the reacting system is surrounded by other groups. Opinion is divided with respect to the manner in which these groups exercise their influence but whether the effect be regarded as spatial or chemical it is generally designated as "Steric Hindrance." In time this hindrance will, doubtless, yield to analysis by general methods, but in the meantime it is important to be able to predict in what form it is most likely to manifest itself and, in particular, whether addition and substitution reactions are affected in like manner. It was this latter question that interested us most in the present investigation.

Most of our work was done upon three ketones, namely, acetomesitylene, dimesityl ketone and dimesityl diketone.

$CH_3COC_6H_2(CH_3)_3$ $(CH_3)_2C_6H_2COC_6H_2(CH_3)_3$ $(CH_3)_3C_6H_2COCOC_6H_2(CH_3)_3$

The first, being a methyl ketone, can enolize when the hindrance to other reactions is prohibitive; the second contains a carbonyl group of which the reactions are subject to the greatest hindrance that can be exercised by methylated aromatic rings; and in the third, the additive power is increased by the interaction of carbonyl groups which are twinned.

One of these compounds, acetomesitylene, has been known and studied heretofore; it gives few of the characteristic reactions of ketones. Its oxime cannot be obtained by any of the ordinary methods,[1] but the ketone doubtless reacts slowly with hydroxylamine at high temperatures, because Feith and Davies[2] found that when it is heated at 160° with hydroxylamine hydrochloride it is converted into acetylmesidine, the product which would be formed by a Beckmann rearrangement of the oxime. Its behavior toward phosphoric acid and toward alkalies is the reverse of that of acetophenone, it being cleaved to mesitylene and acetic acid by the former and completely resistant to the latter,[3] and this resistance to alkalies persists even after all of the hydrogen of the methyl group has been replaced by halogens.[4]

In contrast with this behavior, which indicates a pronounced hindrance to reactions involving addition to carbonyl, acetomesitylene is easily reduced to the carbinol,[5] and according to Klages[6] it also readily combines

[1] Baum, *Ber.*, **28**, 3207 (1895); V. Meyer, *ibid.*, **29**, 830 (1896).

[2] Feith and Davies, *ibid.*, **24**, 3546 (1891).

[3] Klages and Lickroth, *ibid.*, **32**, 1549 (1899).

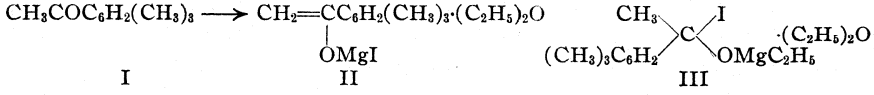
[4] Fuson and Walker, THIS JOURNAL, **52**, 3269 (1930).

[5] Klages and Allendorff, *Ber.*, **31**, 1003 (1898).

[6] Klages, *ibid.*, **35**, 2631 (1905).

with Grignard reagents. Its reduction by sodium and alcohol is not necessarily inconsistent with its general behavior because this mode of reduction may not involve the direct addition of two atoms of hydrogen to the carbonyl group; but the addition of organic magnesium compounds appears completely inexplicable.

In reality, acetomesitylene does not add Grignard reagents. Klages, on treating it with ethylmagnesium iodide in the usual manner, obtained a magnesium compound which he recognized as abnormal because it regenerated acetomesitylene when it was hydrolyzed, but he failed to observe that the reaction is accompanied by evolution of gas. He therefore represented the magnesium compound as an abnormal addition product (III). A quantitative examination of the reaction showed, however, that one mole of gas was evolved and that but one mole of reagent disappeared. The process therefore involves enolization and the product is the magnesium derivative represented by II.



I II III

Many cases are known in which ketones are partially enolized by Grignard reagents but acetomesitylene alone of all ketones that have been examined forms no addition product at all and gives a quantitative yield of hydrocarbon. It appeared possible that this difference in the behavior of acetomesitylene and other ketones might be due to greater ease or rapidity of enolization, but this proved not to be the case. It does not contain enough of the enolic modification to be detectable by the Kurt Meyer method, and at the ordinary temperature it reacts with methylmagnesium iodide slowly, liberating gas for nearly an hour. Moreover, we prepared 2,4,6-trimethylbenzoylacetic ester and found that it does not differ materially from benzoylacetic ester with respect to the extent to which it is enolized. The mesitylene group, therefore, neither hinders nor promotes enolization and it is reasonable to conclude that acetomesitylene is completely enolized by organic magnesium compounds because the hindrance to addition is great enough to allow ample time for the process.

The non-volatile product of this reaction, the iodomagnesium salt of the enolic modification (II), was accurately described by Klages. Unlike many other enolates of ketones it neither combines with oxygen to form a peroxide nor undergoes autoxidative cleavage. It combines with carbon dioxide to form a carbonate which loses carbon dioxide and regenerates acetomesitylene when it is acidified. It also reacts very readily with acid chlorides. With the chlorides of carboxylic acids—acetyl chloride, benzoyl chloride and even chlorocarbonic ester—the products are invariably diacyl derivatives, regardless of the quantities of the reactants employed or the order in which they are brought together

$(CH_3CO)_2CHCOC_6H_2(CH_3)_3$ $(C_6H_5CO)_2CHCOC_6H_2(CH_3)_3$ $(CH_3)_3C_6H_2COCH(CO_2C_2H_5)_2$
IV V VI

p-Toluenesulfonyl chloride likewise reacts readily but as usual forms a halogen compound which subsequently couples with a second molecule of the enolate

$$2CH_2{=}CC_6H_2(CH_3)_3 + C_7H_7SO_2Cl \longrightarrow (CH_3)_3C_6H_2COCH_2CH_2COC_6H_2(CH_3)_3 + C_7H_7SO_2MgX + MgX_2$$
$\quad\quad\quad

Dimesityl carbinol was obtained from dimesityl ketone by other reactions which throw more light on the manner in which it is formed. In benzene the ketone readily combined with sodium to form a greenish blue ketyl which, on hydrolysis, gave the usual equimolar mixture of ketone and secondary alcohol

$$(CH_3)_3C_6H_2COC_6H_2(CH_3)_3 \longrightarrow \underset{\text{VIII}}{(CH_3)_3C_6H_2CC_6H_2(CH_3)_3} \xrightarrow[H_2O]{} \underset{\text{IX}}{(CH_3)_3C_6H_2CHOHC_6H_2(CH_3)_3} + \underset{\text{X}}{(CH_3)_3C_6H_2COC_6H_2(CH_3)_3}$$

(ONa)

The ketone also reacted with Gomberg and Bachmann's[9] binary combination of magnesium and magnesium iodide, forming a dark purple ketyl which was obtained in crystalline form and which, on hydrolysis, likewise yielded equivalent quantities of ketone and carbinol. These metal ketyls showed no tendency to associate to ethane derivatives and no pinacol could be detected in the product of hydrolysis. Experiments are under way to determine whether substituents in the ortho positions actually promote the formation of free radicals, but the foregoing facts show clearly that they have no effect on the formation of metal ketyls. In view of the ease with which these ketyls are formed and the difficulty of saturating the carbonyl group by direct addition, it seems probable that they are intermediates in the rapid reduction of the ketone by sodium or pure sodium amalgam. A train of addition, hydrolysis and rearrangement products that would be consistent both with the general behavior of the ketone and the action of pure sodium amalgam[10] is represented by the scheme

$$(CH_3)_3C_6H_2COC_6H_2(CH_3)_3 \longrightarrow (CH_3)_3C_6H_2C(O\ldots Na)C_6H_2(CH_3)_3 \longrightarrow$$

$$CH_3C_6H_2C(OH)C_6H_2(CH_3)_3 \longrightarrow (CH_3)_3C_6H_2CHC_6H_2(CH_3)_3 \longrightarrow$$

(O)

$$(CH_3)_3C_6H_2CHC_6H_2(CH_3)_3 \longrightarrow (CH_3)_3C_6H_2CHOHC_6H_2(CH_3)_3$$

(O . . . Na)

The hindrance which is so conspicuous in the addition reactions of the ketone appears to be lacking completely in the metathetical reactions of the carbinol. The combination of hydrogen iodide and red phosphorus has no effect on the ketone at the boiling point of the acid but it readily reduces the

$$\underset{\text{XI}}{(CH_3)_3C_6H_2CH_2C_6H_2(CH_3)_3} \longleftarrow \underset{\text{X}}{(CH_3)_3C_6H_2CHOHC_6H_2(CH_3)_3} \longrightarrow \underset{\text{XII}}{(CH_3)_3C_6H_2CHC_6H_2(CH_3)_3}$$

($OCOC_6H_5$)

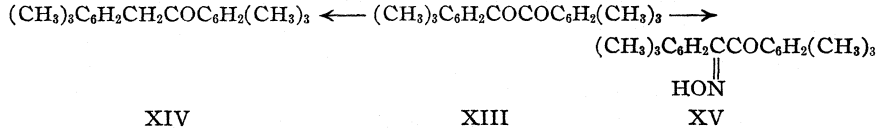
[9] Gomberg and Bachmann, THIS JOURNAL, **49**, 286 (1927).

[10] Willstätter, Seitz and Bumm, *Ber.*, **61**, 871 (1928).

carbinol to dimesitylmethane. And the carbinol is benzoylated as easily as it is reduced.

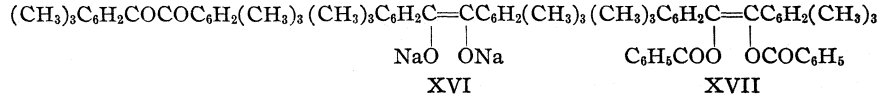
The last of our ketones—dimesityl diketone or hexamethyl benzil—was of special interest because it has long been known that mesityl glyoxylic acid forms hydrazones and that its esters form oximes. By many this behavior of the glyoxylic acid and its esters has been regarded as anomalous because they have compared these substances with mesitylenic ketones, ignoring the fact that the twinning of carbonyl groups greatly increases their additive power—as illustrated, for example, in the stability of the hydrates of glyoxylic aldehydes, mesoxalic acid and diphenyl triketone. In order to get a correct estimate of the hindrance due to the mesityl group it is necessary, therefore, to compare the glyoxylic ester with other glyoxylic esters and the diketone with other α-diketones.

Dimesityl diketone can be reduced to the desoxy compound with zinc and alcoholic potassium hydroxide and it forms a monoxime when it is digested for a long time with excess of strongly alkaline hydroxylamine. These are the only reactions that we could find which presumably involve addition to carbonyl



XIV XIII XV

The diketone neither combines with Grignard reagents nor forms a quinoxaline derivative with ortho phenylenediamine. It also does not undergo the benzilic acid rearrangement, confirming the view of those who hold that the first step in this rearrangement consists in the addition of an alkaline hydroxide to a carbonyl group. One of the most useful reactions of α-diketones is their cleavage to acids with sodium peroxide. Weitz and Scheffer,[11] the originators of the reaction, claimed that it is specific for α-diketones and wrote a mechanism which involves addition to the ends of the conjugated system. The behavior of dimesityl diketone brings support to this view because it is cleaved quantitatively to two molecules of trimethylbenzoic acid. The diketone also enters into another reaction that involves addition to the ends of the conjugated system, namely, addition of alkali metals; it combines with sodium forming a brown disodium compound which reacts with benzoyl chloride to form the corresponding dibenzoate-hexamethyl isobenzil



XVI XVII

[11] Weitz and Scheffer, *Ber.*, **54**, 2327 (1921).

In these three mesitylenic ketones the sole effect of the two methyl groups in the diortho positions is a hindrance to reactions that involve addition to the carbon atom which is in direct union with the mesityl group. The diortho substitution neither promotes nor hinders enolization of alkyl mesityl ketones and it does not affect the chemical properties of the enolates formed from these ketones. It also interferes neither with addition to the oxygen of the carbonyl group nor with 1,4-addition to the two oxygen atoms in α-diketones. In general the hindrance is adequate to prevent all reactions involving addition to the alpha carbon atom excepting, possibly, reduction; but it may be overcome, in part, by the action of a carbonyl group in the alpha position.

Experimental

I. Acetomesitylene

In the quantitative study of the reaction between acetomesitylene and organic magnesium compounds described in an earlier paper[12] the reagent as usual was methylmagnesium iodide. In the present work a standard quantity of the bromomagnesium enolate of acetomesitylene was made by adding an ethereal solution of 10 g. of acetomesitylene, drop by drop, to a solution of ethylmagnesium bromide which had been prepared from 2.2 g. of magnesium, and warming until gas was no longer evolved. The enolate began to crystallize by the time half of the ketone had been added and at the end most of it had separated as a fine white crystalline powder. The suspension obtained in this manner was employed in the subsequent operations.

Acetylation. Diacetyl-2,4,6-trimethylbenzoylmethane (IV).—An ethereal solution of 8 g. of acetyl chloride was added slowly to the suspension of the enolate. An olive-green color developed in the solution and a thick paste accumulated on the bottom of the flask. After heating for half an hour the magnesium derivatives were decomposed with iced acid and the organic products collected in ether in the usual manner. When the ethereal solution was shaken with excess of saturated aqueous copper acetate, it assumed the rich dark blue color of the copper derivative of the triketone, which is surprisingly soluble in ether, but which was precipitated as a blue-gray powder by addition of petroleum ether. The washed and dried powder was recrystallized from ether, from which it separated in dark blue crystals.

Anal. Calcd. for $(C_{15}H_{17}O_3)_2Cu$: C, 65.0; H, 6.2; Cu, 11.5. Found: C, 64.2; H, 6.5; Cu, 11.4.

For the purpose of isolating the triketone the copper derivative, which is insoluble in water, was warmed with moderately concentrated hydrochloric acid until it was completely disintegrated. The colorless ethereal extract of the resulting liquid was washed, dried, concentrated to small volume and finally diluted with petroleum ether. It deposited crystals which after recrystallization from ether and petroleum ether melted at 66–67°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.2; H, 7.3. Found: 73.6; H, 7.2.

[12] Kohler, Fuson and Stone, THIS JOURNAL, **49**, 3181 (1927).

In another experiment the suspension of the enolate was siphoned slowly into a large excess of acetyl chloride dissolved in ether. The product was collected in ether in the usual manner and, after removing the ether, distilled under diminished pressure. Acetomesitylene distilled first, then the temperature rose rapidly to the boiling point of the diacetyl derivative. The distillate solidified and the solid melted at 64–66°—sufficient evidence that no other products had been formed.

The triketone is insoluble in sodium bicarbonate solution, readily soluble in sodium carbonate. When it was examined quantitatively in the "machine"[13] it liberated one mole of methane and consumed three moles of methylmagnesium iodide.

Benzoylation. Dibenzoyl-2,4,6-trimethylbenzoylmethane (VI).—An ethereal solution of 13 g. of benzoyl chloride was added slowly to the usual suspension of the enolate. It precipitated a gray-green gummy magnesium derivative which on treatment with iced hydrochloric acid changed to a colorless crystalline solid. The weight of the solid was 9 g. and the mother liquor on distillation with steam gave 5 g. of acetomesitylene, making a total yield of about 85%. The solid was purified by recrystallization from acetone.

Anal. Calcd. for $C_{25}H_{22}O_3$: C, 81.1; H, 6.0. Found: C, 81.4; H, 6.0.

The dibenzoyl derivative is moderately soluble in benzene and in acetone, sparingly soluble in ether and in alcohol, insoluble in petroleum ether. It crystallizes in stout prisms and it melts at 192°. Its copper derivative was obtained by shaking a solution in benzene with saturated aqueous copper acetate. It is sparingly soluble in most organic solvents, forming solutions which are olive green in color except in the case of benzene where the solution is yellow or brown. It separates from benzene in minute olive-green prisms.

Anal. Calcd. for $C_{50}H_{47}O_6Cu$: C, 74.8; H, 5.3; Cu, 7.9. Found: C, 75.3; H, 5.0; Cu, 7.9.

Reaction with *p*-Toluene Sulfone Chloride: Di-2,4,6-trimethylbenzoylethane (VII).—An ethereal solution of 17.5 g. of *p*-toluene sulfone chloride was added to the usual suspension of the enolate. It reacted vigorously, the solution became pink in color and deposited a crimson solid. The organic products of the reaction were collected in ether in the usual manner. From the ethereal solution sodium carbonate extracted *p*-toluene sulfinic acid, which was identified by comparison with a sample on hand. The extracted solution, on concentration, yielded a solid which melted at 138–139°, the melting point of the ethane reported by Conant and Lutz.[14]

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 82.0; H, 8.2. Found: C, 81.6; H, 8.6.

Reaction with Ethyl Chlorocarbonate: 2,4,6-Trimethylbenzoylmalonic Ester (VI).—An ethereal solution of 7 g. of the chloro compound was added to the usual suspension of the enolate. The reaction was vigorous but the solution remained clear. It was boiled for half an hour, then treated with ice water and a very small quantity of sodium carbonate. The resulting magnesium derivative was thoroughly washed with water and ether, then repeatedly recrystallized from aqueous alcohol, and finally recrystallized from benzene. It then melted at 147°.

Anal. Calcd. for $Mg(C_9H_{11}COC(CO_2C_2H_5)_2)_2$: C, 64.4; H, 6.6; Mg, 3.8. Found: C, 64.2; H, 6.5; Mg, 4.2.

The composition showed that this substance must be the magnesium derivative of trimethylbenzoylmalonic ester, and this conclusion was confirmed by an ethoxyl determination which gave a value of 25.9 instead of 28.4, calculated for two ethoxyl

[13] Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).

[14] Conant and Lutz, *ibid.*, **45**, 1303 (1923).

groups. All attempts to obtain the free ester were unsuccessful because all methods that we could devise for removing the magnesium led to the loss of one of the ester groups and resulted in the formation of 2,4,6-trimethylbenzoylacetic ester.

2,4,6-Trimethylbenzoylacetic Ester, $(CH_3)_3C_6H_2COCH_2CO_2C_2H_5$.—An attempt to prepare this ketonic ester by Claisen's general method,[15] namely, by the action of trimethylbenzoyl chloride on sodium acetoacetic ester, was unsuccessful, the only product being the ethyl ester of mesityl carbonic acid—a liquid which boiled at 139–141° (20 mm.).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 75.0; H, 8.4. Found: C, 74.8; H, 8.3.

Having failed to secure the ketonic ester by general methods, we proceeded to prepare it by means of the reaction between chlorocarbonic ester and the magnesium enolate of acetomesitylene. To this end we operated with sufficient quantities to enable us not only to isolate the magnesium derivative, but also to separate the liquid products by distillation. From 50 g. of acetomesitylene we obtained 25 g. of pure magnesium derivative, and a liquid which by distillation under diminished pressure was separated into 16.5 g. of acetomesitylene and 10 g. of 2,4,6-trimethylbenzoylacetic ester. The presence of this relatively large quantity of the ketonic acetic ester in the liquid suggests the possibility that in the case of chlorocarbonic ester a part of the product may be formed in accordance with the equation

$$(CH_3)_2C_6H_2C(OMgX)=CH_2 + ClCO_2C_2H_5 \longrightarrow (CH_3)_2C_6H_2C(OCO_2C_2H_5)=CHCO_2C_2H_5$$

The ketonic ester, whether obtained from the liquid products or by the acidification of the pure magnesium derivative of 2,4,6-trimethylbenzoylmalonic ester, was a pale yellow liquid which boiled at 150° (11 mm.).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 71.8; H, 7.7. Found: C, 71.7; H, 7.8.

3-Mesityl-pyrazolone-5: $(CH_3)_3C_6H_2C(=CH)-C(=N)-NH$ (with $=O$ and $-H$ on the ring) .—Diortho substitution evidently interferes in no way with the common condensation reactions of beta ketonic esters because trimethylbenzoylacetic ester reacted readily with an alcoholic solution of hydrazine. The product, which separated in very pale yellow plates, was purified by recrystallization from absolute alcohol. It decomposed, without melting, at 290–300°.

Anal. Calcd. for $C_{12}H_{14}ON_2$: C, 71.3; H, 7.0; N, 13.9. Found: C, 71.1; H, 7.2; N, 14.1.

The pyrazolone likewise gave no indication that its properties were in any way affected by the mesityl group. It was readily condensed with benzaldehyde, forming 3-mesityl-4-benzal-pyrazolone-5—yellow plates which decomposed at about 280°.

Anal. Calcd. for $C_{19}H_{18}N_2O$: C, 78.6; H, 6.2. Found: C, 78.2; H, 6.2.

Enolization of 2,4,6-Trimethylbenzoylacetic Ester.—The enol content was determined by the Kurt Meyer method both in the equilibrium ester and in alcoholic solutions which had been kept until they had attained equilibrium. In the case of the equilibrium ester six determinations, made with two different samples, gave a mean value of 24.5%, the maximum deviation from the mean being 0.7%. The alcoholic solutions gave a somewhat higher value—five determinations giving a mean value of 27.3% with a maximum deviation of 0.6%.

Behavior of the Enolate of Acetomesitylene toward Oxygen and Carbon Dioxide.—Oxygen free from moisture and carbon dioxide was passed through a suspension of the

[15] Claisen, *Ann.*, **291**, 65 (1896).

enolate without producing any effect, subsequent hydrolysis yielding only unchanged acetomesitylene. Carbon dioxide on the other hand manifestly changed the appearance of the magnesium compound, and subsequent addition of acetyl chloride failed to effect acetylation. It was not possible, however, to isolate a carbonated product. When the curdy precipitate which was formed by passing the gas through the usual suspension of the enolate was decomposed with acid it evolved carbon dioxide; the ethereal solution contained nothing that could be extracted with bases, and when the residue, left after removing the ether, was distilled with steam it yielded 9.0 g. of acetomesitylene.

II. Dimesityl Ketone

Dimesityl ketone can be prepared without much difficulty both by the action of trimethylbenzoyl chloride on mesitylene in the presence of aluminum chloride and by the action of mesitylmagnesium bromide on the same acid chloride. We prefer the second method because it yields a product which can be purified without distillation. Inasmuch as the steps leading from mesitylene to mesitylmagnesium bromide have since been published it is unnecessary to describe them here. Mesitylene carbonic acid is most easily obtained by passing carbon dioxide into a solution of mesitylmagnesium bromide, and it is most easily converted into its chloride by means of thionyl chloride. Our yields were as follows.

After passing carbon dioxide through a solution of mesitylmagnesium bromide, prepared from 360 g. of the bromide, for twenty-five hours we isolated 211 g. of mesitylene carbonic acid and recovered 64 g. of mesitylene, the amount of acid corresponding almost exactly to the amount of active magnesium compound found by titration. The acid, on treatment with 250 g. of thionyl chloride, yielded 173 g. of acid chloride boiling at 102–104° (1 mm.). The acid chloride was added slowly to a solution of the magnesium compound prepared from 280 g. of mesityl bromide and 34 g. of magnesium. The reaction was vigorous and a red-purple color appeared in the solution. When the solution was decomposed with iced acid, most of the product separated as a solid, the ethereal layer containing, mainly, mesitylene, mesityl bromide and mesityl carboxylic acid which were recovered. The yield of solid ketone was 149 g. It was recrystallized from a benzene–alcohol mixture.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.6; H, 8.3. Found: C, 85.3; H, 8.5.

Dimesityl ketone crystallizes in stout needles or prisms. It melts at 136–137° and it boils at 200° (2 mm.). It is very soluble in benzene, moderately soluble in boiling alcohol and sparingly soluble in ether. It was recovered *in toto*, both after prolonged boiling with a strongly alkaline alcoholic solution of hydroxylamine, and after it had been heated for five hours to 150–170° in a sealed tube with alcoholic hydroxylamine hydrochloride.

Reduction with Sodium in Alcohol.—To a solution of 10 g. of the ketone in 100 cc. of boiling alcohol, 10 g. of sodium was added, piece by piece, the solution being heated toward the end when the reaction was no longer sufficiently vigorous to cause boiling. The solution was saturated with carbon dioxide, concentrated and gradually diluted with water. It yielded 9.6 g. of a crystalline solid melting at 149°.

Reduction with Sodium Amalgam.—Pure 0.5% sodium amalgam was prepared from distilled mercury and sodium. To 440 g. of this amalgam were added in succession 100 cc. of boiling alcohol and 10 g. of the ketone. The reaction was vigorous at the outset but there was no appreciable escape of hydrogen. The solution was boiled for

four hours, then decanted and manipulated as in the preceding experiment. Here also the yield was quantitative and the product melted at 149–150°.

Dimesityl Carbinol (X).—The product obtained from the two preceding experiments was purified by recrystallization from alcohol and also from benzene and petroleum ether.

Anal. Calcd. for $C_{19}H_{24}O$: C, 85.1; H, 9.0. Found: C, 84.6; H, 9.2.

In freezing benzene the molecular weight was found to be 296 instead of 268 calcd.

The carbinol crystallizes in small prisms and it melts at 150°. At 60° it reduces a solution of chromic acid in glacial acetic acid and reverts to the ketone. In the "machine" it consumes one mole of gas and liberates one mole of methane.

The Benzoate (XII).—A suspension of two grams of the carbinol and 5 g. of benzoyl chloride in 40 cc. of 10% aqueous sodium hydroxide was warmed on a steam-bath and then left overnight. The resulting solid was collected on a filter, washed, dried and recrystallized from petroleum ether. It separated in needles and melted at 154°.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 81.5; H, 7.4. Found: C, 81.4; H, 7.6.

Reduction, Dimesitylmethane (XI).—A suspension of 5 g. of dimesityl carbinol and an equal weight of red phosphorus in 50 cc. of constant boiling hydriodic acid was boiled for twenty-five hours. Most of the acid was then removed by distillation. The residue was extracted with ether, the extract washed, dried and allowed to evaporate slowly. The resulting solid softened at 130°, then melted at 135°.

Anal. Calcd. for $C_{19}H_{24}$: mol. wt., 252; C, 90.4; H, 9.6. Found: mol. wt., 234; C, 90.6; H, 10.1.

The analytical values indicated dimesitylmethane and the product was completely identified by comparison with a sample that was synthesized by Baeyer's method.[16]

Action of the Combination, Magnesium + Magnesium Iodide on the Ketone.—In a 100-cc. globular flask 3 g. of powdered magnesium was mixed with 8 g. of iodine. A little benzene and some absolute ether were added and also, after the reaction between the metal and the halogen had subsided, 10 g. of dimesityl ketone in absolute ether. The air in the flask was displaced by boiling off a part of the ether and then the flask was securely stoppered. A royal-purple color developed rapidly and when the flask was cooled in a freezing mixture purple-black crystals separated from the solution.

As soon as the reaction appeared to be complete, the flask was warmed again, the stopper removed and the solution poured rapidly into ammonium chloride solution. The organic products were collected in ether, and the washed and dried ethereal solution was concentrated in a current of air. It left a solid from which 4.0 g. of pure dimesityl ketone and 3.5 g. of pure carbinol were separated, and an oil that could not be crystallized further.

Action of Sodium on the Ketone in Benzene.—A large excess of sodium in the form of wire was added to a solution of 10 g. of the ketone in 100 cc. of benzene. A blue-green color developed and rapidly became so dark as to make the liquid opaque. The mixture was shaken mechanically for about sixteen hours, and the solution was then decanted into water. The benzene layer was washed, dried and concentrated. It deposited 10 g. of a colorless crystalline product. This was partially separated into pure ketone and pure carbinol—further fractional crystallization being abandoned when it became evident that no other substances could be present in the mixture.

III. Dimesityl Diketone XIII

The diketone is extremely difficult to secure. After trying a great many methods which appeared feasible, but were not, we finally prepared it by the

[16] Baeyer, *Ber.*, **5**, 1908 (1873).

action of mesitylmagnesium bromide on mesityl glyoxylic ester. The procedure was as follows.

To a solution of the magnesium compound prepared from 50 g. of mesityl bromide, 25 g. of mesityl glyoxylic ester was added drop by drop and then 100 cc. of benzene. The mixture was distilled until its boiling point rose to 75° and then heated at this temperature for three hours. The mixture was decomposed in the usual manner with iced acid. The benzene layer was first freed from mesityl glyoxylic acid by extraction with sodium carbonate, then washed, dried and distilled fractionally under diminished pressure. It was thus separated into mesitylene, mesityl glyoxylic ester, dimesityl, dimesityl diketone and some higher boiling yellow oil. The diketone fraction boiling at about 200° (6 mm.) partially solidified when it was diluted with methyl alcohol. The total yield of pure diketone obtained from this and higher fractions was 3 g. The substance was purified by recrystallization from methyl alcohol.

Anal. Calcd. for $C_{20}H_{22}O_2$: mol. wt., 294; C, 81.5; H, 7.5. Found: mol. wt., 289; C, 81.5; H, 7.7.

The diketone is much more highly colored than most other aromatic α-diketones, crystallizing in golden yellow plates that melt at 122°. It is moderately soluble in most organic solvents including petroleum ether.

Reduction. Mesityl-acetomesitylene (XIV).—The reduction of the diketone is much more difficult than is that of benzil. Zinc and acetic acid—Clemmensen combination of amalgamated zinc and concentrated hydrochloric acid—and catalytic hydrogenation were tried without success, the diketone being recovered in each case. The substance is, however, slowly attacked by zinc and alkali. A mixture composed of 0.5 g. of the diketone, 10 cc. of alcohol, 2 cc. of water, 1 g. of potassium hydroxide and 2.5 g. of zinc dust was boiled for thirty-six hours, at the end of which time it was light brown in color. It was then freed from alcohol and extracted with ether. The ethereal extract, on concentration, first deposited 0.3 g. of diketone, then a mixture from which 0.04 g. of a white crystalline compound was finally isolated by systematic fractional crystallization. The desoxy compound is moderately soluble in alcohol, sparingly soluble in ether. It melts at 141°.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.7; H, 8.6. Found: C, 85.8; H, 8.7.

Oxidation.—A solution of sodium hydrogen peroxide obtained by dissolving sodium peroxide in ice water was added to a solution of 0.02 g. of the diketone in methyl alcohol. The mixture was digested on a steam-bath for an hour, then cooled and extracted with ether. The ethereal extract contained some unchanged diketone, but the aqueous layer on acidification yielded 0.015 g. of mesitylene carboxylic acid.

Action of Alkali.—An aqueous alcoholic solution containing 0.25 g. of the diketone and 0.4 g. of water was heated for an hour, alcohol being added from time to time to maintain solution. Under these conditions benzil reacts rapidly but the diketone was not affected. Even fused potassium hydroxide failed to effect a benzilic acid rearrangement. Thus 1.3 g. of potassium hydroxide and 0.6 g. of water were heated in a porcelain crucible until most of the water had evaporated. After the addition of 0.2 g. of the diketone, the heating was continued but the molten substance failed to dissolve in the alkali and when the brown melt was cooled nearly all of the diketone was recovered by treatment with water and ether.

The Monoxime (XV).—All attempts to prepare a quinazine derivative by treating the diketone with ortho phenylenediamine were unsuccessful, as were also all attempts to prepare a dioxime. The monoxime, however, could be obtained without much difficulty. For this purpose a solution of 0.55 g. of potassium hydroxide and 0.45 g. of hydroxylamine hydrochloride in a little water was added to a solution of 0.3 g. of

the diketone in 10 cc. of alcohol. The mixture was boiled for nine hours, then diluted and made feebly acidic. It deposited a colorless solid which, after crystallization from carbon bisulfide, and finally from ether–petroleum ether, melted at 209–210°. The yield of crude product was 0.23 g.

Anal. Calcd. for $C_{20}H_{25}O_2N$: C, 77.6; H, 7.5. Found: C, 77.9; H, 7.5.

Beckmann Rearrangement.—In order to determine whether the substance was really an oxime, 0.07 g. of the pure material was heated with formic acid for four hours, then diluted and extracted with ether. From the ethereal extract sodium bicarbonate removed 0.05 g. of mesitylene carbonic acid, and the ether, on evaporation, left 0.01 g. of unchanged oxime. In configuration, the substance, therefore, corresponds to the alpha oxime of benzil.

Reaction of the Diketone with Sodium.—A suspension of 0.1 g. of sodium in a solution of 0.65 g. of the diketone in 15 cc. of dry toluene was boiled in a current of pure nitrogen. The solution first turned brown in color, then deposited a brown solid. After two hours, 0.7 g. of benzoyl chloride was added. No reaction was apparent in the cold but when the mixture was heated the brown solid disappeared rapidly and the solution became yellow, the color being due to unchanged ketone which remained because the first reaction had not been carried to completion. The solution was decanted from the unused metal, freed from sodium chloride by filtration and evaporated.

The residue was a mixture of unchanged diketone and a colorless product. The mixture was separated by fractional crystallization from ether–petroleum ether.

Anal. Calcd. for $C_{34}H_{32}O_4$: C, 81.3; H, 6.4. Found: C, 81.4; H, 6.3.

Hexamethyl Isobenzil (XVII).—The dibenzoate obtained as described in the foregoing account is insoluble in petroleum ether, sparingly soluble in methyl and in ethyl alcohol, readily soluble in benzene and in ether. It crystallizes in needles and it melts at 190°. Like isobenzil it is readily hydrolyzed with alcoholic alkalies but the process is accompanied by oxidation and the products are benzoic acid and the diketone instead of benzoic acid and hexamethylbenzoin. Thus, using the method of Klinger and Standke,[17] 0.2 g. of powdered potassium hydroxide was added to a solution of 0.15 g. of the dibenzoate in 10 cc. of hot alcohol. The solution became yellow immediately. It was warmed for a few minutes, then cooled in a freezing mixture, whereupon it deposited the yellow plates of the diketone. The yield of diketone was practically quantitative and benzoic acid was isolated from the filtrates.

Summary

The results of a study of three mesitylenic ketones, acetomesitylene, dimesityl ketone and dimesityl diketone, show that the two methyl groups in the di-ortho positions affect only those reactions which involve addition to the carbon atom that is in direct union with the mesityl group. These methyl groups neither promote nor hinder the enolization of acetomesitylene, trimethylbenzoylacetic ester and similar substances. They also do not interfere with reactions which involve only addition to the oxygen of the carbonyl group.

In general the hindrance is adequate to prevent all addition reactions that involve the alpha carbon atom excepting reduction; but it may be overcome, in part, by another carbonyl group in the alpha position.

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[17] Klinger and Standke, *Ber.*, **24**, 1264 (1891).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE DEVELOPMENT OF A METHOD FOR THE RESOLUTION OF RACEMIC AMINES AT LOW TEMPERATURES

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We may suppose[1] that optical activity has not definitely been found for trisubstituted amino or quaternary nitrogen $(R_1)(R_2)(R_3)N$, $[(H)(R_1)(R_2)(R_3)N]^+$, either because the groupings are intrinsically not optically asymmetric, or because attempts to resolve racemic mixtures have failed.

By analogy with the behavior of active completely substituted quaternary nitrogen, which very commonly tends to racemize with great ease, and with the extreme mobility of hydrogen in comparison with other radicals, we should expect tri-substituted ammonium compounds—if capable of assuming enantiomorphic forms due to the central nitrogen—to racemize with great rapidity at ordinary temperatures. The velocity of racemization is, however, in general considerably decreased by decreasing temperature.[2]

The question arises, therefore, as to whether tri-substituted quaternary or amino nitrogen[3] could be found asymmetric by a resolution process and examination of products conducted entirely at a low temperature.

The present investigation consists of the development of a means of effecting and detecting resolution at low temperature applicable to the resolution of amino compounds, together with a testing of the method employing a known resolvable amino compound containing asymmetric carbon.

Brief mention only can be made of previous work. In 1927 E. Wedekind and Klatte[4] gave a clear and complete statement of the status of the problem of the stereochemistry of saturated trivalent nitrogen and reported some evidence for the existence of a tri-substituted ammonium ion which

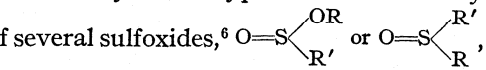
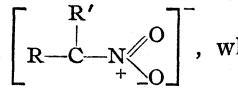
[1] For excellent presentations of the theory of natural rotation from a stereochemical standpoint, see (a) F. M. Jaeger, "Lectures on the Principle of Symmetry," Elsevier Pub. Co., Amsterdam, 1920, pp. 204 *et seq.*; (b) J. B. Cohen, "Organic Chemistry," 5th Ed., Part II, Structure, Longmans, Green and Co., London, 1928, pp. 173 *et seq.*; (c) Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929); (d) Born, *ibid.*, **16**, 251 (1915); *Ann. Physik*, [4] **55**, 177 (1918); Oseen, *ibid.*, [4] **48**, 1 (1915). See also Gans, *Z. Physik*, **27**, 164 (1924); *Ann. Physik*, [4] **79**, 547 (1926). Compare Bursian and Timorev, *Z. Physik*, **38**, 473 (1926). Note that the corrections to Born's theory made by Gans do not affect Born's stereochemical conclusions.

[2] Ref. 1 (b), p. 200.

[3] The structural similarity between tri-substituted amino and quaternary nitrogen should be noted. If H^+ could be added to the grouping $(R_1)(R_2)(R_3)N$, or removed from the grouping $[(H)(R_1)(R_2)(R_3)N]^+$ by a process during which racemization did not take place, or did not take place completely, we might expect to obtain one active form from the corresponding one.

[4] Wedekind and Klatte, *Ber.*, **60**, 2325 (1927).

cannot be considered as conclusive. They agreed with Meisenheimer[5] that "a stabilization results only if the fourth coördination position of nitrogen is occupied either by a positively charged hydrogen atom or alkyl group, or by an oxygen atom, or by a complex metal group."

That a molecular structure of the tertiary amine type could conceivably be asymmetric is seen in the case of several sulfoxides,[6]  and what appears to be an analogous case of carbon attached to three radicals—the ion of 2-nitro-octane,  , which has been reported.[7] It should be noted, however, as the investigators of the sulfoxides have mentioned, that it seems characteristic of the above cases that there is present in the molecule a permanent dipole moment[6,7,8] involving the central atom.

Moreover, in addition to the fact that completely substituted quaternary nitrogen has been shown, by investigations of optical activity, to be tetrahedral, we have also the fact that tertiary nitrogen has been shown, by other evidence,[9] to be at any rate non-planar in structure. There is still reason, therefore, to expect tri-substituted amino and quaternary nitrogen to have a tetrahedral structure[10] and exhibit optical activity.

In our investigation the original intention was to agitate a solution of a suitable amine in contact, at a low temperature, with a finely powdered appropriate optically active acid, employing a solvent in which the amine, but not the acid or salt, would be soluble. Any activity then appearing in the solution would be due to the enantiomorph which was slower to react with the acid. It was intended, moreover, to keep the reaction mixture under observation in a polarimeter so that any transient activity could be detected. This process was found to be impractical however; salt formation appeared to occur extremely slowly if at all under such conditions.

The final method of salt formation consisted in dissolving the acid and base at room temperature in a solvent in which the salt would not be very

[5] Meisenheimer and co-workers, *Ber.*, **57**, 1744 (1924).

[6] Phillips, *Trans. Chem. Soc.*, **77**, 1072 (1900); Harrison, Kenyon and Phillips, *ibid.*, **129**, 2079 (1926); see also Clarke, Kenyon and Phillips, *ibid.*, **131**, 188 (1927).

[7] Kuhn and Albrecht, *Ber.*, **60**, 1297 (1927). Shriner and Young, THIS JOURNAL, **52**, 3332 (1930); see also Heubaum and Noyes, *ibid.*, **52**, 5070 (1930).

[8] For a recent discussion, see Fuson, *Chem. Rev.*, **7**, 359 (1930).

[9] For example, triethylamine has a permanent dipole moment. The space isomerism of multiply bonded N^{III} (as in oximes, etc.) indicates also a non-planar structure of the nitrogen.

[10] Other cases reported by Harries, *Ann.*, **417**, 107 (1918), and by Hess, *Ber.*, **52**, 964, 1622 (1919); **53**, 129 (1920); and Hess and Gran, *Ann.*, **441**, 101 (1925), have been disposed of by Orthner, *ibid.*, **456**, 225 (1927), and by Meisenheimer and Mahler, *ibid.*, **462**, 301 (1928).

soluble, at concentrations such that considerable salt would precipitate as crystals upon cooling; then, after seeding if possible, cooling the solution and keeping it cold until cessation of crystallization. By this means we could utilize differences in solubility of the non-enantiomorphic salts, as well as differences in rates of formation. Activity in the solution could now be due not only to partial resolution but also to unprecipitated acid or salt. For amines racemizing rapidly at room temperatures, solutions showing activity after separation of the salt could be heated to room temperature, then cooled to the original low temperature and again examined. A difference in the original and final activity would then be evidence of racemization and hence of some resolution. Methods were developed to examine the crystalline phase also, at the low temperature.

A rather delicate solvent–concentration balance[11] was necessary in order to obtain solutions which when cooled would deposit crystals and leave optically clear supernatant solutions.

Discussion of the Experiments

We have given our early experiments in considerable detail, because they form a study of salt formation in non-aqueous and slightly aqueous media. Employing a racemic amine (Expt. I), the antipodes of which are quite stable, and which is readily resolvable under a variety of conditions by the optically active acid employed, the amine was dissolved in a solvent in which the optically active acid is insoluble and the solution kept in contact with the solid acid for a long time. No resolution was attained by this procedure. What we found in this initial set of experiments could not have been predicted. We do not know whether or not the forces active at the surfaces of asymmetric crystals could themselves have any property of asymmetry. We know nothing regarding the symmetry or asymmetry of any forces associated with the boundary between a strongly optically active strong acid in the solid state and a readily resolvable strong base in solution.

Our second and third sets of experiments (see Expts. II and III) indicate the following: (1) Our optically active acid was somewhat soluble in the solvent media employed and some partial resolution was attained. (2) The formation of crystals rather than sirups seems necessary for resolution. (3) The initial formation of sirups which later turn into crystals may hinder the resolution process in two ways. The amount of time required is lengthened by the time necessary for the crystals to be formed from the sirup. The extent of resolution may be reduced by the sirup itself acting

[11] The effect of the presence of water in our solvents is interesting. A little water present before precipitation appeared to facilitate crystal formation (if moisture entered the solution, however, after precipitation was well under way, the solution became fogged).

as a solvent medium for the process and being a less favorable solvent than the main solution.[12]

The second point noted above is of particular interest. Several examinations of the sirups (and congealed sirups formed at low temperature) and of the supernatant solutions were made during this investigation. In all cases it was found that no detectable resolution had been brought about by the precipitation of the sirups. In the crystals formed from the sirups, however, except when pure ether was employed as solvent, partial resolution had been attained. This indicates that the actual *crystalline* salt must be obtained in order to bring about resolution by a salt formation process.

The next set of experiments (see Expt. IV) shows that upon employing a solvent more polar than the previous media we were able to obtain a much higher percentage resolution. Also, the time required for the crystal formation was materially reduced.

In the next set of experiments (see Expt. V) we find that: (1) neither the salt of the dextro antipode nor of the levo antipode of the amine we were using with the optically active acid employed was detectably soluble in dry ether.

(2) A mixture consisting of equal amounts of the salts of the amine isomers in contact with an excess of the dissolved racemic amine finally reaches a state in which an excess of the dextro amine is present in the solution and a corresponding excess of the salt of the levo amine is present in the solid phases. The data indicating this interesting result were not verified. Only a single experiment (of the type Vb) was carried out. We are not certain that we reached equilibrium in this experiment. We believe that the success of our resolution process depended upon a difference between the amine isomers in their *rate* of forming salt *crystals* with the optically active acid. The non-enantiomorphic salts of the base and optically active acid we were using should differ in solubility in any solvent. Although this relative difference in solubility might be appreciable in the solvent media we employed, so that with the racemic base and active acid initially in solution, one salt would be precipitated in greater amount to attain equilibrium, we do not regard such equilibrium considerations as particularly pertinent under the conditions of our resolution procedure. In a number of cases we found we were working with supersaturated solutions. Clear solutions decanted from good crops of crystals, after crystallization had been occurring for twelve hours or so, would slowly deposit more crystals over a period of several days or even weeks.[13]

[12] On numerous occasions sirup was thrown against the walls of containers (by shaking) above the reaction mixture and stuck there. This sirup, out of contact with the main solution, would give crystals directly, simultaneously with the appearance of crystals from the sirup in contact with the solution. This indicates that crystal formation took place in the sirup as solvent.

[13] The containers were stoppered; moreover the mother liquors, after long standing

Moreover, during our work at low temperature we frequently observed the unusual phenomena of crystals being deposited while solutions[14] were warming up. Clear solutions decanted from crystals at −70° would give small additional crops during one or two hours' warming to room temperature.

We suppose, but we did not prove, that salt formation took place much faster than crystal formation in our ethereal solutions. In more concentrated solution—in solvent media high in alcohol or ethyl acetate or acetone content—the addition of amine to acid was accompanied by a very obvious heat effect. In the more dilute solutions, no heat of neutralization was noticed, but we did not try experiments in a calorimeter.

The next series of experiments (see Expt. VI) and the last three series (see Expts. VIII, IX and X) describe the low temperature resolution of 1-amino-1-phenylethane and summarize the unsuccessful attempts to resolve benzylethylaniline.

We wish to comment on our method of freeing amines at low temperature (see Expt. VII). By the use of a relatively strong (optically inactive) amine we were able to liberate our resolved amine at low temperatures from a salt into a solvent permitting of polarimetric examination. The process would appear to be serviceable in many cases. However, a comprehensive investigation with a large number of resolved amines would be necessary to demonstrate the general applicability of the method. The solvent media might have to be changed somewhat depending upon the amine investigated. The method given is considered an improvement over the older method of liberating rapidly racemizing amines by ether extraction from a basic aqueous solution of a salt.

Experimental Part

Polarimeter.—A Laurent polarimeter was equipped with quarter-wave plate for sodium light. The trough for supporting ordinary polarimeter tubes was removed and the polarizing and analyzing mechanisms mounted firmly on a steel base with guides and screws for adjustment. Space and rests were provided between the polarizer and analyzer so that either the trough and ordinary tubes or the heat-insulated low temperature tubes could be accommodated at will.

The polarimeter tube consisted of a copper tube gold-plated inside, 17.43 cm. in length between end disks and 1.8 cm. inside diameter. Vertical side tubes—offset from the center line—were attached for the thermometer and for introducing and removing solutions. A glass tube ran down one side tube to the bottom of the polarimeter tube and extended some distance in the upward direction; from this a horizontal branch connected with a reaction vessel containing the solution whose activity was to be measured. The other side tube, in addition to accommodating a thermometer, had a vertical glass tube attached. The two vertical glass tubes were connected to drying towers.

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and further crystallization, would frequently have lower rotations. If accidental evaporation had occurred and the crystallization took place in response to this, the final solutions should have the same or higher rotations.

[14] Protected against appreciable evaporation or the entrance of moisture by long tubes filled with drying agent.

The windows were simply ordinary polarimeter tube disks 2.4 cm. in diameter, held tightly—protected by washers[15]—by means of threaded brass rings, into threaded depressions at the ends of the tube. Hard rubber tubes were attached to each end of the tube to prevent currents of moist air from striking the windows. The polarimeter tube was set into a heat-insulated box.

The reaction vessels were simply glass containers in the shape of large test-tubes closed by stoppers bearing siphons and short connections to drying tubes. These vessels were placed in larger test-tubes containing some light liquid for thermal contact and the larger test-tubes surrounded by freezing mixture in gallon Dewar jars. A reaction vessel could be removed momentarily from the cold bath for examination without any freezing mixture adhering.

By applying gentle air pressure through the drying tube attached to the reaction vessel, solution could be forced over into the polarimeter tube. Applying dry air over the solution in the polarimeter tube, the tube could be emptied. The contents of the polarimeter tube could be stirred by sending portions of the solution up and down the vertical glass tubes attached. The polarimeter tube windows were freed from condensed moisture by spraying them with alcohol; a time interval of from five to ten minutes—ample for making an observation—would elapse during which the window would be absolutely clear. When solutions were removed from the polarimeter tube for boiling and re-cooling, flasks with long reflux condensers, capped by drying tubes, were used.

Dewar and Jones, and Molby[16] have used low temperatures in measuring optical activity. Molby found successful a glass polarimeter tube equipped with double windows. The windows were sealed by water-glass joints to rings, forming window chambers which were evacuated, or dried by phosphorus pentoxide. We found a glass polarimeter tube equipped with two side tubes, all carefully annealed, to be subject to some distortion upon cooling, unless the freezing mixture were carefully applied. Molby needed only one side connection and encased the glass tube in close fitting copper tubing to obtain uniform conduction, so very likely did not experience any distortion. By using washered, rather than sealed-in or cemented-in windows, we could be sure that we would never have any distortion giving rise to rotations which we might attribute to mutarotation.

The temperature was measured by ligroin or pentane thermometers checked against one calibrated by the Bureau of Standards. We used acetone and carbon dioxide snow for keeping the reaction vessels cold. Instead of acetone we employed a mixture of acetone (60%) with carbon tetrachloride (20%) and chloroform (20%) by volume for cooling the polarimeter tube. The latter mixture (with solid carbon dioxide) would give temperatures around $-78°$ and was not flammable.

The Light Source.—It appeared early in our work that we would need a light source of very high intensity. We found entirely satisfactory a simple modification of a light originally used by Perkin.[17] Perkins vaporized sodium in a current of hydrogen and burned the sodium-laden hydrogen in air. Our modification consisted of burning the sodium-laden hydrogen in a current of oxygen, thus increasing the intensity many fold. The light consists of a horizontal piece of 5-cm. pipe about 30 cm. long with, at one end, a capped vertical elbow (for introducing sodium every few days) pierced horizontally by a small pipe carrying hydrogen; the other end terminated also in a vertical elbow, pierced vertically by a small pipe carrying oxygen, the oxygen pipe ending flush with the elbow

[15] Fiber-like washers were found best: rubber washers would often crack when cold, leather or asbestos-like washers would leak solvents when cold.

[16] Dewar and Jones, *Proc. Roy. Soc.* (London), [A] **80**, 236 (1908); Molby, *Phys. Rev.*, **28**, 57 (1909); **30**, 84 (1910); **31**, 291 (1910).

[17] Perkin, *Trans. Chem. Soc.*, **45**, 421 (1884); **69**, 1027 (1896).

around it to form the burner. The sodium is vaporized by an electric furnace element surrounding the horizontal pipe.

The light given by the modified Perkins lamp is of approximate spectral purity, no monochromator or filter was necessary.

Preparation of Materials. 1-Bromo-*d*-camphor-10-sulfonic Acid.—Bromocamphor, white crystals, m. p. 76–77°, was sulfonated by the method of Pope and Read[18] except that a better yield was obtained through the use of a less concentrated sulfonating mixture. For 150 g. of bromocamphor, 110 cc. of 95% sulfuric and 165 cc. of 30% fuming sulfuric acid were used. This yielded 35% of the theoretical amount of ammonium salt of the acid, against 25% using Pope and Read's reaction mixture. The ammonium salt was recrystallized from water until its rotation rose to the required value; colorless crystals, dec. 270°; 3.8875 g. in 50 cc. of aqueous solution, $[\alpha]_D^{22}$ 86.4°. Washing the moist ammonium salt with cold acetone facilitated the purification. An aqueous solution of the acid was made by Pope and Read's method, and evaporated on a steam-bath to a thick sirup and finally to dryness over phosphorus pentoxide *in vacuo*. The resinous mass was finally obtained as a white powder, m. p. 196°, forming a clear solution in water, only slight trace of barium: 1.050 g. in 50 cc. of aqueous solution, $[\alpha]_D^{22.5}$ 85.3°. To phenolphthalein, 1.050 g. of the acid used 0.003272 equivalent of sodium hydroxide; equivalent weight found, 321; calculated, 311.

***d*-Camphor-1′-sulfonic acid,** from Eastman, was recrystallized twice from moist ethyl acetate and dried over phosphorus pentoxide *in vacuo;* colorless crystals, dec. 195°. To phenolphthalein, 1.000 g. used 0.00409 equivalent of sodium hydroxide, whereas one gram of pure acid should use 0.00431 equivalent, hence it was 94.8% pure. 2.000 g. in 100 cc. of aqueous solution, $[\alpha]_D^{22.5}$ 20.9°.

1-Amino-1-phenylethane was prepared by the reduction of acetophenone oxime,[19] using five times the amounts specified; yield, 70%, b. p. 186°.

Benzylethylaniline from Schering–Kahlbaum, A. G., was twice distilled *in vacuo* over a one-degree range. The light yellow oil distilled at 312–313° at 750 mm. with some decomposition; picrate, m. p. 117°.

Solvents.—The methyl alcohol, ethyl alcohol, ethyl acetate and acetone were of "U. S. P." grade, dried with anhydrous copper sulfate. The ether, denoted in the experiments as "comml. ether" was moist, alcoholic, "U. S. P.," 99% pure. Ether specified as "dry ether" was dried and stored over sodium wire. The petroleum ether was the "U. S. P." grade "Oronite."

TABLE I

DATA USED IN CALCULATIONS

Compound	Mol. wt.	Molecular rotation (dilute aqueous soln.)	Abbreviation
1-Bromo-*d*-camphor-10-sulfonic acid	311	271°	HK
Salt (anion)	...	271°	K^-
d-Camphor-1′-sulfonic acid	232	50°	HR
Salt (anion)	...	50°	R^-
1-Amino-1-phenylethane	121	30.2° 50° (in dry ether)	A
Salt (cation)	...	0°	AH^+
Benzylethylaniline	211	.....	B

Definition of "Per Cent. of Resolution."—Let $[M]_r$ be the molecular rotation of the

[18] Pope and Read, *J. Chem. Soc.*, **97**, 2200 (1910).

[19] Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 361.

completely resolved salt, A·HK, $[M]_u$ that of the unresolved salt and [M] that of the sample in question, each in distinctly alkaline solution, then

$$\text{Per cent. of resolution} = 100\{[M]_u - [M]\}/\{[M]_u - [M]_r\}$$

For a dry ethereal extract of the base A

$$\text{Per cent. of resolution} = 100 \text{ (moles of excess } d \text{ or } l \text{ base)/total base}$$

The total base may be determined by titration and the amount of active base in excess of racemic base from the optical activity. The two methods of determination agree. In water, the rotations of the active acid and base and their ions may be superimposed.

Record of Experiments.—Since all measurements were made with sodium light, the subscript D will be omitted in giving the rotations. A subscript to denote the length of the observation tube in decimeters will be used.

Preparation of (l) A·HK and Tests of the Method of Analysis.—15.5 g. (0.05 mole) (HK) and 12.1 g. (0.1 mole) (A) were added to 50 cc. of 1 *N* (0.05 mole) HCl (aq.) and dissolved by warming. In order to obtain crystals, the solution had to be evaporated to a sirup. After four days' standing, a crop of crystals was formed. The crystals were filtered off, washed with a little cold ethyl acetate and recrystallized twice from ethyl acetate; yield, 6 g. of colorless crystals, m. p. 207–208°.

The ethyl acetate from the crystallizations and washing was added to the sirup, the solution evaporated to a sirupy consistency and let stand. After seven days a large crop of crystals was obtained which was filtered off, washed and recrystallized three times from ethyl acetate; yield, 11 g. of colorless crystals, m. p. 207–208°. The two crops were mixed and recrystallized from water; m. p. 207–208°.

For 0.8652 g. of the crystals made up to 50 cc. aqueous soln., $\alpha_{4\,\text{dm.}}^{22°}$ 4°24′, therefore $[M]^{22°}$ 268. According to the literature, for (*l*) A·HK, m. p. 206–207°, $[M]^{20.5°}$ 271°. Hence the crystals were practically pure (*l*)A·HK.

The Quantitative Separation of A from its Salt.—2.000 grams of (*l*)A·HK, 20 cc. of water, 3 cc. of 12 *N* sodium hydroxide and 30 cc. of ether (comml.) were shaken thoroughly. The ethereal layer was separated (one extraction proved sufficient) and dried with solid potassium hydroxide, by decanting from any aqueous layer to fresh drier and allowing it to stand on the drier in a stoppered vessel for twelve hours. The ether layer was finally decanted from the drier, the latter washed with dry ether and the combined solution and washings measured for volume. The original aqueous layer was analyzed for K^- polarimetrically.

$$\text{Equivalents of salt by weight } 2/432 = 4.63 \times 10^{-3} \text{ eq.}$$
$$\text{Equivalents of salt by rotation} = 4.63 \times 10^{-3} \text{ eq.}$$

The rotation of the ether solution containing the base gave values of $[M]^{22.5°}$ (for three dilutions) of −49.5°, −49.0°, −50.3°, respectively. Blank experiments with a known amount of unresolved base showed that the base could be dissolved in ether, the solution shaken with 4 *N* sodium hydroxide solution, separated and dried as above, the base then extracted from it with a known excess of standard acid and the acid back-titrated to show within 2% the original amount of base. It was shown further that within 1% the molecular rotations of (*l*) A and K^- are additive and independent of wide variations in the alkalinity of the solution and of the presence or absence of alcohol in the solution. The average value of [M] for the base A in dry ether was taken as 50.0° as a result of these experiments.

Experiments in Detail. I. Room Temperature Experiments with (*dl*)A Dissolved and HK Insoluble.—(a) 2.3035 g. of HK was added to 250 cc. of petroleum ether and the mixture left to stand with occasional shaking. (b) 2.1845 g. of HK (0.0073 mole) was added to a solution of 2 cc. of (A) (0.0154 mole) in 250 cc. of petroleum ether and the mixture left to stand with occasional shaking. The two mixtures were examined for ro-

tation (in 2-dm. tube) after standing for one week, two weeks and then after being shaken continuously for an additional week. All rotations were zero. The only change noted was that the HK which remained a loose powder throughout in (a) and was originally a loose powder in (b), became, after ten days' standing in (b), too gummy to move around freely. Similar experiments for shorter periods of time also showed no indication of partial resolution.

II. With HK Originally Undissolved but Soluble; Sirup Formed.—(a) A solution of 1 cc. of A (0.0078 mole) in 50 cc. of ether was kept, with occasional moderate shaking, in contact with 1.21 g. of HK (0.0039 mole). A sirupy coating rapidly formed about the HK. The ethereal solution was examined from time to time for rotation; twenty-four, thirty-six and forty-eight hours after mixing, $\alpha_{2\,\mathrm{dm.}}^{\mathrm{room\ temp.}}$ 8′. After forty-eight hours' standing the solid acid and sirupy coating were mixed together and shaken with the ether solution thoroughly for six hours, then $\alpha_{2\,\mathrm{dm.}}^{\mathrm{room\ temp.}}$ 16′. Examination of the ethereal solution at this point showed it to contain a small amount of K^- and 0.0031 equiv. of A with 0.0009 equiv. excess (*d*)A. Hence the resolution was 29% complete. The solid and semi-solid material contained considerable unused HK. (b) A solution of 2.58 cc. of A (0.02 mole) in 200 cc. of ether was kept, with occasional moderate shaking, in contact with 3.11 g. of HK (0.01 mole). A sirupy coating gathered about the powdered solid acid upon mixing. The mixture did not change in appearance over a period of twenty-four hours. The sirupy substance then, however, began forming powdery crystals. This change appeared to be complete after forty-eight hours (seventy-two hours after mixing) and the mixture was filtered. The solid matter, washed with a little ether, consisted of 3.72 g. of white powdery crystals, melting from about 150° to 185°. Examination of the solid showed it to be practically pure A·HK, about 20% resolved.

III. With HK Originally Dissolved; Sirup Formed.—(a) 1 cc. of A added to 128 cc. of a solution of HK in ether, 0.061 mole/liter (equivalent amounts) gave immediately a great deal of suspension which rapidly gathered into clear sirupy droplets. The clear supernatant solution was decanted twenty minutes after the mixture was made up. Examination of the supernatant solution showed it to be appreciably acidic and that no partial resolution had been effected by precipitating the sirupy phase. (b) 1 cc. of A was dissolved in 19 cc. of ether and the solution added to 128 cc. of a solution of of HK in ether, 0.061 mole/liter (equivalent amounts). A great deal of suspension was immediately produced (just as in the previous case) and soon gathered into sirupy droplets. Twenty-four hours later the sirupy phase had partially solidified and changed into powdery crystals. The powdery substance was loosened from the containing vessel, filtered off and washed with a little ether; 0.82 g. of a white powder, melting from about 103° to about 175°, was thus obtained. Examination showed the powder to be fairly pure A·HK not resolved to more than 2%. A duplicate experiment which stood for seventeen days produced no detectable resolution. (c) 1 cc. of A dissolved in 36 cc. of ether was added to 64 cc. of a solution of HK in ether, 0.061 mole/liter (ratio A/HK = 2). The addition of the amine solution produced a copious suspension which rapidly gathered into sirupy droplets. During three days' standing the sirup changed over into white powdery crystals. The powder, filtered off and washed with a little ether, weighed 0.87 g. and melted at about 105–180°. Examination showed the powder to be practically pure (*dl*) A·HK. (d) Added 1.29 cc. of A, 2.5 cc. of acetone and 2.5 cc. of alcohol to 140 cc. of a solution of HK in ether (comml.), 0.0715 mole/liter (equivalent amounts). A suspension formed upon adding the amine soon disappeared, leaving a clear solution. Upon slight shaking, however, the suspension reappeared. It was found that a separate liquid phase was present, spread out thinly and uniformly along the container in contact with the solution. Within an hour crystals began to form. After twenty-four hours the crystals were filtered off and washed with a little ether: 2.01 g. of colorless crystals, melting 165–178°. Examination showed the solid matter to be prac-

tically pure A·HK, about 27% resolved. (e) 1 cc. of A added to 64 cc. of a solution of HK in ether, 0.061 mole/liter (ratio A/HK = 2), produced a suspension which collected into a sirupy phase. Within an hour the sirupy phase began changing over into a white powder; this change was completed after about eighteen hours. During two weeks' further standing the powdery substance steadily disappeared and a new type of crystals—feathery needle clusters—formed. The feathery needle clusters were filtered off and washed with a little ether: 1.510 g. of colorless crystals, melting at 175–192°. Examination showed the crystals to be practically pure A·HK, 38% resolved.

IV. With (HK) Originally Dissolved; No Sirup Formed.—(a) In 150 cc. of a solution of 2800 cc. of ether (comml.), 100 cc. of acetone and 100 cc. of alcohol, there was dissolved 3.11 g. of HK, then 1.3 cc. of A was added (equivalent amounts). Only a faint turbidity appeared on mixing. Three hours later colorless crystals began to appear and grew rapidly. After forty-eight hours the crystals were filtered off and washed with a little petroleum ether: 0.81 g. of crystals, melting at about 186–207°. Examination showed the crystals to be practically pure A·HK, about 80% resolved. (b) In 150 cc. of a solution of 2800 cc. of ether (comml.), 100 cc. of acetone, 100 cc. of alcohol was dissolved 3.11 g. of HK, then 2.6 cc. of A (ratio A/HK = 2) added. Only a faint turbidity appeared on mixing. Two hours after mixing colorless crystals began forming; forty-eight hours later they were filtered off and washed with a little petroleum ether: 0.75 g. of crystals, melting at about 186–207°. Examination showed the crystals to be practically pure A·HK, about 80% resolved. (c) 2.58 cc. of A, 5 cc. of acetone and 5 cc. of alcohol added to 140 cc. of a solution of HK in ether (comml.), 0.0715 mole/liter (Ratio A/HK = 2), produced only a slight suspension. The mixture seeded with (*l*)A·HK, began depositing crystals within forty-five minutes. Twelve hours later the crystals were filtered off and washed with a little ether: 2.09 g. of white powdery crystals, melting at 175–187°. Examination showed the crystals to be practically pure A·HK, about 75% resolved.

V. Solubility of A·HK in Ethereal Solutions.—(a) 1.802 g. of (*dl*)A·HK was added to 200 cc. of ether and the mixture shaken for ten hours daily on an efficient shaker for four weeks. The ether was examined (in a 2-dm. tube) each week; rotations all zero. No measurable amount of HK or K^- was dissolved. (b) 3.105 g. of (*dl*) A·HK was added to a solution of 1 cc. of A (racemic) in 200 cc. of ether and the mixture shaken for ten hours daily on an efficient shaker for four weeks. The ethereal solution was examined each week for rotation: $\alpha_{2\text{ dm.}}^{\text{room temp.}}$ 06′. Examination of the solution and of the salt recovered indicated that the amine had been partially resolved. (c) 6.14 g. of powdered (*l*)A·HK was added to 300 cc. of a solvent mixture consisting of 280 cc. of ether (comml.), 10 cc. of acetone and 10 cc. of alcohol. The mixture was shaken violently for twelve hours, allowed to stand for twelve hours and then filtered. Examination of the filtrate indicated that the salt had dissolved to the extent of roughly 0.005 mole/liter.

VI. Partial Resolution of A at a Low Temperature.—The investigation of the resolution of A by HK at a low temperature paralleled that at room temperature. The behavior of the reaction mixtures was analogous. The course of the development of the resolution process is clear from the results at room temperature. We shall summarize only the salient findings of the preliminary low temperature investigation.

Solutions of (*dl*)A and HK, 1/1 or 2/1 by mols, saturated at room temperature with respect to (*l*)A·HK in acetone, alcohol, ethyl acetate, or in 25% by volume or 50% by volume alcoholic ether as solvents, could be cooled in contact with and kept in contact with (*l*)A·HK at about −70° for twenty-four hours with thorough shaking from time to time without any noticeable precipitation or crystal growth occurring. These same solutions warmed to room temperature deposited large crops of crystals rapidly—obvious crystal growth getting well under way in each case within thirty minutes after warming to 20°.

The addition of considerable ether to the solvent media reduces the viscosity of the solutions, permitting rapid precipitation and optically clear supernatant solutions.

Pure ether or ether containing only very small amounts of water, alcohol, acetone or ethyl acetate causes precipitation of sirups, separation of sirups not being accompanied by any resolution. The sirups, or congealed sirups, at low temperature change extremely slowly into crystals.

By proper choice of solvents there can be brought about at −70° rapid crystal formation resulting in high resolution and clear mother liquor. The following is an example of a satisfactory low temperature resolution test: 5.16 cc. of A (0.04 mole), 10 cc. of acetone, and 10 cc. of alcohol were added to 280 cc. of a solution of HK in ether (comml.), 0.0715 mole/liter (0.02 mole). The clear solution was seeded with (*l*)A·HK and two hours later when crystal growth was barely visible the mixture was immediately cooled to about −70°. Rapid crystal growth ensued; eleven hours later the mixture consisted of clear solution above a good crop of crystals. A sample of solution was then introduced into the low temperature polarimeter tube

Time	Temp., °C.	
8:25	−72	2°36′ ± 3′
8:35	−73	

The sample was removed, boiled, cooled, re-introduced into the tube

8:55	−72	2°37′ ± 3′
9:05	−71	

The rest of the solution was decanted from the crystals and the latter washed with a little ether. There was obtained 2.53 g. of colorless crystals, melting at 193–207°. Examination showed the crystals to be practically pure A·HK, about 90% resolved.

VII. A Method of Freeing Amines at Low Temperature.—By the use of a relatively strong amine, amines can be liberated from salts at low temperatures into solvents permitting of polarimetric observation. A comparison of the process at room temperature and at −70° follows. (The polarimeter observations in the test below were made at room temperature. For a rapidly racemizing amine, the observations would be made at low temperature.) (a) Two grams of (*l*)A·HK was added to 250 cc. of a solvent consisting of 28 parts ether (comml.), 1 part acetone, 1 part alcohol by volume and the mixture kept, with moderate shaking from time to time, for twelve hours. A sample of solution then showed $\alpha_{4\text{ dm.}}^{22.5^\circ}$ 26′.

One cc. of diethylamine was then added and the mixture shaken; the solid entirely dissolved, giving a clear solution, $\alpha_{2\text{ dm.}}^{23^\circ}$ 1° 9′. Another 1 cc. of diethylamine and shaking, and still another 1 cc. and more shaking, gave in both cases $\alpha_{2\text{ dm.}}^{23}$ 1° 10′. (b) Two grams of (*l*)A·HK was added to 250 cc. of the solvent described in (a) and the mixture cooled to about −70° and kept, with occasional moderate shaking, for twelve hours. A sample of solution (warmed) gave $\alpha_{2\text{ dm.}}^{22.5^\circ}$ 21′.

One cc. of diethylamine was then added at −70° and the mixture shaken (still at about 70°) moderately for an hour; all the solid did not dissolve. A clear sample of solution was withdrawn through cloth (to remove crystals in suspension) and warmed, $\alpha_{2\text{ dm.}}^{23^\circ}$ 52′.

VIII. Experiments with B and HK.—We did not succeed in obtaining crystalline B·HK formed at low temperature. We tried various mixtures of B and HK, 1/1 or 2/1 by mols, in ether, ether (comml.), with and without alcohol, acetone, ethyl acetate or *n*-butanol. The addition of the base to the acid was varied by having the B concentrated or in solution, the HK undissolved or dissolved, the mixtures originally at room temperature then cooled, or originally cold. In all cases in which the solutions were such as to give a precipitate at low temperature, the precipitate was a sirup (or con-

gealed sirup) which would not change into crystals at a measurable rate at the low temperature.

Optical examinations were made shortly after mixing and at intervals during long standing. The solutions above the sirups, and the sirups themselves dissolved in alcoholic ether, were examined for rotation, heated to boiling, cooled, and re-examined. No changes in rotation (greater than 2 or 3′, within our experimental error) were found.

Samples of the crystalline salt, B·HK, were obtained at room temperature from the slow evaporation of an ethyl acetate solution of the base and acid (ratio 2:1). It melted at 103–106°. Examination showed that its optical activity was entirely due to the anion, K^-.

IX. Experiments with B and HR at Room Temperature.—The behavior of solutions of B and HR was entirely analogous to the behavior of similar solutions of A and HK. The same mixed solvent (29 parts ether (comml.), 1 part alcohol, 1 part acetone by volume) which rapidly precipitated crystalline A·HK also rapidly precipitated crystalline B·HR from concentrations of 0.02 mole of B, 0.01 mole of HR in 150 cc. of solvent. A number of crops of B·HR obtained consisted of colorless crystals, each crop melting in a range of approximately 2° from 120 to 127°.

Twenty-one grams of crude salt was crystallized twice, yielding 20 g. of colorless crystals. Two grams of this was retained for examination and the remaining 18 g. again crystallized, the crystallization not being allowed to go to completion. In this way 15 g. was obtained, of which 2 g. was kept and the 13 g. again crystallized, yielding 10 g.

The three crops, after drying, melted, respectively, at 120–122°, 121–124°, 122–124°; 1.000-g. samples were made up to 50 cc. in aqueous solution containing 10 cc. of *N*/10 hydrochloric acid. These solutions gave the following

	Rotation	Vol. *N*/10 NaOH to titrate to phenolphthalein, cc.
i	$\alpha^{22}_{2\,\mathrm{dm.}}$ 26′	32.65
ii	$\alpha^{22}_{2\,\mathrm{dm.}}$ 27′	32.65
iii	$\alpha^{22}_{2\,\mathrm{dm.}}$ 27′	32.63

These results show that the crystals were practically pure salt (containing no solvent of crystallization), not detectably resolved.

X. Experiments with B and HR at Low Temperature.—Experiments entirely similar to those carried out with A and HK were carried out with B and HR. No evidence was obtained of resolution. The crystalline salt, practically pure, was formed (at about −70°) in a number of tests. In no case was any racemization by heat, or any resolution, detected.

Summary

A method has been developed for the resolution of racemic amines at low temperatures, −70°. The resolution process employed was that of salt formation between amine antipodes and optically active acids. The method was tested and proved using 1-amino-1-phenylethane, an amine known to be resolvable and 1-bromo-*d*-camphor-10-sulfonic acid, a suitable acid. In the course of testing the method, it was found that formation of *crystalline* salt was necessary for resolution. Under the conditions most favorable for resolution at low temperatures, success in the resolution process appeared to depend upon a difference between the amine enantiomorphs in their *rate* of forming salt crystals from supersaturated

solutions, rather than upon a difference in the solubility of the non-enantiomorphic salts.

The resolution of an asymmetrically substituted amine, benzylethylaniline, possessing no carbon asymmetry, was finally attempted employing, in turn, 1-bromo-*d*-camphor-10-sulfonic acid, and *d*-camphor-1′-sulfonic acid. No evidence of resolution was found.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE FREE ENERGY OF ENOLIZATION IN THE GASEOUS PHASE OF SUBSTITUTED ACETOACETIC ESTERS

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Previous measurements of the equilibrium constants of the change keto $\longrightarrow$ enol have all been carried out with solutions of the two components or with the equilibrium liquid mixture. K. H. Meyer,[1] the first investigator to obtain satisfactory quantitative results, found that the nature of the solvent affected enormously the equilibrium constant. It was thus difficult to obtain a satisfactory comparison of a series of substituted ketonic esters or diketones; his proposal to compare them all in the same solvent was only partially successful as the comparisons in many cases varied with the nature of the solvent. The use of the pure liquid equilibrium mixtures as a basis of comparison is clearly open to the same sort of error and a serious and unknown solvent effect is introduced into the measurements. It seemed probable that the greatest regularity between structure and free energy of enolization would be found by taking the gaseous phase (preferably at low pressure) as the standard state. Such a choice of the standard state in the reduction of a series of chloroquinones brings out regularities which are obscured by physical forces when the solid state or a solution is used as the standard state.[2] We have therefore undertaken to measure the equilibrium constant of enolization in the gaseous state for acetoacetic ester, eight substituted acetoacetic esters, four β-diketones and a few other related compounds. The results show clearly that there is a regularity between the structure of the compound and the free energy of enolization in the gaseous state.

Since the interconversion of the two tautomeric isomers does not proceed at all readily in the gaseous state at room temperature, it was necessary to use the liquid phase as an intermediary. It is clear that if chemical

[1] Meyer, *Ber.*, **45**, 2846 (1912).

[2] Conant, THIS JOURNAL, **49**, 293 (1927); a further discussion of this point and a preliminary statement of the results of the present investigation are given in *Ind. Eng. Chem.*, **24**, 466 (1932).

equilibrium involving two isomers is maintained in a liquid throughout an experiment and if the liquid in turn is in physical equilibrium with the gas, the composition of the vapor must represent the equilibrium condition in the gaseous state. If condensation of the vapor now takes place without isomerization, the composition of the condensate is a correct measure of the equilibrium corresponding to the gaseous state. The experimental procedure was briefly as follows. The pure liquid compound (a mixture of the two forms) was placed in a Pyrex flask of 50-cc. capacity and a small amount of solid anhydrous barium hydroxide was added as a catalyst. The flask was sealed to a Pyrex receiver immersed in an ether–carbon dioxide bath and evacuated with a pump to a pressure of less than 0.01 mm. of mercury. Physical equilibrium between the liquid and gaseous phases was assured by rocking the flask back and forth mechanically so that the surface was continuously renewed by the agitation. To prevent refluxing the neck of the vessel and connecting tube were warmed by an electric heating coil wound on the apparatus. The temperature of the liquid in the flask was controlled by placing the flask in a small water-bath whose temperature was read throughout the distillation.

A great many experiments were carried out to test the assumptions underlying this method. The Pyrex receiver, which consisted of a tube about 1 cm. in diameter and 10 cm. long, was rendered non-catalytic by the method of Rice and Sullivan.[3] This consists of heating the carefully cleaned tube to the point of collapse in a blast lamp; the Pyrex test-tube into which the distillate was poured and the Pyrex pipet used for transferring a sample for analysis received the same treatment. As a proof of the non-catalytic effect of the receiver, the fact may be cited that 77% enolic acetoacetic ester in such a receiver dropped to 45% only after fifteen hours at room temperature (equilibrium concentration 7%). Since the receiver was at about $-80°$ throughout a determination and the contents were analyzed within five minutes after the receiver had been warmed to room temperature, it is evident that any isomerization in the receiver was negligible. A further test of the point at issue was afforded by the results of successive sampling of the contents of the receiver. In every case except two the results obtained were consistent. In the case of acetylacetone and methyl acetoacetate, however, the pouring from the receiver to the "aseptic" test-tube had to be omitted. With these compounds the receiver was cut off from the apparatus and the material rapidly withdrawn from the cold receiver with an aseptic pipet. Under these conditions successive samples gave results which showed but a slight decrease of enol content within the time required for analysis.

Both the direct and indirect bromine titration procedures were tried as methods of determining the enol content of the distillate. With un-

[3] Rice and Sullivan, THIS JOURNAL, 50, 3048 (1928).

substituted acetoacetic ester and acetylacetone, the indirect method (using beta naphthol, potassium iodide and titrating the iodine evolved) gave slightly higher results than the direct method. With all the other compounds, the direct method when properly carried out was found much more reliable;[4] the difficulty with the indirect method when applied to the substituted acetoacetic esters is that the iodo compound liberates its iodine but slowly and the apparent enol content, therefore, depends on the time of heating of the solution, reaching as a limit a value near that obtained by the direct method. Since we were always working with mixtures richer in enol than the equilibrium mixture, any error caused by the catalytic effect of the added bromine would tend to cause our results to be too low. Actually, however, they were somewhat higher than the limit approached by the indirect method. For this reason, and because of the consistency and reproducibility of the results obtained by the direct titration, we employed it in every case except those mentioned above. The procedure was as follows. The sample was introduced from a calibrated "aseptic" pipet into 20 cc. of ethyl alcohol cooled to $-10°$. The solution was immediately titrated with approximately 0.1 N bromine in methyl alcohol until a yellow color was permanent for several seconds; the titration takes less than a minute. Immediately a volume of the bromine solution of exactly the amount used in the titration is run into another flask, an aqueous solution of potassium iodide added and the mixture titrated with standard thiosulfate solution in the usual manner; the amount of bromine consumed by the sample is calculated from the thiosulfate used.

The assumptions in regard to the attainment of chemical and physical equilibrium during the distillation can be tested by stopping the distillation from time to time and analyzing the distillate. Unless equilibrium conditions prevail, successive distillates would hardly be expected to have the same composition. This is easily shown by omitting the catalyst from the liquid phase, when the first distillate is high in enol and progressively diminishes in enol content with each fraction. Typical results which were obtained under what we believe to have been equilibrium conditions, were as follows: acetoacetic ester, four successive fractions had the following enol content: 45.6, 46.3, 47.9, 47.9%; three successive fractions of α-propyl ethylacetoacetate had the following compositions: 11.9, 12.2, 12.2% enol. In two cases we had clear evidence that we were not dealing with equilibrium conditions; one of these was with α-*sec.*-butyl ethyl acetoactate using the usual barium hydroxide as a catalyst. The enol content of the fractions regularly diminished from 16.5 to about 8%. That the failure was due to insufficient catalytic effect was shown by treating high enol *sec.*-butylacetoacetic ester (10.6%) with barium hy-

[4] Dieckmann, *Ber*, **55**, 2470 (1922), gives a detailed discussion of the two methods.

droxide in Pyrex, it required one hundred and sixty-eight hours for the liquid equilibrium state (8.8%) to be reached. By using a drop of tetramethylammonium hydroxide (a solution concentrated to a sirup on the water-bath) as a catalyst, fairly satisfactory results were obtained with the *sec.*-butyl compound. In the case of tricarbethoxymethane, no conditions were found that yielded a satisfactory equilibrium. Only a rough estimate of the value in the vapor phase could be obtained from an analysis of the very first distillate. The fact that these difficulties manifested themselves so clearly leads us to believe that equilibrium conditions were at hand in all the other cases where consistent results were obtained on the analysis of successive distillates. It should be further mentioned that it was found that the temperature of the neck of the distilling flask was of no influence provided it was sufficient to prevent refluxing and that the rate of distillation was without significance. The usual rate of distillation was about 20 cc. an hour.

The compounds used in this work were all carefully purified by a final fractional distillation under diminished pressure and were used shortly after preparation. Many of them are not stable and after several months' standing had sufficiently decomposed to give unreliable results. The purity of these compounds cannot be checked by means of the usual physical constants since the liquid phase is a mixture of isomers. An analysis of the carbon and hydrogen content, however, is a satisfactory method of detecting any considerable amount of impurity. This is particularly important in the case of the alkyl derivatives made by alkylation which might contain the unalkylated parent compound. Table I lists the compounds we employed, their source, our analytical data, and the enol content of the equilibrium liquid; the previous determination of the enol content of the pure liquid is given in the next to the last column.

Discussion of the Results

The results obtained are summarized in Table II. The first two columns of figures record the results obtained by the method just outlined, the per cent. of enol being the composition of the distillate under equilibrium conditions, the liquid being kept at 25°. The value of $\Delta F(= -RT \ln K)$ for the reaction keto (gas) $\longrightarrow$ enol (gas) is given in kilogram calories per mole in the second column. The corresponding values of the percentage of enol and ΔF for the reaction in the liquid equilibrium mixture, in a 0.1 M hexane solution and a 0.1 M solution in absolute alcohol are given in the other columns. The solutions were allowed to stand till the increase of enol content reached a maximum; this usually required one day. In the case of α-ethylacetoacetic ester, the equilibrium was approached from both sides in hexane solution and in a number of cases piperidine was added to the solution (concn. 0.05 M) in a separate experi-

TABLE I

SUMMARY OF DATA ON PREPARATION AND PURITY OF COMPOUNDS

Substance	Preparation references	Analyses, % Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found		Percentage enol in liquid Found	Percentage enol in liquid Previously determined
$CH_3COCH_2COOC_2H_5$	Eastman product	55.4	55.23	55.31 55.28	7.70	7.79	7.83 7.77	7.3	7.4 *Ber.*, **44**, 2718 (1911)
$CH_3COCH(CH_3)COOC_2H_5$	"Organic Syntheses," Vol. VII, p. 36	58.33		58.30 58.31	8.32		8.37 8.35	4.1	4.1 THIS JOURNAL, **52**, 4358 (1930)
$CH_3COCH(C_2H_5)COOC_2H_5$	"Organic Syntheses," Vol. VII, p. 36	60.80		60.60 60.71	8.86		8.88 8.90	2.95	3.0 *ibid.*, **52**, 4358 (1930)
$CH_3COCH(C_3H_7\text{-}n)\text{-}COOC_2H_5$	"Organic Syntheses," Vol. VII, p. 36	62.75		62.45 62.58	9.30		9.35 9.30	7.0	
$CH_3COCH(C_3H_7\text{-iso})\text{-}COOC_2H_5$	Bischoff, *Ber.*, **28**, 2620 (1895)	62.75		62.77 62.64	9.30		9.36 9.32	4.9	
$CH_3COCH(C_4H_9\text{-}n)\text{-}COOC_2H_5$	"Organic Syntheses," Vol. VII, p. 36	64.5		64.42 64.36	9.68		9.36 9.44	6.1	
$CH_3COCH(C_4H_9\text{-sec.})\text{-}COOC_2H_5$	THIS JOURNAL, **30**, 1149 (1908)	64.5		64.7 64.9	9.68		9.62 9.55	8.4	
$CH_3COCH(C_6H_5)COOC_2H_5$	Beckh, *Ber.*, **31**, 3160 (1898); Dimroth, *ibid.*, **36**, 2243 (1903); Post, THIS JOURNAL, **52**, 4358 (1930)	69.9		70.1 70.3	6.80		7.00 7.09	30.5	39.2 *ibid.*, **53**, 1496 (1931) 30.0 *ibid.*, **54**, 1963 (1932)
$CH_3COCH(CH_2C_6H_5)COOC_2H_5$	"Organic Syntheses," Vol. VII, p. 36	70.9		71.3 71.0	7.27		7.31 7.27	4.9	4.9 *Ber.*, **45**, 2854 (1912)
$CH_3COCH_2COCH_3$	Kahlbaum preparation used	B. p. 137.5–139°			B. p. 137.5–138.5°			76.5	76 *ibid.*, **45**, 2857 (1912) 82 *Ann.*, **426**, 161 (1922)
$CH_3COCH(CH_3)COCH_3$	THIS JOURNAL, **52**, 3212 (1930); *J. Soc. Chem. Ind.*, **44**, 462 (1925)	63.2		63.3 63.4	8.77		8.95 8.84	29.5	31.2 *Ber.*, **45**, 2859 (1912) 31.0 *Ann.*, **426**, 161 (1922)
$CH_3COCH(C_2H_5)COCH_3$	THIS JOURNAL, **52**, 3212 (1930); *J. Soc. Chem. Ind.*, **44**, 462 (1925)	65.6		65.3 65.3	9.38		9.28 9.44	26.4	31 *ibid.*, **426**, 161 (1922)
$CH_3COCH(CH_2C_6H_5)COCH_3$	THIS JOURNAL, **52**, 3212 (1930); *J. Chem. Soc.*, **127**, 797 (1925)	75.8		75.45 75.65	7.37		7.48 7.67	61	
$CH_3COCH(COOC_2H_5)_2$	*Ann.*, **266**, 110 (1891); *Am. Chem. J.*, **14**, 495 (1892); *Ann.*, **426**, 161 (1922)	53.5		51.8 51.9	6.93		6.81 6.86	66.5	64 *Ber.*, **45**, 2854 (1912) 70 *Ann.*, **426**, 161 (1922)
$CH(CO_2CH_3)_3$		M. p. 45–46°.			M. p. 43°; B. p. 111°–112° (4 mm.)			1.16	
$CH(CO_2C_2H_5)_3$	*Am. Chem. J.*, **14**, 495 (1892)	51.7		51.6 51.5	6.90		6.75 7.09	0.7	0.2 *Ber.*, **45**, 2864 (1912)
$CH_3COCH_2COOCH_3$	*Ann.*, **257**, 355 (1890)	51.7		51.65 51.95	6.90		7.14 7.28	5.7	4.9 *ibid.*, **45**, 2869 (1912)

TABLE II

A TABLE OF THE FREE ENERGY CHANGE OF ENOLIZATION, EXPRESSED IN LARGE CALORIES, OF THE COMPOUNDS STUDIED. THESE ARE REFERRED TO FOUR DIFFERENT STANDARD STATES AT 25°

Substance	Gaseous phase		Pure liquid		0.1 *M* solution in hexane		0.1 *M* solution in abs. alcohol	
	% enol	ΔF	% enol	ΔF	% enol	ΔF	% enol	ΔF
$CH_3COCH_2COOCH_3$	53.7–55.0	−0.1	5.7–6.0	1.6				
$CH_3COCH_2COOC_2H_5$	45.3–46.9	0.1	7.3–7.8	1.5	48–50	0.0	9–11.0	1.2
$CH_3COCH(CH_3)COOC_2H_5$	13.5–14.5	1.1	4.0–4.2	1.9	10.3–12.9	1.1	5.1	1.7
$CH_3COCH(C_2H_5)COOC_2H_5$	9.8–10.2	1.3	2.9–3.1	2.1	14.0–15.0	1.1	3.0–4.0	2.0
$CH_3COCH(C_3H_7\text{-}n)\text{-}COOC_2H_5$	13.1–13.4	1.1	6.8–7.2	1.5	14.3–14.5	1.1		
$CH_3COCH(C_3H_7\text{-iso})\text{-}COOC_2H_5$	6.0– 6.25	1.6	4.8–5.0	1.8	5.85–6.1	1.6		
$CH_3COCH(C_4H_9\text{-}n)\text{-}COOC_2H_5$	13.0–15.0	1.1	6.0–6.2	1.6	9.0–11.	1.3	5.7–6.4	1.6
$CH_3COCH(C_4H_9\text{-sec.})\text{-}COOC_2H_5$	*8.0–10.0	*1.4	8.3–8.5	1.4	8.6–9.9	1.3	9.0–9.5	1.4
	[a](54.0–56.0)	[a](−0.15)						
$CH_3COCH(C_6H_5)COOC_2H_5$	*78–82	*−0.8	29.5–31.5	0.5	66–68	−0.4	30.4–31.0	0.5
	[a](9.0–10.0)	[a](1.6)						
$CH_3COCH(CH_2C_6H_5)COOC_2H_5$	11.0–14.0	1.2	4.8–5.0	1.8	11–13	1.2	5.0–5.5	1.7
$CH_3COCH_2COCH_3$	91–93	−1.3	76–80	−0.7	91.4–92	−1.3	82.5–83.5	−1.0
$CH_3COCH(CH_3)COCH_3$	43.5–44.5	0.1	30–31	0.5	58.5–59.4	−0.2	30.6–32.3	0.4
$CH_3COCH(C_2H_5)COCH_3$	*34.0–37.0	*0.3	26–27	.6	26.2–26.7	0.6	27.0–30.4	.5
	[a](58.0–60.0)	[a](−0.25)						
$CH_3COCH(CH_2C_6H_5)COCH_3$	68.0–72.0	−0.5	61–62	−0.25	66–70.0	(−0.4–0.6)	45.0–47.5	−0.1
$CH(COOCH_3)_3$	8–16	1.0–1.4	1–1.2	2.6				

[a] The three groups of results marked with an asterisk are of a lower order of accuracy since they are extrapolated from higher temperatures. The values in parentheses are those actually determined at 95°.

ment and the solution allowed to stand for twelve hours to ensure equilibrium. The probable accuracy of the method is indicated by giving the range of the analytical figures for the percentage of enol; the average has been taken as the most probable. The free energy values are significant we believe in most cases to within a tenth of a kilogram calorie. The values for phenyl- and benzylacetoacetic ester and benzylacetylacetone are subject to the uncertainty of an extrapolation from a higher temperature since the compounds were not sufficiently volatile at 25°. In all cases no experiment was accepted unless at least two successive fractions gave the same value of the enol content, and several separate experiments with fresh samples of material gave consistent results. In most cases more than one piece of apparatus was employed and in a few instances the results were duplicated several months later with a freshly prepared sample of ester.

A study of the data presented in Table II reveals that there is great regularity in the values of ΔF referred to the gaseous phase but this regularity disappears when the liquid equilibrium mixture or a solution is used as a basis of comparison. This is very clearly brought out in the summary of the effect of substitution on the values of ΔF referred to the different standard states given in Table III. It is evident that the liquid

TABLE III

Groups involved	ΔF (gas)	ΔF (liq.)	ΔF (Hexane)	ΔF (C_2H_5OH)
1. Replacement of H by primary alkyl group				
(a) In acetoacetic ester series				
CH_3	1.0	0.4	1.1	0.5
C_2H_5	1.2	.6	1.3	.8
C_3H_7	1.0	.0	1.0	
C_4H_9	1.0	.1	1.3	.4
$CH_2C_6H_5$	1.1	.3	1.2	.5
(b) In acetylacetone series				
CH_3	1.4	1.2	1.1	1.4
C_2H_5	1.6	1.3	1.9	1.5
$CH_2C_6H_5$	0.8	0.45	0.7–0.9	0.9
2. Replacement of H by secondary alkyl				
In acetoacetic ester series				
(sec.)-C_3H_7	1.5	0.3	1.6	
(sec.)-C_4H_9	1.3	−0.1	1.3	0.2
3. Replacement of carbethoxy by acetyl in compound $ACOOC_2H_5$ where A is:				
CH_3COCH_2–	−1.4	−2.2	−1.3	−2.4
$CH_3COCH(CH_3)$–	−1.0	−1.4	−1.3	−1.2
$CH_3COCH(C_2H_5)$–	−1.0	−1.5	−0.7	
$CH_3COCH(CH_2C_6H_5)$–	−1.7	−2.0		
4. Replacement of H by phenyl in acetoacetic ester				
C_6H_5	−0.7	−1.1	−0.4	−0.7
Average deviation from ΔF (gas)	...	0.64	0.17	0.48

phase results are the most irregular and the values obtained with dilute alcoholic solutions are nearly as bad. On the other hand, a dilute hexane solution seems to approximate the gaseous state in most instances. The regularity with this solvent is, however, less than with the gaseous phase, and one could not be certain that with other compounds the errors might not be larger. For ketonic esters and diketones, the use of a dilute hexane solution will probably yield results significant to ± 0.3 kg. cal. It is clearly useless to make measurements with the liquid equilibrium mixture if one is interested in energy differences less than 1.5 kg. cal. (a power of ten in the equilibrium constant).

The relation between structure and ΔF(gas) shown by the data in Tables II and III needs but little discussion. The difference between the ethyl and methyl esters of acetoacetic ester is negligible (0.2) as would be expected. The primary alkyl groups are practically equivalent and only slightly more effective in decreasing enolization in the diketones than in the ketonic esters. The *sec.*-alkyl group is appreciably more effective in decreasing enolization than a primary group. The benzyl group is very like an alkyl group in its effect, but the phenyl group has a marked action in the opposite direction decreasing ΔF by 0.7 (increasing enolization). The acetyl group is more effective in increasing enolization than the carbethoxy by about one large calorie in a number of compounds. A few measurements with acetylmalonic ester (ethyl) and tricarbethoxymethane were not satisfactory and are not included in Table II but they indicated values of ΔF(gas) of about -0.5 and 1.8, respectively. Malonic ester showed no definite enol content in the distillate and ΔF(gas) is therefore greater than $+6$ since 0.006% of enol could have been determined. A comparison of malonic ester and acetylacetone (ΔF gas $= -1.3$) shows that the replacement of two carbethoxy groups by two acetyl groups decreases ΔF by at least 7 Cal., or 3.5 Cal. per group. This is much larger than the effect summarized in Table III (3), where a similar replacement decreases ΔF by about 1–2 Cal. A comparison of acetylmalonic ester and tricarbethoxymethane shows a similar large effect of 2.8 Cal. caused by the change of one ester group to a methyl ketonic group. Even these approximate results are sufficient to show that no simple additive relation holds in regard to the effect of groups on ΔF of enolization. This is not strange considering that the enol form must have some such structure as that of a chelate ring,[5] and that all the groups attached to the ring may exert a mutually dependent influence. (In every case which we have investigated the enol form is the more volatile which would certainly not be the case if the simple formula $RC(OH)=CHCOR'$ were correct.)

[5] N. V. Sidgwick, *J. Chem. Soc.*, **127**, 907 (1925).

A number of experiments were performed keeping the temperature of the liquid in the distilling flask at different temperatures. The effect of change of temperature on the composition of the distillate is very slight and it was found impossible, therefore, to obtain significant values of the temperature coefficient of K(gas) and hence of ΔH(gas). Errors which are negligible in determining ΔF are enormously magnified in determining ΔH by this method when it is small and only a short range of temperature is available. There is every reason to believe that the entropy change in the reaction keto (gas) $\longrightarrow$ enol (gas) is very small although one isomer is a chelate ring compound and the other an open-chain ketone or ketonic ester. We should expect that ΔH(gas) would be very close to ΔF(gas), therefore. In every case that we examined, except ethylacetylacetone, there was a definite decrease of K(gas) with increase of temperature; with ethylacetylacetone there was no appreciable change. The values of ΔH(gas) varied from -2.3 to 0, which, combined with the values of ΔF-(gas) for the appropriate compound, gave values for $T\Delta S$ (298°K.) of from -0.3 to -2.7, with many values near the latter figure. These indicate a much larger entropy change in the reaction than seems reasonable but in view of the uncertainties of the determination we are not inclined to attach much significance to this finding. Unfortunately, there seems no way of refining the method to yield significant information on this point.

The uncertainty in the temperature coefficient of K(gas) is reflected to a less extent in the extrapolation to 25° of the values obtained at 95° for the phenyl and benzyl compounds; they render the values for these compounds, however, much less certain than the others given in Table II. Possibly the irregularity between the effects of the benzyl group in the acetoacetic ester series and the acetylacetone series is due to experimental error caused by the uncertainties of the extrapolation (see Table III, where the benzyl group has the same effect as the alkyl groups in the acetoacetic ester series, but 0.8 kg. cal. less than the methyl or ethyl group in the acetylacetone series).

Summary

The free energy of enolization in the gaseous phase of a series of substituted acetoacetic esters and certain related compounds has been measured. A comparison of these results with the free energy change referred to the liquid equilibrium mixture or a dilute solution shows that regularities between structure and free energy are often obscured by solvent effects which may be as large as 1 kilogram calorie.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A STUDY OF THE RATE OF ENOLIZATION BY THE POLARISCOPIC METHOD

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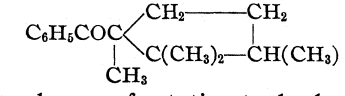
It is a well-known fact that optically active ketones, esters and acids are racemized by alkaline reagents only if the alpha carbon atom is the center of the asymmetry and carries a hydrogen atom. The generally accepted explanation of this phenomenon is the formation of an inactive enol in very small quantities which then reverts to the optically inactive keto form. In particular the investigation of McKenzie[1] using ketones, esters and amides have provided us with numerous examples in support of this theory. Dakin[2] has shown that an hydantoin cannot be racemized unless there is a hydrogen atom on the asymmetric alpha carbon atom; the same is true of alpha amino acids.[3] The evidence is so overwhelming that there seems to be no escape from the conclusion that the phenomenon of racemization by alkaline reagents occurs only if the asymmetric carbon atom carries a hydrogen atom capable of enolization. If this is the case the rate of racemization may be considered as the rate of enolization and by the use of optically active substances a very convenient method is available for studying the latter process. It should be noted that the rate of enolization cannot be faster than the rate of racemization (whatever mechanism is assumed) since the enol must be an inactive compound because of its structure.

Before proceeding with the study of the rate of enolization of a series of ketones and esters by the polariscopic method, we decided to test once again the possibility of racemizing a ketone which had no hydrogen in the alpha position. In particular we wished to try more vigorous conditions than those we knew to be effective in causing rapid racemization of ketones having an alpha hydrogen. We therefore prepared *d*-campholyl phenyl ketone,[4]



and *d*-methylphenylbutylacetophenone. No change of rotation took place when these compounds were dissolved in solutions of 1.3 *M* sodium butylate in butyl alcohol and allowed to stand for a week, or even when heated for three hours at 100° with a dilute solution (0.017 *M*) of the butylate (higher concentrations of catalyst caused so much discolorization at 100° that no measurements could be made). The

[1] McKenzie and Smith, *J. Chem. Soc.*, **121**, 1348 (1922); McKenzie, Martin and Rule, *ibid.*, **105**, 1585 (1914); McKenzie and Dennler, *Ber.*, **60**, 222 (1927), and other papers. See also Wren, *J. Chem. Soc.*, **113**, 210 (1918).

[2] Dakin, *Am. Chem. J.*, **44**, 48 (1910).

[3] E. Fischer, *Ann.*, **406**, 1 (1914).

[4] Rupe and Jäggi, *ibid.*, **428**, 164 (1922).

d-methylphenylbutylacetophenone, which is new, was made by the following series of reactions

$$C_6H_5C(CH_3)(C_4H_9)OCH_3 \xrightarrow{Na-K} [C_6H_5C(CH_3)(C_4H_9)]K \xrightarrow{CO_2}$$

$$C_6H_5C(CH_3)(C_4H_9)COOH\ (d \text{ separated through quinine salt}) \xrightarrow{SOCl_2}$$

$$d\text{-}C_6H_5C(CH_3)(C_4H_9)COCl \xrightarrow{C_6H_5ZnCl} d\text{-}C_6H_5C(CH_3)(C_4H_9)COC_6H_5$$

The five compounds prepared for the study of their rates of enolization by the polariscopic method were phenylbenzylacetophenone, phenylmethylacetophenone, benzylmethylacetophenone, phenylbenzylacetomesitylene, phenylmethylacetomesitylene and the methyl ester of methylbenzylacetic acid. The ketones were all prepared from the corresponding optically active acids by the action of the aryl zinc halide on the acid chloride. Attempts to prepare optically active phenyltolylacetophenone by the same method failed because complete racemization occurred in the last step in spite of all precautions; this fact deprived us of the most interesting member of our intended series but indicated clearly the increased rate of enolization caused by the presence of two aryl groups on the alpha carbon atom.

Our final experiments with basic catalysts are given in Table I; in addition to these a number of preliminary experiments were carried out which gave essentially the same values but were discarded because the concentration of the catalyst was not sufficiently accurately controlled. The value of k (the monomolecular constant, time expressed in minutes) was determined graphically from a plot of the log of the rotation against the time; the best straight line was run through the points and the reciprocal of its slope multiplied by 2.30. These are the values given in column 5 of Table I. In all the experiments the points fell closely on a line corresponding to a monomolecular reaction; this was found to hold even up to 95% racemization, though in most cases the experiment was continued only to 50–70% conversion. The concentration of catalyst is given in column 3 and the catalytic constant obtained by dividing k by the concn. of catalyst is given in column 6. The initial concentration of optically active material was varied irregularly from 0.007 to 0.05 molar, since the rate was not dependent on this variable.

The constancy of the catalytic constant (Col. 6) within the various sections of Table I is a measure of the validity of the generalization that the rate is proportional to the concentration of the catalyst. This was tested over a ten-fold range in most cases and a twenty-fold range in a few. The proportionality was within the experimental error with sodium butylate, but in the case of sodium methylate an increase as great as 60% in the catalytic constant with a ten-fold increase of concentration occurred in two cases. Aside from these two cases one may conclude that the proportionality holds with the alcoholates within 25%. With piperidine the con-

TABLE I

SUMMARY OF RESULTS

(A) Catalyst, Sodium *n*-Butylate in *n*-Butyl Alcohol

Expt.	Substance	Concn. cat.	Temp., °C.	$k \times 10^2$	Catalytic constant	Activation energy in kg. cal.
1	*l*-Phenylbenzylaceto-	0.00157	22.5	0.246	1.56	14.0 (1, 2)
2	phenone	.00157	37.5	.784		
3		.0157	7.5	.630		14.2 (3, 5)
4		.0157	22.5	2.28	1.45	14.0 (3, 4)
5		.0157	38.0	7.76		14.4 (4, 5)
6	*d*-Phenylbenzylaceto-	.0157	23.0	0.491	0.31	
7	mesitylene	.0157	38.5	1.93		16.1 (6, 7)
8		.1297	8.0	1.25		
9		.1297	24.5	4.63	0.36	13.1 (8, 9)
10	*d*-Phenylmethylaceto-	.00129	22.0	0.407	3.16	
11	phenone	.0129	9.0	1.42		
12		.0129	22.5	4.51	3.50	14.2 (11, 12)
13		.0157	8.0	1.34		
14		.0157	22.5	5.10	3.24	15.1 (13, 14)
15	*d*-Phenylmethylaceto-	.00157	11.0	0.983		12.1 (15, 17)
16	mesitylene	.00157	23.0	2.56	16.3	13.3 (15, 16)
17		.00157	38.0	6.70		12.4 (16, 17)
18		.0157	23.0	28.8	18.3	
19	*d*-Methylbenzylaceto-	.0157	10.5	0.274		15.9 (19, 21)
20	phenone	.0157	22.5	0.800	0.51	14.9 (19, 20)
21		.0157	38.0	3.20		16.6 (20, 21)
22		.1593	24.5	9.16	0.575	

(B) Catalyst, Sodium Methylate in CH_3OH

23	*l*-Phenylbenzylaccto-	0.0144	23.0	0.601	0.42	16.6 (23, 25)
24	phenone	.0144	33.0	1.53		16.7 (23, 24)
25		.0144	38.0	2.36		16.4 (24, 25)
26		.0160	23.0	0.589	.37	
27		.0726	23.0	3.13	.43	
28		.1602	6.0	1.37		
29		.1602	22.5	7.50	.47	16.8 (28, 29)
32	*d*-Phenylmethylaceto-	.0144	7.5	0.320		
33	phenone	.0144	23.5	1.56	1.08	16.4 (32, 33)
34		.0160	24.5	1.79	1.12	
35	*d*-Phenylmethylaceto-	0.00144	7.5	0.238		
36	mesitylene	.00144	22.5	0.685	4.76	11.6 (35, 36)
37		.00144	24.5	0.770	4.68	11.4 (35, 37)
38		.0144	7.5	3.30		
39		.0144	22.5	11.2	7.77	13.4 (38, 39)
40	*d*-Methylbenzylaceto-	0.0144	25.5	0.181	0.09	
41	phenone	.0726	22.5	0.810	.11	
42		.1453	7.0	.364		
43		.1453	22.5	1.62	.11	16.4 (42, 43)

TABLE I (*Concluded*)

(C) Catalyst, Piperidine in Butyl Alcohol

Expt.	Substance	Concn. cat.	Temp., °C.	$k \times 10^2$	Catalytic constant
44	*l*-Phenylbenzyl-	0.963	24.0	0.094	0.97×10^{-3}
45	acetophenone	1.997	25.0	.234	1.18×10^{-3}
46		4.004	25.0	.458	1.14×10^{-3}
47	*d*-Phenylmethyl-	1.977	24.0	.509	2.57×10^{-3}
48	acetophenone	4.004	24.5	.956	2.39×10^{-3}
49	*d*-Phenylmethyl-	0.963	25.5	5.48	
50	acetomesitylene	1.977	24.0	8.46	
51		4.004	23.0	15.70	

(D) Catalyst, Piperidine in Methyl Alcohol

54	*l*-Phenylbenzyl-	0.992	25.0	0.217	2.18×10^{-3}
55	acetophenone	2.005	23.0	.361	1.80×10^{-3}
56	*d*-Phenylmethyl-	0.992	25.0	.572	5.76×10^{-3}
57	acetophenone	2.005	23.0	.710	3.54×10^{-3}
58	*d*-Phenylmethyl-	0.992	22.5	7.67	7.74×10^{-2}
59	acetomesitylene	2.005	24.0	14.10	7.04×10^{-2}
60	*d*-Methylbenzyl-	0.992	25.0	0.062	6.25×10^{-4}
61	acetophenone	2.005	22.0	0.066	3.02×10^{-4}

centration was varied only four-fold and in most cases only two-fold, the catalytic constants showed divergencies of 20%, in some cases decreasing, in others increasing with concentration of catalyst. In spite of certain irregularities which seem to be greater than the experimental error, there seems to be no doubt but that the racemization (enolization) is a pseudo monomolecular reaction, the real reaction being bimolecular between the substrate and the catalyst, the differential expression being as follows where $C_{cat.}$ is the concentration of catalyst and $k_{cat.}$ the true bimolecular constant which is equal to the monomolecular constant divided by the concentration of catalyst. On the whole this bimolecular equation seems to hold as well as in most organic reactions.

$$\frac{dx}{dt} = k_{cat.}\, C_{cat.}\, (a - x)$$

Only a few experiments were performed using acid catalysts, which were found to be much less effective than the alcoholates, but of the same order of effect as piperidine. Thus the catalytic constants at 26° with benzylphenylacetophenone were: H_2SO_4 in $CH_3OH < 1 \times 10^{-5}$; H_2SO_4 in acetic acid 2.7×10^{-4}; HCl in CH_3OH, 6.5×10^{-3}, as compared with 1.45 for sodium butylate and 1×10^{-3} for piperidine in butyl alcohol for the same compound. Two experiments in which the hydrochloric acid concentration in methyl alcohol was varied two-fold indicated that the rate was roughly proportional to the apparent catalyst concentration $k_{cat.} = 5.6 \times 10^{-3}$ and 7.1×10^{-3}. It seems clear that the phenomenon of enolization is a case of acid

and basic catalysis similar to the mutarotation of glucose studied by Brönsted and Lowry and the ideas of these investigators can be applied at least as a first approximation. A proton acceptor and a proton donator seem to be required for the reaction. With the alcoholates, the acid catalyst is the alcohol, the alcoholate ion the base; in acid catalysis in alcohol solution, there are probably a number of species of acid catalysts (the hydrated proton, undissociated acid, alcoholated proton, etc.), and the alcohol itself the base. The rate of enolization is at a minimum in "neutral solvents" where the concentrations of the acid and base are both very low.

In such complicated non-aqueous solvents with the solvent and catalyst both changing, only a qualitative application of Brönsted's ideas can be expected to hold. It is interesting, however, to note that the alcoholates of ethyl, *n*-propyl, *n*-butyl and *sec.*-butyl are all about the same in their effect ($k_{cat.}$ = 2.1 − 1.6 for phenylbenzylacetophenone) whereas with sodium methylate $k_{cat.}$ = 0.4 and with piperidine $k_{cat.}$ = 0.001. The catalytic constants thus parallel the basicity since the pK values[5] of C_2H_5OH and $C_6H_{11}NH^+$ are estimated as 19 and 11, respectively, and methyl alcohol would certainly be expected to be somewhat the strongest acid of the series of alcohols.

In Table II are collected the data of Table I and certain other experiments with other catalysts. For convenience the results are all expressed

TABLE II

RELATIVE RATES OF ENOLIZATION AT 25°

(A) Acetophenone Derivatives [$XYCHCOC_6H_5$]

Substituents on α-carbon atoms (X,Y)	Relative catalytic constants referred to I with: $NaOCH_3$ in CH_3OH	$NaOC_2H_5$ in C_2H_5OH	$NaOC_3H_7(n)$ in $C_3H_7OH(n)$	$NaOC_4H_9(n)$ in $C_4H_9(OH)n$	$NaOC_4H_9(sec.)$ in $C_4H_9OH(sec.)$	$NaOCH_3$ in $C_4H_9(OH)tert.$	$C_6H_{10}NH$ in CH_3OH	$C_5H_{10}NH$ in C_4H_9OH	HCl in CH_3OH
I C_6H_5, $C_6H_5CH_2$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
II C_6H_5, CH_3	3.0		3.0	2.3	2.3	2.1	2.6	2.2	
III $C_6H_5CH_2$, CH_3	0.26	0.31	0.67	0.35	0.34	0.40	0.29	0.06	7.0

(B) Acetomesitylene Derivatives [$XYCOC_6H_2(CH_3)_3$]

IV C_6H_5, $C_6H_5CH_2$	0.35			0.21					
V C_6H_5, CH_3	21	10.5	10.8	12.7	14.4	12.8	35.5	36.2	

(C) Methyl Ester [$XYCHCOOCH_3$]

VI $C_6H_5CH_2$, CH_3	0.003

The constants were determined with a concentration of catalyst of approximately 0.01 molar in the case of the alcoholates, about 2 *M* with piperidine and 2 *M* with hydrochloric acid. In each case the concentration of catalyst was accurately measured and this value used in determining the catalytic constant.

[5] Danner, THIS JOURNAL, **44**, 2841 (1922), gives $k = 7 \times 10^{-20}$ for C_2H_5OH in ethyl alcohol.

as rates relative to that of phenylbenzylacetophenone with the same catalyst. It is clear from a brief inspection of the table that the relative rates are not independent of the catalyst. Even with the series of closely related catalysts, the alcoholates, there are divergencies as much as 100% in a number of cases and 20 to 50% in many others; these divergencies seem to be beyond any possible experimental error. When we turn to such different catalysts as piperidine and hydrochloric acid, enormous irregularities occur. For example, with piperidine in *n*-butyl alcohol, methylbenzylacetophenone is enolized only about one-twentieth as fast as the reference compound, whereas with most other alkaline catalysts the ratio of the two rates is about one-third. With hydrochloric acid, the compound actually racemized faster than the reference substance, instead of more slowly. When we consider the complicated nature of the reaction which involves the interaction of the ketone with a proton donator and a proton acceptor, the results are not at all surprising. They show, however, *the impossibility of making any generalizations about the rate of enolization without regard to the solvent or catalyst.* It is, of course, quite probable that the actual mechanism of proton transfer may be different under different conditions.

In view of the difficulties mentioned above, it is possible to compare the effect of substituent groups on the rate in only a very rough and approximate way. Taking the average of the alcoholate results as a basis of comparison, it is clear that substitution of methyl or benzyl by phenyl increases the rate by three- to six-fold (III *vs.* I and III *vs.* II). This increase in the rate of enolization parallels the greater degree of enolization caused by the introduction of a phenyl group in acetoacetic ester[6] ($K = 0.45$) as compared with α-methylacetoacetic ester ($K = 0.05$) or α-benzylacetic ($K = 0.06$, all equilibrium constants in dilute alcohol at 25°). A similar parallelism with the free energy measurements is seen with the low rate of enolization of the ester (VI) compared to the corresponding ketone; here the ratio is about a hundred times. The ratio of the equilibrium constants of acetoacetic ester and acetylacetone varies from 10 to 40 depending on the standard state chosen;[6] (though this is the best comparison available it is not very satisfactory as in the replacement of $COOCH_3$ by $—COCH_3$ a methyl and not a phenyl ketone is involved). The difference caused by the replacement of a benzyl by a methyl group (I *vs.* II and IV *vs.* V) does not find its analogy in the free energy measurements, where the two groups are nearly equivalent. The substitution of the phenyl group by the mesityl group in one series (I *vs.* IV) decreases the rate, in the other (V *vs.* II) it increases the speed of enolization by basic catalysts.

The irregularities exhibited in Table II are in part due to the small range between the most rapidly enolized and the least (only about 10^4). Complications due to the effect of solvent would be expected to obscure relation-

[6] Conant and Thompson, THIS JOURNAL, **54**, 4039 (1932).

ships between compounds differing less than five-fold in the rate, for even if there were a parallelism between the equilibrium constant and the rate of enolization (due to the fact that the rate of ketonization was independent of structure), the solvent effects would amount to ± 500 cal.,[6] which corresponds to about two to three-fold difference in k. While there is, perhaps, some such general parallelism indicated by the discussion of the preceding paragraph, it is clear that there must be many disturbing factors. Unless one wishes to assume that entirely different forces are at work here than in the case of the substituted acetoacetic ester, one must conclude *that the relation between free energy of isomerization and structure is more regular than that between rate of isomerization and structure.*

The activation energy calculated from the temperature coefficient is given in the last column of Table I. The average value is about 14,000 cal.; it was not possible to obtain sufficiently accurate and reliable values to test the question of whether or not there was a relation between the rates and activation energies. By an extrapolation of the free energy measurements of diketones and keto esters,[6] one feels quite confident that $\Delta F > +6000$ for the acetophenone derivatives and ΔH is not far from this value (since ΔS for an isomeric change is small). This sets a lower limit to the values of ΔF and ΔH for the enolization; an upper limit can be placed on the value of ΔH by a consideration of the fact that the heat of activation of the ketonization cannot be less than zero and since $\Delta H = E_1 - E_2$, ΔH cannot be greater than $+14{,}000$ cal., the activation energy of enolization. These considerations are independent of the catalyst since approximately the same value of E was obtained with piperidine and with hydrochloric acid in methyl alcohol; they only depend on the correctness of two assumptions, (1) that the rate of racemization is a measure of the rate of enolization and (2) that there are not several consecutive reactions involved in the enolization. Since ΔF is probably within a thousand calories of ΔH for an isomeric change of this sort, we may place the value of ΔF for the enolization of acetophenone derivatives as between 6000 and 14,000 cal., which correspond to values of K of 10^{-5} to 10^{-10}. It seems worth while to set such limits since there seems to be no way of measuring ΔF or ΔH for this type of isomeric change (where the one isomer is in extremely small concentration at equilibrium) or calculating it from the third law. It is interesting that if one takes a figure nearer the upper limit of ΔF, say $K = 10^{-9}$ and assumes that the enol form is itself an acid of the strength of phenol, the value of K for the equilibrium ketone $\longrightarrow$ enol ion $+ H^+$ is $10^{-9} \times 10^{-10} = 10^{-19}$. The value of 10^{-20} was taken as a probable approximate value for the acidity constant of acetophenone from entirely other considerations in a recent paper from this Laboratory.[7] Preliminary experiments on the rate of racemization of the methyl ester of methyl-

[7] Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

benzylacetic acid with sodium methylate gave values of 18,000 for the activation energy. The fact that this is larger than the average value for the ketones cannot be considered as significant without further work, but an upper limit for ΔH and ΔF of enolization can be set by the considerations just mentioned. Using such approximations, together with the quantitative information in the preceding paper[6] and the qualitative behavior of the compounds, the following table may be constructed to summarize our present information about enolization.

TABLE III

ESTIMATED VALUES OF ΔF OF ENOLIZATION IN GASEOUS PHASE

ΔF for liquid phase or solutions may differ from these values by ± 0.7 kg. cal.

Type of compound	ΔF in kilogram calories	Type of compound	ΔF in kilogram calories
$R_2CHCOOC_2H_5$	16–14	$CH_3COCHRCOCH_3$	0
$R_2CHCOCH_3$	10–12	$CH_3COCH_2COOC_2H_5$	
R_2CHCHO	10– 7	$CH_3COCH(C_6H_5)COOC_2H_5$	−1
$CH_2(COOC_2H_5)_2$	7	$CH_3COCH_2COCH_3$	−1.3
$CH_3COCHRCOOC_2H_5$	1	$(RCO)_3CH$	less than 3

(R = C_nH_{2n+1}; if R = aryl, it is probable that ΔF of enolization will be about 1.5 kg. cal. more negative.)

Experimental

(a) Preparation of Compounds

Methylbutylphenylcarbinol.—A Grignard reagent prepared from 137 g. of *n*-butyl bromide and 24.3 g. of magnesium was treated at 0° with 120 g. of acetophenone dissolved in an equal volume of ether. The product of reaction was hydrolyzed with ice and sulfuric acid. The aqueous layer was extracted three times with ether and the ether extract washed with a concentrated sodium carbonate solution. The dried and filtered solution was evaporated and the residue vacuum distilled. The carbinol (110 g.) had the following physical properties: b. p. 129–130° at 4 mm., n_D^{20} 1.5091, d_{20} 0.9592; mol. ref. calcd., 55.54; found, 55.42.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.89; H, 10.18. Found: C, 81.09; H, 10.32.

Methyl (α-Methyl-α-phenyl-*n*-amyl) Ether.—A solution of 17.8 g. of the carbinol in 30 cc. of methyl alcohol containing 1 cc. of concentrated sulfuric acid separated into two layers on standing overnight. The product of reaction was dissolved in ether, washed with water and a sodium carbonate solution, dried and the ether distilled; the residue was distilled in a vacuum. Twelve grams of product was obtained having the following properties: b. p. 105–106° at 6 mm., n_D^{20} 1.4940, d_{20} 0.9275; mol. ref. calcd., 60.27; found, 60.27.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.25; H, 10.41. Found: C, 81.02; H, 10.38.

α-Methyl-α-phenyl-*n*-caproic Acid.—Five grams of methyl-(methylphenylamyl) ether was dissolved in 150 cc. of dry ether and treated with 5–6 cc. of liquid sodium–potassium alloy in an atmosphere of nitrogen. The reaction started immediately and proceeded without shaking. The red potassium derivative was treated with carbon dioxide until all color disappeared. Excess alloy was decomposed by adding moist ether and alcohol. The alcohol-ether solution was then extracted several times with water. The alkaline solution was acidified and the liberated acid extracted with ether. After drying over sodium sulfate the ether was distilled off and the residue combined

from two similar experiments vacuum distilled. The yield was 6.5 g.; b. p. 155° at 4 mm. In a larger run 40 g. of acid was obtained from 55 g. of ether.

Neutral equivalent. Calcd. for $C_{13}H_{18}O_2$: 206. Found: 194.7. *Anal.* Calcd. for $C_{13}H_{18}O_2$: C, 75.68; H, 8.78. Found: C, 75.83; H, 8.94.

α-Methyl-α-phenylmethylcaproate.—Four grams of α,α-methylphenylcaproic acid as the potassium salt was methylated with dimethyl sulfate at the temperature of the steam-bath. Two fractions of product were collected (1) 1.4 g., boiling point 112–113° at 1 mm.; (2) 1.85 g., b. p. 115° at 2 mm. The last fraction was odorless and had the following physical properties: n_D^{20} 1.4964, d_{20} 0.9938; mol. ref. calcd., 64.78; found, 64.70. Molecular weight by the freezing point method in benzene: mol. wt. calcd., 220; found, 206.

Anal. Calcd. for $C_{14}H_{20}O_2$; C, 76.36; H, 9.09. Found: C, 76.21; H, 9.13.

***d*-α-Methyl-α-phenylcaproic Acid.**—Ten grams of methylphenylcaproic acid and 16 g. of quinine were dissolved in 75 cc. of hot alcohol and filtered. The filtrate was diluted with water until turbid and sufficient alcohol then added until the solution became clear. After three crystallizations the salt was decomposed by dilute sulfuric acid. The free acid gave the following value for the specific rotation in alcohol solution

$$[\alpha]_{5461} = 13.65° = \frac{0.70° \times 100}{2 \times 2.559}$$

To determine whether the ease of resolution was greater with some other alkaloid, 10 g. of the acid and 14.3 g. of cinchonidine were dissolved in 100 cc. of hot alcohol and the solution filtered. The filtrate was diluted with water and set aside to crystallize. After three crystallizations the salt was decomposed with dilute hydrochloric acid. The free acid in this case gave a slightly lower specific rotation in alcohol solution.

$$[\alpha]_{5461} = 10.68° = \frac{0.26° \times 100}{2 \times 1.219}$$

***d*-α-Methyl-α-phenylcaprophenone.**—Five grams of thionyl chloride and 2.5 g. of *d*-α-methyl-α-phenylcaproic acid (α_{5461} = 13.65°) were mixed in a 100-cc. Erlenmeyer flask attached to a reflux condenser provided with a calcium chloride tube. The reaction was completed by warming on the steam-bath for ten to fifteen minutes. Excess thionyl chloride was distilled off at the pressure of the water pump. The residual acid chloride was dissolved in 25 cc. of toluene and the flask tightly stoppered.

A Grignard reagent prepared in the usual manner from 0.3 g. of magnesium and 2 g. of bromobenzene was treated with 2 g. of freshly fused zinc chloride dissolved in a minimum quantity of ether. The phenyl zinc chloride formed separated from solution as a fine gray powder. Twenty-five cc. of toluene was added and the flask connected with the condenser set for downward distillation. Most of the ether was distilled from the zinc compound and replaced by an equal volume of toluene. The acid chloride previously prepared was added slowly to the suspension of the phenyl zinc chloride in boiling toluene. A rather vigorous reaction occurred and a gummy mass was formed which held the stirrer fast in some cases. After one hour, hydrolysis was effected by 50 cc. of a saturated ammonium chloride solution. The toluene layer was washed with water, a dilute sodium carbonate solution, and finally with dilute hydrochloric acid, dried and evaporated at the pressure of the water pump. The residue was dissolved in several solvents but showed no tendency to crystallize from any one even at low temperature. Attempts to crystallize the ketone were abandoned and after evaporating the solvent the residue was distilled in vacuum. The yield was 1.7 g. of ketone having a boiling point of 150–152° at 0.5 mm. specific rotation in alcohol solution

$$[\alpha]_{5461} = 30.78° = \frac{0.62° \times 100}{2 \times 1.008}$$

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.66; H, 8.33. Found: C, 85.48; H, 8.55.

***d*-Methylbenzylacetophenone.**—The acid chloride was prepared by the usual procedure from 7.2 g. of *d*-methylbenzylacetic acid ($[\alpha]_{5461} = 31.5°$ for the sodium salt) and 21 g. of thionyl chloride. A Grignard reagent prepared from 7.5 g. of bromobenzene and 1.2 g. of magnesium was treated with 6.6 g. of freshly fused zinc chloride dissolved in a minimum quantity of ether. The ether was replaced with toluene. The acid chloride prepared above was dissolved in toluene and added to the boiling toluene suspension of phenyl zinc chloride. After one hour the product was hydrolyzed by a saturated ammonium chloride solution and the toluene layer washed with a dilute sodium carbonate solution, dilute hydrochloric acid, and finally with water. The dried and filtered toluene solution was evaporated under diminished pressure and the residue vacuum distilled. The yield was 5.5 g. of ketone having a boiling point of 148–150° at 6 mm. When cooled the distillate was solid, but melted at room temperature. The solidified distillate was transferred to a small chilled porous cell and centrifuged at a high speed at the temperature of the cold room. In this manner 2.5 g. of white crystalline ketone of m. p. 42–43° was obtained. The ketone had the following specific rotation in alcohol solution

$$[\alpha]_{5461} = 87.5° = \frac{4.66° \times 100}{2 \times 2.669}$$

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.72; H, 7.45.

1-Phenylbenzylacetomesitylene.—A petroleum ether solution of 6 g. of 1-benzylphenylacetic acid ($[\alpha]_{5461} = -70.48°$) was treated with 10 g. of thionyl chloride at room temperature. The reaction was completed by warming on the water-bath; excess thionyl chloride was evaporated at reduced pressure and the residual acid chloride dissolved in 25 cc. of toluene.

A Grignard reagent prepared from 10.6 g. of mesityl bromide and 1.3 g. of magnesium was treated with 7.5 g. of freshly fused zinc chloride dissolved in a minimum quantity of ether. The ether was replaced by toluene and the hot suspension of mesityl zinc chloride treated with the solution of acid chloride previously prepared. After one hour the product was hydrolyzed with a saturated ammonium chloride solution and the toluene layer washed with dilute sodium carbonate, dilute hydrochloric acid, and finally with water. The dried and filtered solution was evaporated at reduced pressure. Mesitylene and mesityl bromide were distilled off at 2–3 mm. by immersing the flask in a metal bath maintained at 100° and the residue crystallized from methyl alcohol. Five grams of mesityl ketone of m. p. 113–114° was obtained. The ketone had the following specific rotation in acetone solution

$$[\alpha]_{5461} = -8.06° = \frac{-0.10° \times 100}{2 \times 0.620}$$

Anal. Calcd. for $C_{24}H_{24}O$: C, 87.75; H, 7.36. Found: C, 87.74; H, 7.60.

***d*-Phenylmethylacetomesitylene.**—Twenty-five grams of thionyl chloride and 9.5 g. of the *d*-phenylmethylacetic acid ($[\alpha]_{5461} = 61.75°$ in alcohol) were mixed in the usual apparatus at room temperature. Excess thionyl chloride was evaporated off and the residual acid chloride dissolved in 25 cc. of toluene.

The acid chloride was added to a boiling toluene suspension of mesityl zinc chloride prepared as usual from 20 g. of mesityl bromide, 2.5 g. of magnesium, and 14 g. of freshly fused zinc chloride. After one hour the product was hydrolyzed with a saturated ammonium chloride solution and the toluene layer washed with a dilute sodium carbonate solution, dilute hydrochloric acid, and finally with water. The dried and filtered solution was evaporated at reduced pressure and the residue crystallized from methyl alcohol at −20°. The yield was 6.5 g. of mesityl ketone of m. p. 59–60.5°; specific rotation (in methyl alcohol)

$$[\alpha]_{5461} = 71.5° = \frac{1.88° \times 100}{2 \times 1.268}$$

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.66; H, 7.99. Found: C, 85.39; H, 8.01.

***l*-Methylbenzylmethylacetate.**[8]—The compound used in the rate measurements had the following rotation

$$[\alpha]_{5461} = -18.00 = \frac{-18.31°}{1 \times 1.0174}$$

1-Benzylphenylacetophenone.—The compound used in the final rate measurements was prepared from the chloride of the completely resolved acid by the action of phenyl zinc chloride. Some racemization must have occurred during the preparation as the m. p. was 115–116° and $[\alpha]_{5461} = -168.2° = (3.49° \times 100)/(2 \times 1.038)$ as compared with m. p. 121–121.5° and $[\alpha]_D = -268°$ recorded by McKenzie.[9]

***d*-Phenylmethylacetophenone.**—The compound used in the rate measurements melted at 32–33° and had a rotation in methyl alcohol of $[\alpha]_{5461} = 242.1 = (5.06 \times 100)/(2 \times 1.045)$ as compared with m. p. 34–35° and $[\alpha]_{5461} = 260$ (in $CHCl_3$) recorded by McKenzie and $[\alpha]_D = 210.8$ in alcohol.[10] The analytical data for the compound were satisfactory.

(b) Measurements

The measurements were made with a Schmidt and Haensch polariscope which was read to 0.01°, a mercury arc light with suitable filters giving light of $\lambda = 5461$ was used. The polariscope tube was jacketed and the temperature kept constant by circulating water; the temperature was read on a thermometer immersed in the liquid in the polariscope tube itself. Anhydrous solvents were used throughout. The alcoholates were prepared by dissolving metallic sodium in the alcohol in question, the concentration being finally determined by titration of an aliquot sample with standard acid. The piperidine used in the final experiments was distilled from solid potassium hydroxide; thus prepared it was about 30% less effective than piperidine which had not been given this treatment. A number of experiments indicated that it was more difficult to obtain reproducible results with various samples of purified piperidine than with the alcoholates.

Summary

1. The rates of enolization of five optically active aryl ketones and one closely related ester were determined under a variety of conditions by noting the rate of racemization. The rate was found to be nearly directly proportional to the concentration of catalyst when the sodium alcoholates were used as the catalytic substances. The most effective catalyst was sodium methylate using tertiary butyl alcohol as the solvent; this catalyst was about 2000 times as effective as piperidine in methyl alcohol, which was the least effective base and 1000 times as effective as hydrogen chloride in methyl alcohol.

2. The relative rates of enolization depended on the catalyst and solvent although with all the alcoholates the relative rates only varied about 50%. Using these values as a basis for comparison, it was found that the ester enolized much more slowly than the ketones but that there was no clear regularity between the rate of enolization of the ketone and its structure.

[8] This Journal, **48**, 169 (1926).

[9] McKenzie, *J. Chem. Soc.*, **129**, 779 (1926).

[10] McKenzie, Roger and Wells, *ibid.*, **129**, 787 (1926).

3. The heat of activation of the enolization is about 14 ± 1 kg. cal. The free energy of enolization of the acetophenone derivatives is estimated to be between +5 and +14 kg. cal.

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

THE REACTION BETWEEN TRIARYLMETHYL HALIDES AND PHENYLMAGNESIUM BROMIDE. I

BY C. S. SCHOEPFLE AND S. G. TREPP[1]

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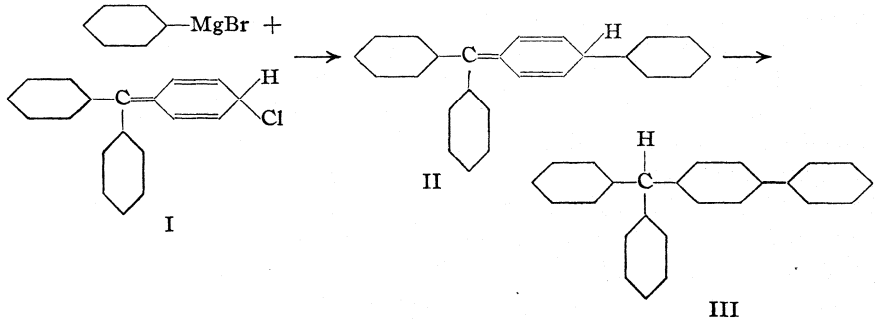
In a previous communication[2] the apparently abnormal reaction of tetraphenylethylene dichloride and phenylmagnesium bromide, which results in the formation of *p*-phenyltetraphenylethylene and tetraphenylethylene,[3] was explained on the assumption that the dichloride reacts in the para quinonoid form. Another Grignard reaction of this type has been described by Gilman and Jones,[4] who treated triphenylchloromethane with phenylmagnesium bromide and obtained a 47% yield of biphenyldiphenylmethane in addition to a small amount of the expected product, tetraphenylmethane. Again, as in so many other reactions of the triarylmethyl salts, the products of this reaction can be readily explained by a simple mechanism involving quinoidation of the triphenylchloromethane. If the quinonoid modification of triphenylchloromethane (I) reacts



with the Grignard reagent, there will be formed an unstable intermediate product (II) which will rearrange to give biphenyldiphenylmethane (III); the benzenoid modification of the chloride of course gives tetraphenyl-

[1] This paper represents the first part of a dissertation submitted to the Graduate School by Mr. Trepp in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Schoepfle and Ryan, THIS JOURNAL, **54**, 3687 (1932).

[3] Norris, Thomas and Brown, *Ber.*, **43**, 2955 (1910).

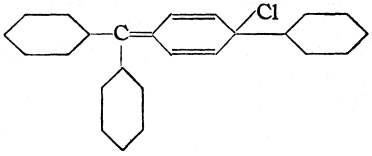
[4] Gilman and Jones, THIS JOURNAL, **51**, 2840 (1929).

methane. The fact that biphenyldiphenylmethane is the principal product indicates that the reaction with the quinonoid modification predominates.

The purpose of the present investigation was to show that the suggested mechanism of the reaction between triarylmethyl halides and phenylmagnesium bromide is correct.[5] If, instead of triphenylchloromethane, 4-chlorotriphenylchloromethane (IV) were used, then in the reaction with excess phenylmagnesium bromide not only the chlorine on the central carbon atom but also some of the chlorine in the ring should be removed, resulting in an increased number of reaction products. Assuming that only para quinoidation takes place, one intermediate and five final products should be formed. The chloride may react in the benzenoid form to give 4-chlorotetraphenylmethane (V), or it may react in the quinonoid form, in which case there are two possibilities. If a ring (a or b) not containing chlorine becomes quinonoid and reacts, 4-chloro-4′-phenyltriphenylmethane (VI) will result. Since this compound no longer has a halogen atom attached to the central carbon atom, it cannot react further with the Grignard reagent, which fact was established by experiment. However, if in the original chloride the ring (c) containing the chlorine atom becomes quinonoid and reacts with one mole of phenylmagnesium bromide, the chlorine atom remaining will migrate back to the central carbon atom to give biphenyldiphenylchloromethane (VII).[6] This compound may then react further with the Grignard reagent in one of three ways; (1) in the benzenoid form to give 4-phenyltetraphenylmethane (VIII); (2) in the quinonoid form where the halogen has migrated to the biphenyl ring to give terphenyldiphenylmethane (IX); or (3) in the other quinonoid form where the halogen has migrated to a benzene ring, in which case dibiphenylphenylmethane (X) should result.

This reaction has been studied with the result that the following compounds have been isolated, the average yields being stated: 4-chlorotetraphenylmethane (V), 10%; 4-chloro-4′-phenyltriphenylmethane (VI), 28%; dibiphenylphenylmethane (X), 9%. Approximately the same results were obtained with 4-chlorotriphenylbromomethane, the average yields of the three products being 9, 27 and 17%, respectively. 4-Bromotriphenylchloromethane and phenylmagnesium bromide also were found

[5] It may be remarked that in this work we are interested in quinoidation of the triarylmethyl halides and not in quinoidation of the Grignard reagent. Several examples of quinonoid Grignard reagents have been recorded and their structures established by experimental evidence. See Schmid lin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, Germany, 1914, p. 204.



[6] The possibility exists that the intermediate product, of structure indicated, might react with another molecule of phenylmagnesium bromide before it has time to rearrange to VII, but such a reaction is not considered likely.

* The structures of the intermediate quinonoid forms are omitted.

to react in a similar manner. The products obtained and the average yields were: 4-bromotetraphenylmethane, 13%; 4-bromo-4′-phenyltriphenylmethane, 7%; and dibiphenylphenylmethane, 20%. 4-Bromo-4′-phenyltriphenylmethane, however, was isolated in only a few runs due to the difficulty with which it crystallizes even when pure.

Inasmuch as 4-phenyltetraphenylmethane (VIII) and terphenyldiphenylmethane (IX) could not be isolated in the above experiments, it was necessary to determine whether these products are formed in appreciable amounts in the reaction between biphenyldiphenylchloromethane and phenylmagnesium bromide. It was found that dibiphenylphenylmethane (X) is the principal product, being obtained in yields of 60 to 70%, while the yield of 4-phenyltetraphenylmethane was less than 10%; terphenyldiphenylmethane could not be isolated at all from the reaction mixture. Since terphenyldiphenylmethane is formed by the quinoidation of the biphenyl group and dibiphenylphenylmethane by the quinoidation of the phenyl group, it follows that a phenyl group apparently becomes quinonoid more easily than a biphenyl group when the two are present in the same molecule.

In the light of these results, it is not at all surprising that terphenyldiphenylmethane is not found among the reaction products of the mono para halogenated triphenylchloromethanes, for it probably is formed only in extremely small amounts; 4-phenyltetraphenylmethane should be present, but again is formed in such small amounts that failure to crystallize it from the complex reaction mixture is readily understood.

The experimental evidence obtained in these reactions is thus in entire agreement with the quinonoid interpretation of the reaction mechanism. Since 4-bromo- or 4-chloro-triphenylchloromethane presumably exists in ether or benzene solution principally or entirely in the benzenoid form, it is probable that the reacting product is a quinonoid addition compound of the chloride with either magnesium bromide or phenylmagnesium bromide itself. This question will be discussed further in a separate communication which concerns a study of the wide variation in yield in the preparation of different tetraaryl methanes by the Grignard reaction.

It should be noted that the reaction between triarylmethyl halides and phenylmagnesium bromide can also be explained on the theory of the formation of intermediate free radicals, but only on the basis that the free radicals themselves exist partly in the quinonoid form.

Experimental

4-Chlorotriphenylchloromethane and Phenylmagnesium Bromide.—An ether solution of phenylmagnesium bromide (3 moles) was rapidly filtered through a small piece of cotton and then slowly poured, with swirling, into a benzene solution of 4-chlorotriphenylchloromethane. The usual sized sample of chloride was 15 g. The reaction mixture assumed a red color, considerable heat was developed, and a flocculent precipi-

tate of magnesium salts settled out. Although the reaction proceeds rapidly, the mixture was usually allowed to stand for a day or two at room temperature, after which it was decomposed with ice and dilute acid in the usual manner. The ether–benzene layer was washed with sodium carbonate solution and with water, and then concentrated and steam distilled. The residue was dissolved in benzene, and the solution dried and concentrated, whereupon 4-chlorotetraphenylmethane crystallized in fairly pure form and was separated. Addition of ligroin to the mother liquor gave a further small amount of this compound, the total yield being 8.5–10.5%. The solution was then allowed to concentrate by spontaneous evaporation of the solvent, and deposited fairly pure crystals of dibiphenylphenylmethane. When no further material could be crystallized, the residue was distilled in a high vacuum still designed by Hickman and Sanford.[7] The temperature was usually about 200° and never exceeded 225°, and there was no evidence of decomposition during the distillation. The distilled product was dissolved in benzene, ligroin added and the solution concentrated as before by spontaneous evaporation. By this means, a trace of 4-chlorotetraphenylmethane and a further quantity of dibiphenylphenylmethane were recovered, giving a total yield of 6.5–10.0% of the latter compound. In addition, 4-chloro-4′-phenyltriphenylmethane was obtained from the distillate in a yield of 27–28%.

The 4-chlorotetraphenylmethane was purified by recrystallization from benzene, from which it is obtained in colorless needles which melt at 227–227.5°. It is soluble in carbon tetrachloride, somewhat soluble in benzene, and insoluble in ether, petroleum ether and acetic acid.

Anal. Calcd. for $C_{25}H_{19}Cl$: C, 84.60; H, 5.40; Cl, 10.00. Found: C, 84.49; H, 5.46; Cl, 10.00.

Dibiphenylphenylmethane and 4-chloro-4′-phenyltriphenylmethane were identified by mixed melting point determinations with authentic samples.

Several experiments were also carried out with 4-chlorotriphenylbromomethane, which was prepared from the corresponding carbinol by treating a benzene solution of the latter with acetyl bromide. After concentrating the solution and adding ligroin, the bromide crystallized in colorless prisms which after recrystallization melted at 111–112°.

Anal. Calcd. for $C_{19}H_{14}BrCl$: Br, 22.36. Found: Br, 22.72.

The reaction of 4-chlorotriphenylbromomethane and phenylmagnesium bromide was similar to that of the chloride except that no precipitate of magnesium salts was formed when the reactants were mixed. The same products were isolated, the following yields being obtained: 4-chlorotetraphenylmethane, 6–9%; dibiphenylphenylmethane, 16.5–18%; and 4-chloro-4′-phenyltriphenylmethane, 18–35%.

4-Bromotriphenylchloromethane and Phenylmagnesium Bromide.—The procedure was the same as described in the preceding experiments, and upon crystallization of the product, dibiphenylphenylmethane in 15–25% yield, and 4-bromotetraphenylmethane in 10–18% yield were obtained. The latter compound melted at 245°;[8] its solubility is similar to that of 4-chlorotetraphenylmethane.

Anal. Calcd. for $C_{25}H_{19}Br$: C, 75.17; H, 4.80; Br, 20.03. Found: C, 74.77; H, 4.75; Br, 19.78.

The non-crystallizable residue was distilled in the Hickman still, and from the distillate a trace of 4-bromotetraphenylmethane and a few tenths of a gram of dibiphenylphenylmethane were recovered. In a few runs, 4-bromo-4′-phenyltriphenylmethane was also obtained from the distillate in a yield of 5–10%. Failure to isolate this com-

[7] Hickman and Sanford, *J. Phys. Chem.*, **34**, 643 (1930), Fig. 6.

[8] Gomberg and Cone, *Ber.*, **38**, 2456 (1905).

pound in other runs is undoubtedly due to the fact that it crystallizes with great difficulty. It was identified by a mixed melting point with an authentic sample.

Biphenyldiphenylchloromethane and Phenylmagnesium Bromide.—The reaction was carried out by mixing a benzene solution of the chloride with an ether solution of phenylmagnesium bromide (2 moles) at room temperature. As in the other reactions studied, a heating effect was observed, the solution became cherry-red in color, and a precipitate of magnesium salts was obtained. After standing for several hours, the reaction mixture was decomposed in the usual manner, the organic layer separated, washed, evaporated to dryness and steam distilled. The product was fractionally crystallized from benzene plus ligroin by gradual concentration of the solution. The only products which could be isolated were 4-phenyltetraphenylmethane in 7–10% yield, and dibiphenylphenylmethane in 58–70% yield. Both compounds were identified by mixed melting point determinations with authentic samples.

Synthesis of 4-Chloro-4′-phenyltriphenylmethane.—4-Chloro-4′-phenylbenzophenone was prepared by the method used by Gomberg and Bailar[9] for the corresponding bromo derivative. The acid chloride obtained from 10.4 g. of 4-chlorobenzoic acid was dissolved in 150 cc. of carbon disulfide, and 30 g. of biphenyl added, followed by 25 g. of anhydrous aluminum chloride in small portions. The reaction mixture was warmed on the steam-bath for three days, and then hydrolyzed. The excess of biphenyl was distilled off under reduced pressure, and the residue dissolved in benzene, from which the ketone crystallized in 63% yield. Upon recrystallization from alcohol, colorless plates were obtained which melted at 169.5–170.5°. The compound is fairly soluble in hot benzene and somewhat soluble in hot alcohol.

Anal. Calcd. for $C_{19}H_{13}OCl$: C, 77.94; H, 4.48; Cl, 12.12. Found: C, 77.65; H, 4.44; Cl, 12.17.

4-Chloro-4′-phenyltriphenylcarbinol was prepared by adding 15 g. of 4-chloro-4′-phenylbenzophenone to a slight excess of phenylmagnesium bromide. The ketone was added as a solid because of its limited solubility in cold solvents. The mixture was refluxed for six hours, and hydrolyzed and worked up in the usual manner. The carbinol did not crystallize readily, therefore the impure product was reduced by shaking the benzene solution for two days with an excess of 57% hydriodic acid. The benzene layer was washed with sodium bisulfite solution and water, and then dried and concentrated. The residue was dissolved in petroleum ether, from which 4-chloro-4′-phenyltriphenylmethane crystallized in colorless rosets in 62% yield. The compound melts at 102–103° and is soluble in the common organic solvents except cold alcohol and cold petroleum ether.

Anal. Calcd. for $C_{25}H_{19}Cl$: C, 84.60; H, 5.40; Cl, 10.00. Found: C, 84.80; H, 5.38; Cl, 9.83.

Synthesis of 4-Bromo-4′-phenyltriphenylmethane.—4-Bromo-4′-phenyltriphenylcarbinol was prepared from 4-bromo-4′-phenylbenzophenone[9] and phenylmagnesium bromide, but could not be made to crystallize. It was therefore treated with hydriodic acid, following the procedure just described. The product obtained was dissolved in petroleum ether, from which 4-bromo-4′-phenyltriphenylmethane crystallized after long standing, a 53% yield being obtained. After recrystallization from petroleum ether or from a mixture of benzene and absolute alcohol, it melted at 82–84°. It is soluble in the common organic solvents except cold alcohol and cold petroleum ether. The compound crystallizes with difficulty even when pure; it may not begin to crystallize until twenty-four hours after being seeded and crystallization from a concentrated petroleum ether solution is seldom complete in less than three or four days. This is in contrast to the corresponding chloro derivative, which crystallizes readily.

[9] Gomberg and Bailar, THIS JOURNAL, **51**, 2233 (1929).

Anal. Calcd. for $C_{25}H_{19}Br$: C, 75.17; H, 4.80; Br, 20.03. Found: C, 75.52; H, 4.95; Br, 20.30.

Synthesis of 4-Phenyltetraphenylmethane.—This compound was prepared by diazotizing 4-amino-4′-phenyltetraphenylmethane and treating the diazonium salt with absolute alcohol to replace the amino group by hydrogen. The method is analogous to that used by Ullmann and Münzhuber[10] for the synthesis of tetraphenylmethane.

To prepare 4-amino-4′-phenyltetraphenylmethane, 20 g. of biphenyldiphenylchloromethane and 35 g. of aniline hydrochloride were dissolved in acetic acid and the solution refluxed for several hours. The solution was then poured into water, neutralized with sodium carbonate, heated to boiling and the precipitated amine filtered off. The compound crystallized from toluene on addition of ligroin in long thin colorless prisms which melted at 192°. The yield was 90%. It is soluble in toluene, benzene and acetic acid when hot, but insoluble in these solvents when cold.

Anal. Calcd. for $C_{31}H_{25}N$: N, 3.41. Found: N, 3.51.

Four grams of 4-amino-4′-phenyltetraphenylmethane was diazotized by means of amyl nitrite at 30°[10] and the solid diazonium sulfate, obtained by precipitation with ether, was washed and dried; yield, 3 g. This was added in small quantities to 200 cc. of boiling absolute alcohol, and upon concentration of the solution, 4-phenyltetraphenylmethane crystallized in 70% yield. Recrystallization from benzene plus ligroin gave colorless rosets which melted at 197–198°. The compound is soluble in carbon tetrachloride, slightly soluble in benzene and in hot acetic acid, and insoluble in acetone, ether and alcohol.

Anal. Calcd. for $C_{31}H_{24}$: C, 93.89; H, 6.11. Found: C, 93.99; H, 6.23.

In connection with this work, N-phenyl-biphenyldiphenylmethylamine was desired. Ten grams of biphenyldiphenylchloromethane and 10 g. of aniline were dissolved in separate portions of benzene, and then mixed. The mixture was heated on the steam-bath for a few minutes after which the precipitated aniline hydrochloride was filtered off, the solution concentrated and ether added. The anilide was obtained in long colorless prisms, which upon recrystallization melted at 154–155°. The yield was 86%. It is soluble in benzene, very slightly soluble in ether and insoluble in alcohol.

Anal. Calcd. for $C_{31}H_{25}N$: N, 3.41. Found: N, 3.36.

N-Biphenyl-triphenylmethylamine was prepared in a similar manner from triphenylchloromethane and 4-aminobiphenyl in 84% yield. Recrystallized from benzene plus alcohol, colorless hexagonal prisms were obtained, which melted at 179.5–180.5°. It agrees with N-phenyl-biphenyldiphenylmethylamine in solubility. Attempts to rearrange this compound to 4-(4-aminophenyl)-tetraphenylmethane were unsuccessful.

Anal. Calcd. for $C_{31}H_{25}N$: N, 3.41. Found: N, 3.40.

Summary

A theory postulating quinoidation of triarylmethyl halides has been advanced to explain the supposedly abnormal reaction of these compounds with phenylmagnesium bromide.

The reaction of 4-chloro- and 4-bromotriphenylchloromethane with phenylmagnesium bromide has been studied and the reaction products are shown to be in agreement with this theory.

ANN ARBOR, MICHIGAN

[10] Ullmann and Münzhuber, *Ber.*, **36**, 404 (1903).

[CONTRIBUTION NO. 96 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

ACETYLENE POLYMERS AND THEIR DERIVATIVES. III. THE ADDITION OF HYDROGEN CHLORIDE TO VINYLACETYLENE

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Vinylacetylene (I) constitutes the simplest possible example of a conjugated enine system. Recorded information concerning the addition reactions of such systems is exceedingly meager. It has already been reported[1] that chloroprene (chloro-2-butadiene-1,3, III) can be obtained by the addition of (aqueous) hydrogen chloride to vinylacetylene, and the present paper is concerned with a further description of the mechanism of this reaction and the nature of the products to which it leads.

It is shown that the initial step consists in 1,4 addition, and the primary product thus formed is chloro-4-butadiene-1,2, (II) (b. p. 88°), a new compound of rather unusual structure and curious properties. Under certain conditions this chloro-4-butadiene-1,2 can be isolated as the major reaction product, but it readily undergoes an isomerization involving migration of the chlorine atom and a shift of a double bond. Chloroprene (b. p. 59.4°) is formed thus, and the transformation occurs with such facility in the presence of hydrogen chloride that chloroprene always constitutes a part of the reaction product. Certain salts reinforce the catalytic effect of hydrogen chloride on this transformation, and when cuprous chloride is present no chloro-4-butadiene-1,2 is found in the reaction product. When sufficient amounts of hydrogen chloride are present the reaction proceeds further with the formation of dichloro-2,4-butene-2 (IV).

$$\underset{\text{I}}{CH{\equiv}C{-}CH{=}CH_2} \xrightarrow{HCl} \underset{\text{II}}{CH_2{=}C{=}CH{-}CH_2Cl} \longrightarrow$$

$$CH_2{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \xrightarrow{HCl} CH_3{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2Cl$$

III IV

Influence of Conditions on the Reaction.—The reaction between vinylacetylene and hydrogen chloride is conveniently carried out in the following manner. Fifty grams of vinylacetylene and 175 cc. of concentrated hydrochloric acid (about 2.2 moles of hydrochloric acid) are placed in a pressure bottle, and the bottle is shaken to promote contact between the aqueous and the hydrocarbon layers. After the completion of the reaction the oily layer is separated, dried, mixed with a small amount of an antioxidant such as catechol or pyrogallol, and distilled *in vacuo* through an efficient column. Data from a very large number of experiments of this

[1] Carothers, Williams, Collins and Kirby, THIS JOURNAL, 53, 4203 (1931).

type are available. Owing to the fact that in most cases neither the temperature nor the speed of shaking was precisely controlled these data cannot be used as a basis for a quantitative description of reaction velocities; nevertheless, they give a clear idea of relative rates.

In a typical experiment of the kind described above, about 43% of the vinylacetylene was utilized in seven hours, and analysis of the reaction product yielded chloro-4-butadiene-1,2 and chloroprene in the ratio 2.2:1.

In general this ratio is diminished by increase in the temperature, concentration of hydrogen chloride, or time of contact; and the proportion of the chloro-4-butadiene-1,2 in the product is less the more completely the vinylacetylene is utilized. This fact demonstrates that part at least of the chloroprene is formed by the isomerization of the chloro-4-butadiene-1,2 during the course of the reaction, and it seems reasonable to conclude that all of it is formed by this demonstrated mechanism.

The reaction is considerably accelerated by the presence of certain salts. Thus when 25 g. of calcium chloride is present in the reaction mixture the time required to obtain 40% conversion is decreased by about one-half, but the ratio of the two isomeric chlorobutadienes present in the reaction product at a given percentage conversion remains practically unaffected. Cuprous chloride is a much more powerful catalyst. When 25 g. of this salt is present in the reaction mixture, about 90% of the vinylacetylene reacts in four hours at 20°. In this case the product consists for the most part of chloroprene, and no chloro-4-butadiene-1,2 is present. It is, however, not necessary to assume that the cuprous chloride directs the reaction so that addition occurs at the acetylenic linkage. Separate experiments show that cuprous chloride reinforces the catalytic effect of hydrogen chloride on the isomerization of chloro-4-butadiene-1,2 and this effect seems adequate to explain the absence of chloro-4-butadiene-1,2 in the reaction product.

Chloroprene reacts further with hydrogen chloride to produce dichloro-2,4-butene-2. This reaction is also catalyzed by cuprous chloride, and the relative velocities are such that any conditions of concentration, temperature, and time of contact that suffice to convert all of a given sample of vinylacetylene result in the formation of a certain amount of the dichlorobutene. The following experiment is illustrative. Fifty grams of vinylacetylene, 175 cc. of concentrated hydrochloric acid, 25 g. of cuprous chloride, and 10 g. of ammonium chloride were placed in each of forty bottles. The bottles were gently shaken in a bath at 20° for four hours and then allowed to stand for twelve hours at 0°. The contents of all the bottles were combined and the mixture was steam distilled *in vacuo* into a receiver placed at the bottom of a 2-meter jacketed, carborundum-packed column provided with a dephlegmator and a second receiver each cooled to −80°. The pressure was kept at about 150 mm. until all of the unchanged vinyl-

acetylene had collected in the second receiver, and the pressure was then gradually reduced to 10 mm. until all of the chloroprene had collected in the second receiver. The dichlorobutene remained in the first receiver. The yields were: unchanged vinylacetylene, 115 g.; chloroprene, 2862 g.; dichlorobutene, 117 g. In mole percentages these values are 5.7, 84.2, and 2.5, respectively. The deficit amounting to 7.6 mole per cent. was mostly comprised in intermediate fractions. When this deficit is distributed proportionately among the three major fractions, the percentage yields become: unreacted vinylacetylene, 6.1%; chloroprene, 91.2%; dichlorobutene, 2.7%. The corresponding figures for the calculated yields based upon unrecovered vinylacetylene are chloroprene, 97%, and dichlorobutene, 3%. Further experiments indicate that the conditions of this experiment lie very close to the optimum for the conversion of vinylacetylene to chloroprene in a batch process: a higher ratio of chloroprene to dichlorobutene can be obtained only by utilizing a smaller proportion of the applied vinylacetylene, and a more complete utilization of the vinylacetylene results in a larger proportion of dichlorobutene.

The Properties of Chloro-4-butadiene-1,2 and the Proof of its Structure.—Chloro-4-butadiene-1,2 is a colorless liquid boiling at 87.7 to 88.1°. It is only slightly soluble in water but miscible with most of the common organic solvents. It has a peculiar, sharp odor. Some other properties are: n_D^{20} 1.4775; d_4^{20}, 0.9891; M_R calcd., 24.61; M_R found, 25.30.

Anal. Calcd. for C_4H_5Cl: C, 54.23; H, 5.64; Cl, 40.11. Found: C, 55.04, 55.11; H, 5.70, 5.90; Cl, 39.75, 40.03.

Its chlorine atom is exceedingly reactive. When mixed with alcoholic silver nitrate it rapidly yields a copious precipitate of silver chloride. This fact in itself indicates that the compound is not a 1,3-diene, since in such a structure the chlorine atom would, of necessity, be attached to a doubly bonded carbon. Furthermore, the compound does not react with maleic anhydride or with naphthoquinone. It is not a true acetylenic compound either since it does not yield any derivative with ammoniacal cuprous chloride. When treated with ozone it yields formaldehyde and (after oxidation with potassium permanganate) chloroacetic acid. The compound has also been directly oxidized with potassium permanganate. The only product obtained was chloroacetic acid. Acetic acid and oxalic acid were absent. This behavior demonstrates the presence of the groups $CH_2{=}$ and ${=}CH{-}CH_2Cl$, and the compound must therefore have the structure chloro-4-butadiene-1,2. This structure is further confirmed by the fact that under the action of cold concentrated sulfuric acid, chloro-4-butadiene-1,2 is readily converted into chloro-4-butanone-2.[2]

The transformation of chloro-4-butadiene-1,2 into chloroprene exempli-

[2] *Cf.* Gustavson and Demjanoff, *J. prakt. Chem.*, [2] **38**, 201 (1888); Bouis, *Ann. chim.*, [10] **9**, 402 (1928).

fies a type of reaction that is common to many substituted allyl halides. Such halides (*e. g.*, $CH_3CHXCH{=}CH_2$ or $CH_3CH{=}CHCH_2X$) arise quite generally by the addition of halogens or hydrogen halides to 1,3-dienes, and in these cases the possibility of isomerization frequently makes it difficult or impossible to determine whether the primary product is the result of 1,2 or 1,4 addition. Chloro-4-butadiene-1,2, however, differs from other allyl halides: the α,γ shift brings the adjacent double bonds into the more stable conjugated configuration and the chlorine atom becomes attached to a doubly bonded carbon where its mobility is lost. A reversal of the isomerization is therefore impossible, and chloro-4-butadiene-1,2 cannot be other than a primary product of the addition of hydrogen chloride to vinylacetylene.

The transformation of chloro-4-butadiene-1,2 into chloroprene has been observed under a variety of conditions: by the action of powdered potassium hydroxide, by the action of hot quinoline (140–150°), by the action of heat (290°) in the presence of silica gel, and by the action of hot dilute hydrochloric acid.[3] However, the isomerization occurred most smoothly and rapidly in the presence of hydrochloric acid containing cuprous chloride. Fifty grams of chloro-4-butadiene-1,2 was refluxed for three and one-half hours with 20 g. of cuprous chloride in 100 cc. of 18% hydrochloric acid. The oily layer was decanted, dried and distilled. The entire specimen except for a small amount of undistillable residue came over between 59 and 63° and the distillate was pure chloroprene. When the chloro-4-butadiene-1,2 was similarly treated with aqueous cuprous chloride alone it was recovered unchanged.

Chloro-4-butadiene-1,2 unlike its isomer chloroprene shows no tendency to polymerize. It can be distilled unchanged at ordinary pressure, and specimens stored under the ordinary laboratory conditions for many months remain unaltered. It undergoes no change even when submitted to a pressure of 6000 atmospheres for forty-five hours at 50°.[4]

Experimental Part

Oxidation of Chloro-4-butadiene-1,2.—To a mixture of 30 g. of chloro-4-butadiene-1,2 with 250 cc. of water containing a little sodium carbonate was added in small portions with constant stirring 214 g. of potassium permanganate. The mixture was filtered, the filtrate acidified and continuously extracted with ether for several hours. The ether solution on distillation gave a liquid boiling at 185° which solidified on cooling. This was chloroacetic acid, identified by its melting point, neutralization equivalent (found, 96; calcd., 94.5) and transformation into chloroacetamide, m. p. 119°. No acetic or oxalic acid was found.

Ozonization of Chloro-4-butadiene-1,2.—A solution of 20 g. of chloro-4-butadiene-1,2 in 20 cc. of chloroform was treated with ozone for twelve hours at 0°. The solvent and the unchanged material were evaporated *in vacuo* and the remaining ozonide

[3] We are indebted to Dr. D. D. Coffman for some of these observations.

[4] We are indebted to Dr. H. W. Starkweather for this observation.

was decomposed with water. Formaldehyde was detected in the aqueous solution by its strong odor and the formation of methylene-di-β-naphthol; white needles melting at 204° (corr.).

Chloroacetaldehyde was not detected directly. The aqueous solution was treated gradually with 50 g. of potassium permanganate, the excess permanganate destroyed with sulfur dioxide, and the filtrate extracted with ether. Distillation of the ether solution left a residue which crystallized on cooling. This product was chloroacetic acid, identified by its melting point and neutralization equivalent.

Hydration of Chloro-4-butadiene-1,2.—Into 250 cc. of concentrated sulfuric acid 88.5 g. of chloro-4-butadiene-1,2 was added dropwise with stirring, the temperature being maintained at −5 to 3°. The dark reaction product was poured onto cracked ice, partly neutralized with sodium carbonate and extracted with ether. The ethereal solution was washed, dried and distilled, yielding 58 g. of crude chloro-4-butanone-2, b. p. 110–123°. On redistillation it boiled at 120 to 122° at 760 mm.

Anal. Calcd. for C_4H_7OCl: C, 45.07; H, 6.57; Cl, 33.33. Found: C, 45.42, 45.42; H, 6.81, 6.47; Cl, 32.26, 32.42.

When treated with phenylhydrazine it gave a derivative having the correct melting point (77°) and analysis for phenylmethylpyrazoline.[5]

Anal. Calcd. for $C_{10}H_{12}N_2$: C, 75.00; H, 7.50; N, 17.50. Found: C, 74.32; H, 7.60; N, 17.10.

Dichloro-2,4-butene-2.—This material is obtained as a by-product in the preparation of chloroprene and it is readily prepared in quantity by shaking vinylacetylene with an excess (4 moles) of hydrochloric acid containing cuprous chloride. It is a colorless liquid having a characteristic odor; other properties are: boiling point 127–129° at 756 mm., 61–63° at 70 mm., 53 to 54° at 50 mm., d_4^{20} 1.1591, n_D^{20} 1.47239, n_C^{20} 1.46988, n_F^{20} 1.48187, M_R calcd. 29.94, M_R found 30.27.

Anal. Calcd. for $C_4H_6Cl_2$: C, 38.40; H, 4.80; Cl, 56.80. Found: C, 38.53; H, 4.87; Cl, 56.90.

The proof of the structure of this compound will be presented in a future paper dealing with its reactions.

Acknowledgment.—The writers are indebted to Mr. O. R. Kreimeier for assistance in the experiments on the addition of hydrogen chloride to vinylacetylene.

Summary

The results of experiments on the action of aqueous hydrogen chloride on vinylacetylene are described. The initial step consists in 1,4 addition and the primary product is chloro-4-butadiene-1,2. This readily undergoes isomerization, yielding chloroprene, which always constitutes a part of the reaction product. When cuprous chloride is present in the reaction mixture the isomerization proceeds more rapidly and no chloro-4-butadiene-1,2 is found in the reaction product. When sufficient hydrogen chloride is present the reaction proceeds further, yielding dichloro-2,4-butene-2.

WILMINGTON, DELAWARE

[5] Maire, *Bull. soc. chim.*, [4] **3**, 272 (1908).

[CONTRIBUTION NO. 98 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

HOMOLOGS OF CHLOROPRENE AND THEIR POLYMERS (SECOND PAPER ON NEW SYNTHETIC RUBBERS)

BY WALLACE H. CAROTHERS AND DONALD D. COFFMAN

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Chloroprene (chloro-2-butadiene-1,3, I) is obtained by the addition of hydrogen chloride to vinylacetylene.[1]

$$CH_2{=}CH{-}C{\equiv}CH + HCl \longrightarrow CH_2{=}CH{-}\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}{=}CH_2 \qquad (I)$$

In the rate of its spontaneous transformation into a rubber-like polymer it greatly exceeds all previously described dienes.[2] The present paper is concerned with homologs of chloroprene obtained by the addition of hydrogen chloride to homologs of vinylacetylene. As Merling has shown,[3] compounds (III) of the latter class can be obtained by the action of sodium acetylide on aldehydes or ketones, followed by dehydration of the resulting carbinols (II).

$$RCH_2\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}O + CH{\equiv}CH \longrightarrow RCH_2\underset{\displaystyle R'}{\overset{\displaystyle |}{\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}}}{-}C{\equiv}CH \longrightarrow RCH{=}\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}{-}C{\equiv}CH$$

(II) (III)

These reactions were in fact proposed as steps in a process for the synthesis of rubber, since in the case where R = H and R′ = CH_3, the product II can be reduced to the vinylcarbinol and then dehydrated to produce isoprene. The elegancy of this method has been frequently commended, but from our own experience it appears more elegant than useful, since the yields in the first step were rather low. Nevertheless, the isolation of small amounts of the pure carbinols presents no particular difficulties, and under properly selected conditions the dehydration to the substituted vinylacetylene proceeds fairly smoothly.

In the present study the carbinols used were those represented in formulas IV–VI. These and the corresponding vinylacetylenes (VII–IX) have already been described by Merling.[3] The substituted vinylacetylenes were converted into the corresponding substituted chloroprenes (X–XII) by shaking them at room temperature with concentrated hydrochloric acid containing cuprous chloride and ammonium chloride. The reactions proceeded somewhat more slowly than the formation of chloro-

[1] Carothers, Berchet and Collins, THIS JOURNAL, **54**, 4066 (1932).

[2] Carothers, Williams, Collins and Kirby, *ibid.*, **53**, 4203 (1931).

[3] Merling, Friedr. Farbenfab. von Bayer & Co., German Patents 280,226, 286,920, 285,770, 288,271; Scheibler and Fischer, *Ber.*, [2] **55**, 2903 (1922); Sung Wouseng, *Ann. chim.*, [10] **1**, 343–416 (1924).

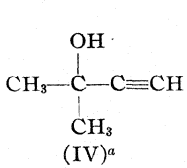
prene itself by the same process. The yields obtained were rather low but this was due chiefly to incomplete conversion. The substituted chloroprenes reacted smoothly with α-naphthoquinone to form crystalline addition products (XIII–XV), which were readily oxidized to the corresponding anthraquinones (XVI–XVIII).

The amounts of the substituted chloroprenes available did not suffice for a very detailed study of their polymerization. The results obtained, however, indicated quite definitely that, of the three dienes, only chloro-2-methyl-3-butadiene (X) is likely to deserve serious consideration as a precursor of rubber. It polymerizes at approximately the same rate as chloroprene; the polymer obtained is definitely rubber-like; a plastic form of the rubber-like product is readily isolated by distilling the unchanged diene from the viscous sirup or the soft jelly obtained by incomplete polymerization; this plastic material is vulcanized by the action of heat alone without the addition of sulfur. Samples thus obtained were strong, very tough and quite elastic, but their extensibility was rather low. The ultimate product of the spontaneous polymerization of the diene in a sealed tube containing a very little air was rather similar in its properties to the vulcanizate described above; it was a black, lustrous solid very strong and tough, but it had a low extensibility.

The dimethyl compound (XI) polymerized very much more slowly than chloroprene—apparently not much more rapidly than isoprene. The product was elastic, but soft and sticky, and attempts to vulcanize it resulted in only partial loss of the plastic properties. The vulcanizate was coherent and rather strong; its extensibility was fairly high (about 500%) but recovery from stretch was slow.

The tetramethylene compound (XII) also polymerized very slowly, and the product obtained was a very soft and plastic mass. The attempt to vulcanize it was almost entirely unsuccessful; the plastic properties were not appreciably affected, but after standing for several months the compounded sample had become quite brittle although it contained an antioxidant.

These observations together with others already available permit some conclusions concerning the effect of the position and the nature of substituting groups on the polymerization of butadiene. Since butadiene, isoprene, and β,γ-dimethylbutadiene do not very greatly differ in the rate of their spontaneous polymerization, it is evident that methyl is not an activating group. The fact that chloroprene polymerizes about seven hundred times as fast as isoprene illustrates the powerful activating effect of a chlorine atom at the β-position. The introduction of a methyl group at the other interior carbon does not greatly modify this effect, although the polymer obtained is somewhat less extensible; but the introduction of a second methyl group at one of the terminal carbons almost completely checks the activating effect of the chlorine atom.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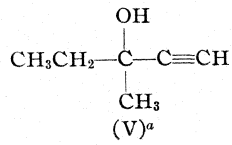
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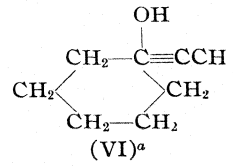
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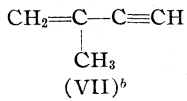
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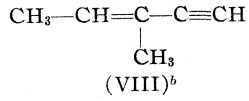
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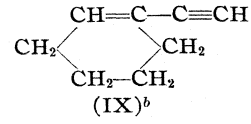
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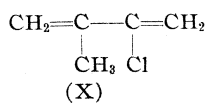
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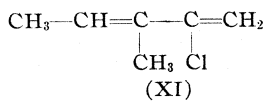
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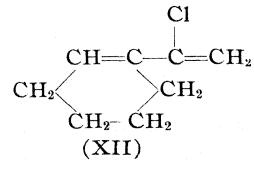
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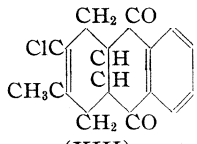
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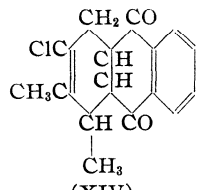
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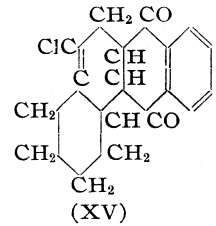
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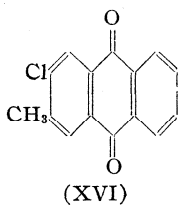
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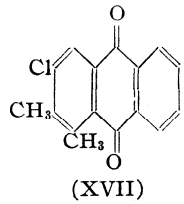
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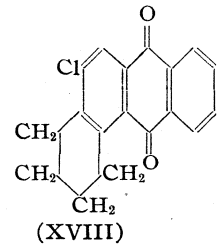

(XVIII)

[a] See Friedr. Farbenfab. von Bayer & Co., German Patents 280,226, 284,764, 286,920, 289,800. [b] German Patent 290,558.

Experimental Part

Acetylenic Carbinols.—The general method used for the preparation of the acetylenic carbinols has already been described in the literature.[4] The ketone (2 moles) was slowly introduced into an ethereal suspension (1 l. abs. ether) of sodamide (2 moles) at −10° with vigorous agitation. After five hours, when the evolution of ammonia had become very slow, acetylene was passed during eight hours into the reaction mixture at −10°, under 10–15 pounds pressure with constant shaking. The reaction mixture was then poured onto crushed ice, acidified with dilute sulfuric acid, subjected to ether extraction, the extract dried and distilled. The yields were: ethinyldimethylcarbinol (IV), b. p. 104–108°, 36%; ethinylmethylethylcarbinol (V), b. p. 119–123°, 33%; ethinyl-1-cyclohexanol-1 (VI), b. p. 174° at 760 mm., 53–55° at 2 mm., 50%.

[4] Sung Wouseng, *Ann. chim.*, [10] I, 343–416 (1924).

In the preparation of ethinyl-1-cyclohexanol-1 two by-products were isolated and identified: di-(hydroxy-1-cyclohexyl-1)-acetylene (10 g. from 2 moles of the ketone); crystals from carbon tetrachloride or benzene–petroleum ether, m. p. 106–107° (copper block). The literature records its melting point as 102°.[5]

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.65; H, 9.90. Found: C, 74.74; H, 10.41.

Cyclohexylidine-2-cyclohexanone-1 (35 g. from 4 moles of the ketone), colorless liquid (b. p. 143–145° at 16 mm.; n_D^{20} 1.5049; d_4^{20} 1.001) which readily formed an oxime, m. p. 146°.[6]

Ethinylmethylphenylcarbinol.—The condensation of acetylene with acetophenone gave in 2% yield ethinylmethylphenylcarbinol which boiled at 69° under 1 mm. The carbinol after three crystallizations from petroleum ether (b. p. 40–60°) melted at 52–53°.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.19; H, 6.85. Found: C, 81.71; H, 6.88.

Dehydration of the Acetylenic Carbinols.—The ethinyldimethylcarbinol was heated at 90° (bath) in a distilling flask with an equal weight of *p*-toluenesulfonic acid for three hours. The methyl-2-butene-1-ine-3 (VII) distilled into the receiver as it was formed, b. p. 34°; yield, 53%.

The ethinylmethylethylcarbinol (60 g.) was slowly added during thirty minutes to 10 g. of *p*-toluenesulfonic acid contained in a distilling flask surrounded by a water-bath at 80°. The operation was carried out at slightly diminished pressure and the methyl-3-pentene-2-ine-4 (VIII) distilled into the receiver as it was formed, b. p. 68 to 71° at 760 mm.; yield, 25%.

Attempts to dehydrate ethinyl-1-cyclohexanol-1 by heating it with iodine, *p*-toluene-sulfonic acid, or anhydrous oxalic acid were unsuccessful, but excellent results were obtained by passing the carbinol in a stream of nitrogen over basic aluminum sulfate (from alum) at 240 to 260°. The yield of ethinyl-1-cyclohexene-1 (IX) boiling at 40 to 43° at 12 mm. was about 35% per passage and the remainder was chiefly unchanged carbinol.

Chloro-2-methyl-3-butadiene-1,3 (X).—Methyl-2-butene-1-ine-3 (40 g.) was shaken in a pressure bottle during four and a half hours at 20° with hydrochloric acid (105 cc., sp. gr. 1.19) containing cuprous chloride (15 g.) and ammonium chloride (6 g.). The reaction mixture was subjected to steam distillation, and the products were dried and distilled. The yield of the chlorobutadiene was 25 g. or 40%; b. p. 93° (760 mm.) with polymerization, 41° (113 mm.), 37° (105 mm.); n_D^{20} 1.4689, d_4^{20} 0.9593, M_R (obs.) 29.75, M_R (calcd.), 29.22.

Anal. Calcd. for C_5H_7Cl: C, 58.54; H, 6.83; Cl, 34.63; mol. wt. 103. Found: C, 58.55; H, 6.72; Cl, 34.39; mol. wt. (in freezing benzene), 126.

Chloro-2-methyl-3-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XIII).—α-Naphthoquinone (0.5 g.) was heated at 100° for half an hour with chloro-2-methyl-3-butadiene-1,3 (1 g.). The reaction mixture was cooled and the crystals were washed with absolute methanol. After crystallization from aqueous acetone, the white needles melted at 165–166° (uncorr.).

Anal. Calcd. for $C_{15}H_{13}O_2Cl$: C, 69.09; H, 4.99. Found: C, 68.72; H, 4.86.

Chloro-2-methyl-3-anthraquinone (XVI).—The tetrahydro compound (XIII) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the blue solution until only a yellow color remained. The suspension was diluted with water, the yellow crystals were filtered and recrystallized from glacial acetic acid. The material

[5] Iotsitch, *J. soc. phys.-chim. r.*, **38**, 656 (1906), G. Dupont, *Ann. chim.*, [8] **30**, 498 (1913).

[6] Wallach, *Ber.*, **29**, 2965 (1896); Mannich, *ibid.*, **40**, 157 (1907).

melted at 214–215° (uncorr.). The melting point of chloro-2-methyl-3-anthraquinone is recorded in the literature as 215° and 219° corrected.[7]

Chloro-2-dimethyl-3,4-butadiene-1,3 (XI).—Methyl-3-pentene-2-ine-4 (25 g.) was shaken in a pressure bottle during five and a half hours at 20° with hydrochloric acid (58 cc., sp. gr. 1.19), containing cuprous chloride (8.5 g.) and ammonium chloride (3.5 g.). The reaction mixture was subjected to steam distillation and the product dried and distilled. The yield of the chlorobutadiene was 9 g. or 22%. A considerable proportion of unreacted hydrocarbon was recovered; b. p. 57–60° (96 mm.), $n_D^{20°}$ 1.4671; d_4^{20} 0.9437, M_R (obs.) 34.26, M_R (calcd.) 33.84.

Anal. Calcd. for C_6H_9Cl: C, 61.80; H, 7.72; Cl, 30.44; mol. wt., 116.5. Found: C, 61.40; H, 7.55; Cl, 29.24; mol. wt., 116.

Chloro-2-dimethyl-3,4-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XIV).—α-Naphthoquinone (0.5 g.) was heated at 100° during one hour with chloro-2-dimethyl-3,4-butadiene-1,3 (1 g.). The reaction mixture was cooled, and the crystals were washed with absolute methanol. After crystallization from aqueous acetone, the white needles melted at 107° (copper block).

Anal. Calcd. for $C_{16}H_{15}O_2Cl$: C, 69.95; H, 5.47. Found: C, 69.41; H, 5.53.

Chloro-2-dimethyl-3,4-anthraquinone (XVII).—The tetrahydro compound (XIV) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the purple solution until only a pale yellow color remained. The ethanol was diluted with water, the yellow crystals filtered and recrystallized from glacial acetic acid. The anthraquinone melted at 171.5° (copper block).

Anal. Calcd. for $C_{16}H_{11}O_2Cl$: C, 70.98; H, 4.07. Found: C, 70.22; H, 4.14.

Chloro-2-tetramethylene-3,4-butadiene-1,3 (XII).—Ethinyl-1-cyclohexene-1 (33 g.) was shaken in a pressure bottle during four and a half hours at 20° with hydrochloric acid (70 cc., sp. gr., 1.19) containing cuprous chloride (10 g.) and ammonium chloride (4 g.). The reaction mixture was subjected to vacuum steam distillation, and the product dried and fractionated. The yield of the chlorobutadiene was 14 g. or 32% of the theoretical, and a considerable amount of unreacted hydrocarbon was recovered; b. p. 55–57° (1 mm.); n_D^{20} 1.5240; d_4^{20} 1.0422; M_R (obs.), 41.84; M_R (calcd.), 40.88.

Anal. Calcd. for $C_8H_{11}Cl$: C, 67.37; H, 7.72; mol. wt., 142.5. Found: C, 67.50; H, 7.90; mol. wt. (in freezing benzene), 143.

Chloro-2-tetramethylene-3,4-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (XV).— α-Naphthoquinone (2 g.) was heated at 100° during twenty minutes with chloro-2-tetramethylene-3,4-butadiene-1,3 (4 g.). On cooling crystals formed which were washed with absolute methanol. After recrystallization from absolute ethanol, the white needles melted at 191–192° (copper block).

Anal. Calcd. for $C_{18}H_{17}ClO_2$: C, 71.88; H, 5.66. Found: C, 71.42; H, 5.86.

Chloro-2-tetramethylene-3,4-anthraquinone (XVIII).—The tetrahydro compound (XV) was suspended in dilute alcoholic sodium hydroxide. Air was bubbled through the purple solution until only a yellow color remained. The ethanol was diluted with water, the crystals filtered and recrystallized from glacial acetic acid. The yellow needles melted at 155–156° (copper block).

Anal. Calcd. for $C_{18}H_{13}ClO_2$: C, 72.85; H, 4.38. Found: C, 72.59; H, 4.53.

Polymerization of Chloro-2-methyl-3-butadiene-1,3 (X).—When a sample of the diene was allowed to stand at the laboratory conditions in a sealed tube containing a trace of air it set up to a stiff jelly in about five days. Later the specimen became dark in color and ten months later when the tube was opened the product was a black, lustrous solid, very strong and tough but having only a slight extensibility. A sample of

[7] Keimatsu and Hirans, *J. Pharm. Soc. Japan*, **49**, 140–147 (1929).

the diene exposed to the light of a Cooper–Hewitt lamp (mercury arc in glass) at ordinary temperature contained 30% of polymer after sixty-five hours. (Under the same conditions chloroprene polymerizes at a greater rate than this—about 30% in forty hours.) The sample was then a soft jelly. The polymer was precipitated, washed with alcohol, and compounded with 1% of phenyl-β-naphthylamine, 5% of zinc oxide, 2% of stearic acid, and heated in a mold at 140 to 145° for fifteen minutes. The resulting sheet was coherent, strong, tough, and rather elastic, but it was deficient in resiliency and extensibility. It appears that the polymer from chloro-2-methyl-3-butadiene-1,3 more closely resembles the products from dimethylbutadiene (methyl rubber) than those obtained either from isoprene or from chloroprene.

Polymerization of Chloro-2-dimethyl-3,4-butadiene-1,3 (XI).—A specimen placed in a sealed glass tube under air and exposed to the light of a 100-watt Mazda lamp for two months at the ordinary temperature was converted to a very soft, sticky, elastic mass which still contained a considerable proportion of volatile material—apparently unchanged monomer. After standing for eight months more in the absence of direct light its properties had not undergone any further change.

A sample of the diene was submitted to a pressure of 8000 atmospheres for 106 hours at 40°. The product was a soft, plastic, elastic mass containing about 70% of polymer. It was compounded with 1% of phenyl-β-naphthylamine, 10% of zinc oxide, 2% of stearic acid, 1% of benzidine and 1% of tetramethylthiuramdisulfide and was then heated in a mold at 120 to 125° for seventy minutes. The product obtained in this way was rather soft and lacking in resiliency and nerve. The extensibility was fairly high (400 to 500%).

Polymerization of Chloro-2-tetramethylene-3,4-butadiene-1,3 (XII).—A specimen in a glass tube under air was exposed to the light of a 100-watt Mazda light for forty-eight days. The product was a thick, dark mass. Removal of the unchanged monomer by washing with alcohol yielded about 70% of polymer. This was very soft, plastic and sticky. It was compounded in the same manner as the polymer described in the preceding paragraph, but after being heated it still remained soft and plastic. After standing for ten months it had become brittle. A specimen of the diene was submitted to a pressure of 6000 atmospheres at 38° during ninety-six hours. The product was quite soft and plastic and when compounded as in the preceding example and heated for seventy minutes at 120° it showed no appreciable signs of vulcanization.

We are indebted to Dr. H. W. Starkweather for the experiments at high pressures.

Summary

Three substituted vinylacetylenes were treated with hydrogen chloride and thus converted to the corresponding chlorobutadienes. Chloro-2-methyl-3-butadiene-1,3 polymerized very rapidly and yielded a rubber-like polymer, which after vulcanization was less extensible than the corresponding product obtained from chloroprene (chloro-2-butadiene-1,3). Chloro-2-dimethyl-3,4-butadiene-1,3 polymerized very slowly and the product, even after vulcanization, was soft and lacking in nerve. Chloro-2-tetramethylene-3,4-butadiene-1,3 also polymerized very slowly and the product was very soft, plastic and sticky.

The structures of the three new chlorobutadienes were established through their reaction with α-naphthoquinone to form crystalline addition products, which were oxidized to the corresponding anthraquinones.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

COMPLEX TYPES INVOLVED IN THE CATALYTIC OXIDATION OF THIOL ACIDS

BY MAXWELL SCHUBERT

RECEIVED JUNE 11, 1932 PUBLISHED OCTOBER 5, 1932

The study of the chemistry of the heavy metal complexes of thiol acids which in previous work[1] has been concerned with thioglycolic acid and cysteine and their compounds with cobalt has now been extended to include complexes of iron and of a thiol compound with no free carboxyl group, that is, thioglycolic ester. This extension makes possible a more detailed and clearer view on the probable mechanism of the catalytic oxidation of thiol acids to disulfide acids in the presence of iron salts by oxygen, noticed by Mathews and Walker and by Warburg and Sakuma.

The iron complexes are of particular interest as being the actual intermediate compounds involved in this catalytic process. The reaction is best shown by the addition of a trace of iron salt to a solution of thioglycolic acid or cysteine at a P_H of 8 to 9. A red color develops with the thioglycolic acid while a violet color appears in the case of cysteine. When the dissolved oxygen has been used up this color gradually fades. Simultaneously some of the thiol acid is transformed to disulfide, but as long as there remains any thiol acid the color may be regenerated by shaking the mixture with air. A time finally comes when this color can no longer be regenerated because the thiol acid has been completely oxidized to the disulfide.

There have been two attempts to work out the mechanism of this catalytic process in detailed steps, the first by Michaelis,[2] the second by Cannan and Richardson.[3] Both theories were based on measurements made on solutions of the complexes, of such physico-chemical properties as reduction potentials, reduction capacity and reaction kinetics. In each case the catalysis was imagined as occurring in three steps: first, a formation of a ferrous complex of the thiol acid; second, an oxidation of this complex by means of oxygen to a ferric complex, which is the cause of the red or violet color observed in the catalytic process; third, an autoreduction of this ferric complex in which the iron is reduced to a divalent condition while the thiol sulfur is oxidized to disulfide with simultaneous breaking up of the complex and fading of the color.

The theory that will be presented in the present paper is similar in outline but differs in the constitution of the complexes assumed as intermediate steps and attempts to present the whole picture in greater detail. The

[1] THIS JOURNAL, **52**, 4418 (1930); **53**, 3851 (1931).

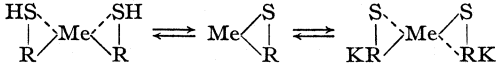
[2] L. Michaelis, *J. Biol. Chem.*, **84**, 777 (1929).

[3] Cannan and Richardson, *Biochem. J.*, **23**, 1242 (1929).

evidence is based on the types of complex actually isolated in crystalline condition from solutions containing iron and thiol acid in which the catalysis could occur if exposed to the air and from similar solutions containing cobalt in place of iron in which no catalysis can occur.

The constitution and relations of the iron complexes can be brought out most clearly by a description of an actual experiment. If an air-free solution of ferrous iron and twice as many mols of thioglycolic acid be mixed in an atmosphere of hydrogen and air-free potassium hydroxide be added drop by drop, there soon develops a yellow color. On further slow addition a yellow crystalline precipitate appears. This has the composition $Fe(SCH_2COO)\cdot 1.5H_2O$. As the potassium hydroxide addition is continued the yellow precipitate dissolves, giving a deep orange to orange-red solution. From this solution a crystalline product has been isolated having the composition $Fe(SCH_2COOK)_2$. The P_H at this stage is in the veronal range or about 9, as will be shown in the experimental section. Finally, if enough potassium hydroxide be added, ferrous hydroxide precipitates and the orange-red color disappears. The same sequence of changes occurs when thioglycolic acid is replaced by cysteine or when iron is replaced by cobalt, the colors being, of course, different. In all these changes the metal always remains divalent as air is rigorously excluded.

This series of changes can be formulated as follows. After enough alkali has been added to bring about ionization of the carboxyl group of the thiol acid and before the appearance of the first yellow color in the solution, it is probable that the normal, and to a certain extent complex, salt I is



$P_H < 4$ I $\quad$ P_H 4–6 II $\quad$ P_H 8–10 III

formed. Further addition of alkali causes ionization of the thiol group to begin and this is facilitated by the tendency of the iron to combine with sulfur. The result is the precipitation of II in which the groups responsible for solubility are not free. That this compound should dissolve on further addition of alkali is very striking. The only way this can be made understandable is to take account of the further ionization of the thiol group and the preference of the iron to combine with sulfur rather than with oxygen. The deep orange-red solution which forms about P_H 9 then must contain the complex in the form III. I and III differ in the distribution of primary and secondary valence bonds and II is the transition state between them, separable because of its insolubility.

This is a point of considerable theoretical importance from the point of view of the structure of these complexes and a little further consideration will be required to see if it has any meaning at all because of the general opinion that in complex ions there is no distinction between primary and

secondary valence links. In the case of symmetrical complex ions such as ammonium or ferrocyanide, there seems to be no difference between primary and secondary bonds. This probably means that the electron pair between the central atom and each coördinating group is held similarly and the electric charge of the ion is not localized at any particular hydrogen or cyanide group but is distributed over the ion as a whole.

On the octet scheme thioglycolic acid is written $H:S:\overset{H}{\underset{H:O:}{\overset{\cdot\cdot}{C}}}:\overset{\cdot\cdot}{C}:\overset{\cdot\cdot}{O}:H$, which for our purpose may be simplified to $H:\overset{\cdot\cdot}{S}:R:\overset{\cdot\cdot}{O}:H$. The hydrogen of the carboxyl group ionizes more readily than that of the thiol group so that on dissolving iron in the thioglycolic acid the salt formed would have the structure $H:\overset{\cdot\cdot}{S}:R:\overset{\cdot\cdot}{O}:Fe:\overset{\cdot\cdot}{O}:R:\overset{\cdot\cdot}{S}:H$ or, since it is at least to a certain extent complex, (A) $H:\overset{\cdot\cdot}{S}:\overset{:\overset{\cdot\cdot}{O}:R}{\underset{R:\overset{\cdot\cdot}{O}:}{\overset{\cdot\cdot}{Fe}}}:\overset{\cdot\cdot}{S}:H$. This corresponds to the complex I, but the electronic formula A shows no difference between primary and secondary bonds. In this condition the thiol group must be un-ionized; otherwise there is no reason why on making more alkaline the complex II should precipitate. The formation of II is perfectly comprehensible, however, if in the first step of the ionization of A, a dibasic complex acid, the resulting more negative character of one of the sulfur atoms makes possible a closer linkage of the iron and this sulfur atom. The preference of the iron for this closer link with the sulfur rather than its link with the oxygen is the cause of what has been called the shift of the main valence bond from oxygen to sulfur in the change of I to II. This can be represented thus

$$H:\overset{\cdot\cdot}{S}:\overset{:\overset{\cdot\cdot}{O}:R}{\underset{R:\overset{\cdot\cdot}{O}:}{\overset{\cdot\cdot}{Fe}}}:\overset{\cdot\cdot}{S}:H + (OH)^- \longrightarrow \overset{:\overset{\cdot\cdot}{O}:R}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Fe}:\overset{\cdot\cdot}{S}}} + (H:\overset{\cdot\cdot}{S}:R:\overset{\cdot\cdot}{O}:)^- + H_2O$$

Now on further making alkaline the reaction

$$(H:\overset{\cdot\cdot}{S}:R:\overset{\cdot\cdot}{O}:)^- + (OH)^- \longrightarrow (:\overset{\cdot\cdot}{S}:R:\overset{\cdot\cdot}{O}:)^- + H_2O$$

is favored and again the iron can exert its preference for the link with sulfur

$$\overset{:\overset{\cdot\cdot}{O}:R}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{Fe}:\overset{\cdot\cdot}{S}:}} + (:\overset{\cdot\cdot}{S}:R:\overset{\cdot\cdot}{O}:)^- \longrightarrow \left[\begin{array}{c} :\overset{\cdot\cdot}{O}:R \\ :\overset{\cdot\cdot}{S}:\overset{\cdot\cdot}{Fe}:\overset{\cdot\cdot}{S}: \\ R:\overset{\cdot\cdot}{O}: \end{array}\right]^- \qquad \text{(B)}$$

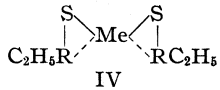
But although the electronic formula B looks like A after complete ionization, it must be understood that a great change has taken place in the way the electron pairs between the sulfur atoms and the iron are held. Physically this is reflected in the great development of color on changing from A to B which could not be explained merely as a result of ionization.

This brings out a defect of both the valence method of representing the

structure of these complexes as exemplified in I, II and III, which emphasizes the difference in the kind of bond, and the electronic method shown in A and B in which there is no difference at all. Actually the difference might be represented roughly by showing the electron pair between iron and sulfur displaced at various distances between these elements as the electronegative character of sulfur changes by ionization. It would seem likely that as the sulfur becomes more negative the electron pair would be pulled further toward the iron. It is only in some such sense as this that the distinction between primary and secondary valence bonds is to be understood in this paper.

This apparent preference of iron to link as closely as possible with sulfur is hindered when the sulfur is already covalently linked with hydrogen, but here the hydrogen is easily removable by ionization. If instead of hydrogen a benzyl group be substituted which is not displaced as the hydrogen, then the formation of more deeply colored complexes is completely hindered. The only compound that could be isolated with the S-benzylcysteine is a pink salt of the composition $Co(OOCCHNH_2CH_2SCH_2C_6H_5)_2$. The formation of the yellow or green complexes like those represented by III does not occur at all.

But if the hydrogen of the carboxyl group be replaced by an alkyl group as in thioglycolic ester then the formation of the yellow and green complexes does occur and in these the main valence links must be between metal and sulfur as



IV

These complexes of both iron and cobalt have been isolated. This is the real reason why the complex A has been identified with I where the main valence link is with the carboxyl group as in the S-benzylcysteine compound with cobalt and B has been identified with III where the main valence link is with sulfur as in IV.

The conditions in solution under which complexes of type III are formed are the same as those in which iron acts as a catalyst for the oxidation of thiol acids in the presence of air. If solutions containing III be prepared under hydrogen with careful exclusion of all oxygen, they can be kept indefinitely. But as soon as they are exposed to the air the color changes, for example, in the case of iron and thioglycolic acid from a red-orange to a much more intense dark red and almost immediately ferric hydroxide begins to precipitate while the color gradually fades. It is at this point that, in attempting to follow the chemistry of these changes made so difficult by the lability of the oxidized iron complexes, the corresponding cobalt complexes are studied instead. Cobalt complexes of the structure II and III have been described previously. The cobalto bis cysteinate of

structure III is an intense blue-green. On exposure to the air it is oxidized like the iron complex and turns to an olive-brown but this olive-brown cobalt complex, unlike the corresponding intensely red oxidized iron complex, is stable.

Let us now consider the structure of these oxidized cobalt complexes which from their close connection with the unstable iron complexes may be expected to give us some information on the structure of these catalytically important compounds.

Kendall and Holst[4] studied the oxidation of cobalto-bis-cysteinate to cobalti-bis-cysteinate and came to the conclusion that there is an intermediate formation of a cobalti-tris-cysteinate according to the scheme

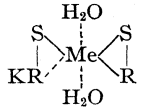
$$3Co^{II}(Cy)_2 \longrightarrow 2Co^{III}(Cy)_3 + Co^{++} \longrightarrow 2Co^{III}(Cy)_2 + \text{Cystine} \qquad (1)$$

The maximum theoretical yield of cobalti-bis-cysteinate calculated on the basis of the cysteine hydrochloride used would then be 67% of the yield to be expected from a simple direct oxidation of the character

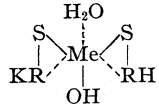
$$3Co^{II}(Cy)_2 \longrightarrow 3Co^{III}(Cy)_2 \qquad (2)$$

Since actual practical yields of 75 to 80% calculated on the basis of (2) have been obtained with both cysteine and thioglycolic acid, the more complicated reaction (1) is not only unnecessary but impossible.

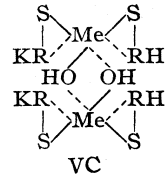
The oxidation of the cobalto-bis-cysteinate according to (2) can be imagined in three ways, giving rise to VA, VB and VC. Now on changing acidity the complex nucleus of VA being a monovalent anion can give rise to only a single potassium salt besides the corresponding free acid; that of VB being a divalent acid ion can form only two potassium salts, the free acid and a hydrochloride of the coördinated hydroxo group, while VC having a tetrabasic acid ion could give rise to at least three different potassium salts as well as the free acid and no chloride is possible.



VA



VB



VC

Working with both cysteine and thioglycolic acid, three salts have been obtained, a primary, a secondary and a quaternary, as well as the free acid. Although this complete series has not been prepared for either the cysteine or thioglycolic acid complexes, this is only a question of difficulty of obtaining them in crystalline form as their behavior on changing P_H is identical, this identity of the complex nucleus being further borne out by the close similarity of their absorption spectra. The impossibility of obtaining a chloride even in strongly acid solutions of the cobalti-

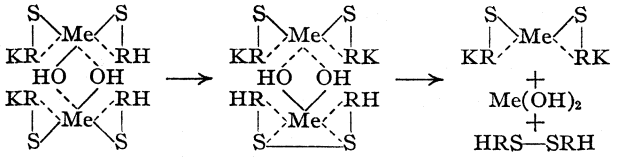
[4] Kendall and Holst, *J. Biol. Chem.*, **91**, 435 (1931).

bis-thioglycolate contributes to discredit VB. The existence of a hydrochloride of the corresponding cysteine complex has been previously shown to be due to the amino groups present.

This chemical evidence then definitely favors the formula VC to represent the structure of the cobalti-bis-thiol acid complexes. The free acid behaves as a fairly strong acid, not being precipitable by acetic acid but requiring hydrochloric acid. On the other hand, the secondary potassium salt is the form isolated at P_H 9 to 10. This would mean that the *pKa* values of the last two of the acid hydrogen atoms must be quite high. In a dilute aqueous solution any one of these forms of VC would be expected to be in equilibrium with several of the others. This might account for the impossibility experienced previously of determining the molecular weight of VC by cryoscopic methods.

As a result of this work the most probable course of the catalytic process seems to be first the formation of the ferrous complex III. This is oxidized by oxygen, giving the ferric complex VC as the second step. The third step consists in a reduction of this ferric complex with a splitting off of the oxidized disulfide acid. This might be due to the generally less stable nature of ferric complexes and the tendency of these to pass into ferrous complexes. A theoretical reason for the greater stability of the ferrous complexes is suggested by Sidgwick's[5] considerations on the electron configurations of metal atoms in complexes. This theory also accounts for the great stability of cobaltic complexes. The theory is, however, open to so many objections and exceptions that although it fits the present case quite well, it cannot be taken too seriously and is mentioned merely as the only available suggestion as to why the ferric complexes undergo the third step completing the catalytic process while the cobaltic complexes stop at the second step and consequently cannot form part of a catalytic cycle.

Only one possible way of representing this third step need be mentioned.



One of the iron atoms pulls in an electron from each of the sulfur atoms with which it is combined and passes one on to the other iron atom giving, after breaking up the naturally unstable intermediate, a molecule of ferrous bis-thiol acid, one of disulfide acid and one of ferrous hydroxide, which combines with thiol acid again, completing the catalytic cycle.

For the preparation of any of the iron complexes it is necessary to carry out the whole procedure in the absence of air. This is accomplished by use of the apparatus,

[5] Sidgwick, *J. Chem. Soc.*, **123**, 725 (1923); also Mann, *ibid.*, 651 (1929).

a diagram of which has already been published,[6] and to which reference will be made in what follows. The test-tube A is omitted; in B is placed either a freshly prepared solution of ferrous chloride or better still a pure grade of iron powder with hydrochloric acid; the flask C contains the cysteine or thioglycolic acid solution and the flask I contains the alkali necessary, which can be added drop by drop. Otherwise the manipulation is as previously described and need not be repeated here.

The complexes of type II are prepared as follows. After complete removal of air the ferrous chloride solution in B, containing about 20 to 25 millimoles of iron, is tipped into C containing from 25 to 50 millimoles of thiol acid. Potassium hydroxide solution is forced back into C from I drop by drop until a permanent light yellow color develops. In the case of thioglycolic acid precipitation of the complex is almost immediate and alkali may be added, while shaking the whole, until this reaches a maximum, but in the case of cysteine the precipitation is slower and it is best to proceed more cautiously. In either case the precipitated compound is light yellow and by warming slightly with a beaker of hot water crystallization is rapid. Filtration and washing are as previously described. The P_H at which this precipitation occurs is probably about 5 as filtrates tested were acid to litmus and alkaline to congo red. After drying over sulfuric acid at less than 1 mm. pressure, these analytical results were obtained.

Anal. Calcd. for $Fe(OOCCHS)\cdot 1.5H_2O$. Fe, 32.35; S, 18.50. Found for different preparations: Fe, 32.89, 32.98; S, 18.81, 19.10. Calcd. for $Fe(OOCCHNH_2CHS)\cdot 1.5H_2O$: Fe, 27.70; N, 6.93; S, 15.84. Found: Fe, 27.89; N, 6.44; S, 16.42.

These complexes after drying are perfectly stable in air. They undergo no apparent change when suspended in water, in which they are quite insoluble. Addition of dilute alkali causes no change but if a little thio acid be added simultaneously in the absence of air, then the deep red color of the complexes III is produced.

The complexes of type III at first seemed much more difficult to prepare. This is due to the great solubility of these complexes, together with their great sensitiveness to oxidation by oxygen so that rigid exclusion of air is essential until the crystalline product is separated from solution and washed.

The potassium salt of this complex has been prepared by a long complicated process involving a preparation of ferrous hydroxide, a thorough washing of this material followed by addition of thioglycolic acid and potassium hydroxide and evaporation of the resulting solution to small volume, an addition of air-free alcohol and a cooling on ice for some twelve hours. The resulting yellow rectangular platelets are filtered and washed with alcohol. This entire set of operations is carried out in closed vessels through which a continuous stream of purified hydrogen is passed. After drying *in vacuo* over sulfuric acid the analysis agreed reasonably, considering the impossibility of any purification procedures, with $Fe(SCH_2COOK)_2\cdot 2H_2O$.

Anal. Calcd.: Fe, 16.87; S, 19.27; K, 23.50. Found, for independent preparations: Fe, 19.42, 16.25; S, 19.26, 20.00; K, 25.14, 25.87.

The sodium salt of this complex can be prepared more easily. In the test-tube B of the special flask set-up are placed 5.5 g. of $FeSO_4.(NH_4)_2SO_4.6H_2O$ and 15 cc. of water and in the main flask 3 cc. of thioglycolic acid and 5 cc. of water. After complete removal of air sodium hydroxide is slowly added from the flask I. At first the yellow precipitate of the complex II appears but this soon redissolves, giving the usual deep red solution from which, after adding 9 to 10 cc. of 7.3 *M* sodium hydroxide, there slowly crystallizes a yellow substance. It is best to shake steadily while this is in progress as the crystals tend to stick to the sides of the flask. This product is filtered, washed with air-free water and alcohol as usual. Dried *in vacuo* its analysis corresponds with $Fe(SCH_2COONa)_2\cdot 2H_2O$. The results of two preparations are given.

[6] THIS JOURNAL, **53**, 3858 (1931).

Anal. Calcd.: Fe, 17.60; S, 20.11; Na, 14.46. Found: Fe, 18.46, 17.26; S, 20.45, 20.20; Na, 15.26, 15.86.

Freshly prepared and before exposure to the air the crystals are yellow and dissolve readily in air-free water, giving a raspberry-red solution which on exposure to air turns to a much deeper red. The dry crystals themselves on exposure to air turn from yellow to yellow-green and finally to an orange-red. Using a Warburg microrespiration apparatus, they were found to absorb oxygen slowly from the air. That this is not merely a case of adsorption of gas due to drying the crystals at less than 1 mm. pressure is shown by the fact that in an atmosphere of hydrogen no gas is taken up at all. In a number of experiments, making the transfer from the desiccator to the Warburg vessel as quickly as possible, which with weighing and allowing the vessel to come to temperature equilibrium in the bath occupied ten to fifteen minutes, 20 to 25 millimoles of the complex absorbed 5 to 10 millimoles of oxygen in three to four hours. About the same oxygen consumption was measured by dissolving the crystals in borate buffer. In either case an orange-red crystalline product was obtained. This product is insoluble in water, borate buffer and dilute acetic acid and when washed and dried shows an iron content of 53.0%, which with the absence of other elements makes it appear as ferric hydroxide. If dissolved in dilute hydrochloric acid and reprecipitated with alkali, the usual form of ferric hydroxide appears.

The cobalt salt of S-benzylcysteine is easily prepared by dissolving 4 g. of benzylcysteine made as described by Suter[7] in 200 cc. of hot water containing 15 g. of secondary sodium phosphate and slowly adding a mixture of 4 cc. of 1 *M* $CoCl_2$ and 25 cc. of saturated Na_2HPO_4, digesting the mixture for an hour at boiling temperature until no more cobaltous phosphate remains, filtering and washing with boiling water; 2 g. of pink crystals consisting of flat plates is obtained.

Anal. Calcd. for $Co(OOCCHNH_2CH_2SCH_2C_6H_5)_2 \cdot H_2O$: Co, 11.87; S, 12.87; N, 5.63. Found: Co, 11.69; S, 13.67; N, 5.50.

The ferrous complexes of the ethyl ester of thioglycolic acid were prepared in a manner similar to that described for complexes of type VI. For example, 7 g. of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and 25 cc. of water are placed in test-tube B, 3.7 cc. of thioglycolic ester in flask C and after deaeration the iron is tipped into the flask C. From I 3.5 *M* potassium hydroxide is added dropwise. On the first addition of alkali a yellow precipitate forms which rapidly crystallizes but there are dark red or brown spots present which disappear for the most part on warming the mixture with a beaker of water. The yellow crystals are filtered, washed and transferred to a desiccator. It is much more difficult to get reasonable analytical data on this complex because as soon as the desiccator is opened there appears to be a rapid combination with oxygen and the dry crystalline product gets quite hot, fumes are given off and in some cases the substance even glows. This action lasts only a minute or two, after which there appears to be no further change. Analytical data on the three best preparations are as follows.

Anal. Calcd. for $Fe(SCH_2COOC_2H_5)_2$: Fe, 19.05; S, 21.77. Found: Fe, 18.74, 19.58; S, 22.07, 20.60. Calcd. for $Fe(SCH_2COOC_2H_5) \cdot 2H_2O$: Fe, 16.97; S, 19.39. Found: Fe, 17.19; S, 19.57.

The same procedure was followed to prepare the corresponding cobalt complex, which separates as thin leaflets of a gold-green color with a metallic sheen. This compound after washing and drying appears to be stable in air.

Anal. Calcd. for $[Co(SCH_2COOC_2H_5)_2]_2HSCH_2COOC_2H_5$: Co, 16.52; S, 22.39. Found: Co, 16.86, 17.45; S, 23.01, 23.03.

[7] Suter, *Z. physiol. Chem.*, **20**, 562 (1895).

This complex dissolves in chloroform to give a deep red solution. If this complex is refluxed with chloroform for a while, filtered and treated with an equal volume of alcohol, a gelatinous precipitate is formed which may be redissolved on gentle warming. On slow cooling a granular deposit of very tiny black crystals forms. The same substance is also formed by mixing a solution of 2.5 cc. of thioglycolic ester in 10 cc. of alcohol with one of 2.5 g. of $CoCl_2.6H_2O$ in 30 cc. of alcohol and bubbling air through the mixture for an hour. After standing for a day a fine granular deposit settles out which is washed most conveniently with alcohol by centrifuging, yielding 1 g. of product after drying. Either method of preparation gives the compound $Co(SCH_2COOC_2H_5)_3$.

Anal. Calcd.: Co, 14.18; S, 23.08. Found: Co, 14.60, 13.90; S, 23.27, 22.99.

Cobalt complexes with nuclei of type VC have already been described, the only one which is new being a tetrapotassium salt of the cysteine complex. The simplest method of preparation is to start with the corresponding free acid, 5 g. of which is dissolved in 15 cc. of 3.7 *M* potassium hydroxide; then 25 cc. more of this potassium hydroxide solution is added, followed by 50 cc. of alcohol, stirring vigorously during this addition. After standing for an hour the mixture becomes almost solid with masses of very fine hair-like crystals which are filtered off and washed with a little cold water and then with alcohol.

Anal. Calcd. for $[Co(SCH_2CHNH_2COOK)_2OH]_2$: Co, 15.05; S, 16.34; K, 19.89. Found: Co, 14.97; S, 16.47; K, 20.11.

Attempts to prepare the corresponding salt of the thioglycolate complexes resulted only in the separation of uncrystallizable liquids. The barium salts prepared at these high alkalinities were different from those made at a P_H range of 8 to 10 but likewise resisted attempts to crystallize and so were unsuitable for analysis.

Thanks are due to Mr. Bitterlich of this Laboratory for all analytical work done in connection with this paper.

Summary

By working in the absence of oxygen a number of complexes of divalent iron with cysteine, thioglycolic acid and ethyl thioglycolate have been prepared and their structures discussed in some detail. The role of these complexes in the catalytic oxidation of thiol acids in the presence of iron salts is pointed out and on this basis as well as that of some previous work a theory of the mechanism of this catalysis is presented.

NEW YORK CITY

[CONTRIBUTION NO. 204 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XXXI. THE ALPHA AND BETA FORMS OF ETHYL-*d*-GLUCOSIDE AND THEIR TETRAACETATES[1]

BY J. H. FERGUSON[2]

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According to Hudson's[3] second rule of isorotation the sum of the molecular rotations of the alpha and beta derivatives of any aldose where only the end asymmetric carbon atom is affected, is equal to the sum for the alpha and beta forms of the aldose itself. Using the best data of the present time for the rotations of the α and β forms of glucose and methylglucoside, one observes that the rule is borne out very well (see Table I), the difference of the sums being less than 3° in specific rotation. In Hudson's 1909 article, similar data were quoted from E. Fischer[4] for α-ethylglucoside and from Koenigs and Knorr[5] for β-ethylglucoside; namely, $(\alpha)_D$ + 151° and −30°, respectively, leading to (151–30) (208) = 25,200 as the molecular rotation sum for these substances. This value is somewhat larger (5 to 7° in specific rotation) than those mentioned, but it is to be noticed that Koenigs and Knorr's measurement is only approximate, having been obtained from an amorphous substance. Crystalline β-ethylglucoside was first prepared through enzymotic synthesis by Bourquelot and Bridel,[6] who reported its $[\alpha]_D$ value to be −33.4° in aqueous solution, and this rotation was later revised by Bourquelot[7] to −35.8°. For α-ethylglucoside Bourquelot[7] reported $[\alpha]_D$ +150.9°, confirming Fischer's measurement. The revised data of Bourquelot lead to the sum (150.9−35.8) (208) = 23,940, which agrees closely with the sums for the forms of glucose and of methylglucoside. The writer has now re-prepared both α- and β-ethylglucoside by chemical synthesis in crystalline condition, and also their crystalline tetraacetates, the alpha isomer of which is a new

[1] The author has arranged with Dr. C. S. Hudson, at whose suggestion this research was carried out, that it be published in this series. No. XXX, by Dale and Hudson, was published in THIS JOURNAL, **52**, 2534 (1930).

[2] Submitted in partial fulfilment of the requirements for the Ph.D. degree in the Graduate School of the University of Pittsburgh.

[3] Hudson, THIS JOURNAL, **31**, 66 (1909), Scientific Papers of the Bureau of Standards, No. 533 (1925). Reports on Carbohydrates, Tenth Conference of the International Union of Chemistry, Liège, 1930, p. 59.

[4] Fischer, *Ber.*, **28**, 1154 (1895).

[5] Koenigs and Knorr, *ibid.*, **34**, 972 (1901). In Hudson's 1909 article this reference should take the place of the one to E. F. Armstrong, for β-ethylglucoside.

[6] Bourquelot and Bridel, *Compt. rend.*, **155**, 86 (1912); *Ann. chim. phys.*, **29**, 190 (1913).

[7] Bourquelot, *J. pharm. chim.*, **14**, 225 (1916).

substance. As is shown in the tables, the rotations of these four substances agree closely with Hudson's second rule of isorotation.

TABLE I

CONFIRMATION OF HUDSON'S SECOND RULE OF ISOROTATION. GLUCOSE AND THE METHYL- AND ETHYLGLUCOSIDES

Substance	$[\alpha]_D$ in H_2O	Mol. wt.	Mol. rot.	Sum
α-*d*-Glucose[8]	113	180	+20,340	
β-*d*-Glucose[8]	19	180	+ 3,420	23,760
α-Methyl-*d*-glucoside[9]	158.9	194	30,830	
β-Methyl-*d*-glucoside[9]	−34.2	194	− 6,630	24,200
α-Ethyl-*d*-glucoside	152	208	31,620	
β-Ethyl-*d*-glucoside	−36.7	208	− 7,630	23,990

TABLE II

CONFIRMATION OF HUDSON'S SECOND RULE OF ISOROTATION. ACETATES OF THE SUBSTANCES

Substance	$[\alpha]_D$ in $CHCl_3$	Mol. wt.	Mol. rot.	Sum
α-*d*-Glucose pentaacetate[10]	101.6	390	39,600	
β-*d*-Glucose pentaacetate[10]	3.8	390	1,500	41,100
α-Methyl-*d*-glucoside tetraacetate[10]	130.6	362	47,300	
β-Methyl-*d*-glucoside tetraacetate[10]	−18.3	362	− 6,600	40,700
α-Ethyl-*d*-glucoside tetraacetate	132.1	376	49,670	
β-Ethyl-*d*-glucoside tetraacetate	−22.7	376	− 8,535	41,135

The present data for the rotation of the acetates of the ethylglucosides can be used for the calculation of the rotations of the two forms of heptaacetylethylmaltoside by Hudson's first rule of isorotation. Hudson and Johnson[11] have shown from the rotational values of the alpha and beta forms of octaacetylmaltose that the value for the B part of the molecule (which concerns itself with all of the molecule excepting the aldehyde carbon atom) should be one-half the sum of the molecular rotations of the two forms or 125,400/2 = 62,700. The value for A (the aldehyde carbon atom with the attached ethyl group) calculated as half the difference of the rotations of the alpha and beta forms of tetraacetylethylglucoside is (49,670 + 8,535)/2 = 29,102. Combining these two values, we have for the alpha form of heptaacetyl methylmaltoside $[\alpha]_D$ = (29,102 + 62,700)/664 = 138°, and for the beta modification $[\alpha]_D$ = (−29,102 + 62,700)/664 = 50.6°, both referred to chloroform solution. From the close agreement of the latter value with that obtained by Fischer and Koegl[12] for a heptaacetylethylmaltoside made from acetobromomaltose in ethyl alcohol solution and silver carbonate, which gave a specific rotation in acetylene tetra-

[8] Hudson and Yanovsky, THIS JOURNAL, **39**, 1013 (1917).

[9] Riiber, *Ber.*, **57**, 1797 (1924).

[10] Hudson and Dale, THIS JOURNAL, **37**, 1264 (1915).

[11] Hudson and Johnson, *ibid.*, **37**, 1277 (1915). See also Hudson, *ibid.*, **47**, 277 (1925).

[12] Fischer and Koegl, *Ann.*, **436**, 226 (1924).

chloride of 48.93°, it is evident that their compound was a beta modification, as would be expected from the method used in its synthesis. It is known that rotations in chloroform and acetylene tetrachloride are closely alike.

Experimental Part

β-Tetraacetylethylglucoside.—Twenty-five grams of pentaacetylglucose was treated with 51 g. of a solution of glacial acetic acid containing 32% by weight of dry hydrobromic acid. The mixture was allowed to stand at 28° until all the pentaacetylglucose had gone into solution and the color of the mixture had become a deep brownish red. The time required was about one hour. The mixture was then diluted with 102 cc. of cooled chloroform and poured into 150 cc. of ice water. The resulting mixture was well shaken and the layers separated. The water layer was next washed with 30 cc. of chloroform in three portions of 10 cc. each. The combined chloroform layers were washed until neutral with a solution of sodium bicarbonate. The sodium bicarbonate was removed by washing with ice water. The chloroform layer was dried over calcium chloride until clear and filtered into a distilling flask. The solution was concentrated under vacuum at 40° to a thick sirup. At this point the sirup was dissolved in 175 cc. of absolute alcohol and the solution shaken in a flask with 32 g. of freshly prepared silver carbonate, until most of the carbon dioxide had been evolved. The flask was stoppered and shaken on a machine for one-half hour until the solution gave a negative test for bromide ion with silver nitrate. The silver residues were removed by filtration and washed with ether. The neutral filtrate was evaporated to one-half volume on a water-bath, cooled and further evaporated with a stream of air until crystals began to separate. The solution was then cooled overnight in an ice box and the crystalline product filtered off. The yield corresponded to 50% of the theoretical. The compound thus prepared melted at 105°. The crude material was recrystallized from absolute alcohol to constant rotation and melting point. The pure substance melted at 106.8°.

Optical Rotation.—2.4688 g. in 25 cc. of chloroform solution in a 2-dm. tube gave $\alpha = -4.474°$; $[\alpha]_D^{22.5}$ −22.67°.

β-Ethylglucoside.—Koenigs and Knorr[13] described a method for the saponification of β-tetraacetylethylglucoside, but stated that they were unable to crystallize the sirup so prepared. Their method was modified as follows. Five grams of β-tetraacetylethylglucoside was suspended in 300 cc. of distilled water, 16 g. of $Ba(OH)_2 \cdot 8H_2O$, which had been recrystallized three times from hot water, was added and the mixture shaken on a machine for fifteen hours. The excess barium hydroxide was then precipitated with carbon dioxide and the resulting barium carbonate centrifuged and filtered. The filtrate was concentrated under reduced pressure using a bath at 45–50° until a thick sirup was obtained. This residue was extracted with absolute alcohol, the precipitated barium acetate filtered by means of a suction funnel containing filter paper covered with a layer of activated carbon, and the filtrate again concentrated *in vacuo* to a thick sirup with a bath at 35°. To this was added a few drops of dry acetone and the solution was allowed to stand in a desiccator over phosphorus pentoxide for fifteen days. At the end of this time, a small crystalline area was observed which after a few days had spread throughout the sirup in a series of radiating needles. These crystals were used thereafter for seeding purposes. All subsequent saponifications were made with sodium ethylate using the general procedure of Zemplén.[14]

Twenty grams of β-tetraacetylethylglucoside was dissolved in 80 cc. of absolute

[13] Koenigs and Knorr, *Ber.*, **34**, 971 (1901).

[14] Zemplén and Pacsu, *Ber.*, **62**, 1613–1614 (1929).

alcohol and 6 cc. of a solution of 0.3 g. of sodium in 25 cc. of absolute alcohol was added. The flask was tightly stoppered with a rubber stopper covered with tin foil and allowed to stand at room temperature for twenty hours. At the end of this time the solution was evaporated *in vacuo* from the original flask, at room temperature, to dryness. Ten cc. of dry acetone was then added slowly with shaking and the solution was seeded and allowed to stand stoppered overnight at room temperature. The next day the bottom was covered with a mass of needle crystals. The flask was then put in the ice box and allowed to stand for ten hours. At the end of this time the solution had solidified. This was quickly filtered on a glass Büchner funnel which was so arranged that all air passing through was previously dried by calcium chloride. The precipitate was washed with a little dry acetone and then quickly transferred to a vacuum desiccator containing phosphorus pentoxide.

On opening the flask preparatory to filtration, the solid mass became quite sticky due to absorbed water (the compound is very hygroscopic) but after desiccation changed to a white amorphous mass. This mass was then treated with a few cc. of acetone and shaken until most of the compound had gone into solution. At this point, small needles could be seen which ultimately disappeared. The solution was cooled in an ice–salt bath and dry ethyl acetate added slowly, with shaking, until the solution became turbid. It was then seeded as before, stoppered, and put away in the ice box. After a few hours, the solution had solidified to a crystalline mass. This was filtered as before, washed with dry acetone and dried in a phosphorus pentoxide vacuum desiccator. The yield was 45% of the theoretical.

Optical Rotation.—0.3575 g. in 25 cc. of water solution in a 2-dm. tube gave $\alpha = -1.05°$; $[\alpha]_D^{29.5}$ $-36.71°$.

The filtrate from the first filtration, which contained a considerable amount of sirup, was diluted with a little acetone. It was poured into a wide-mouthed flask, stoppered and cooled in an ice–salt bath. Ethyl acetate was then added, as before described, until slight turbidity was attained. After crystallization it was again treated with dry acetone, allowed to stand until only a few needle crystals could be seen and then cooled in an ice–salt bath until turbid. The solution at this point was put in the ice box, and after one day contained a mass of fine white needle crystals. These immediately became gummy during filtration, but on desiccation changed into a pure white crystalline mass.

Optical Rotation.—0.3828 g. in 25 cc. of water solution in a 2-dm. tube gave $\alpha = -1.12°$; $[\alpha]_D^{31}$ $-36.57°$.

Another batch prepared in the same manner and recrystallized three times gave a specific rotation of $-36.85°$. Therefore the average rotation has been given in Table I as $-36.7°$. The melting point was 90.4°.

α-Tetraacetylethylglucoside.—In preparing this compound from β-tetraacetylethylglucoside, titanium tetrachloride was used as described by Pacsu.[15] Fourteen grams of β-tetraacetylethylglucoside dissolved in 110.7 cc. of dry chloroform was treated with 4.2 cc. of titanium tetrachloride in 74.7 cc. of absolute chloroform. A yellow solid immediately separated, which slowly dissolved upon standing. The mixture was heated on a water-bath just below the boiling point for three hours under a reflux condenser. It was then cooled, poured into ice water and stirred until the chloroform layer became clear. The layers were separated and the chloroform washed twice with distilled water, and dried over calcium chloride. It was evaporated *in vacuo* in a bath at 45° to a thick sirup. This was treated with 40 cc. of absolute alcohol, filtered through an activated carbon layer by suction, and cooled in an ice–salt bath. On scratching the sides of the beaker with the glass rod, small crystals began to separate. At the end of an hour the solution solidified. After filtering and drying, 13 g. of material melting at 58–59°

[15] Pacsu, *Ber.*, **61**, 1511 (1928).

was obtained. The specific rotation was +118.9°. The product was then recrystallized from absolute alcohol until it gave a constant rotation and melting point. The final melting point was 61.8°.

Optical Rotation.—0.2209 g. in 25 cc. of chloroform solution in a 2-dm. tube gave $\alpha = +2.335°$; $[\alpha]_D^{30}$ 132.13°. The final melting point was 61.8°.

Anal. Calcd.: C, 51.03; H, 6.43; O, 42.54. Found: C, 50.54, 50.81, 50.63; H, 6.43, 6.37; O. 42.94.

α-Ethylglucoside.—This compound was prepared by the saponification of α-tetraacetylethylglucoside with sodium ethylate in the following manner.

Nine grams of α-tetraacetylethylglucoside was dissolved in 40 cc. of absolute alcohol and 2.7 cc. of a solution containing 0.3 g. of sodium in 25 cc. of absolute alcohol was added. The flask was stoppered with a rubber stopper covered with tin foil and allowed to stand for twelve hours at 33°. At the end of one-half hour, the solution had turned slightly yellow and the odor of ethyl acetate was quite strong. The solution was then filtered through an activated carbon layer to decolorize, and concentrated *in vacuo* in a bath at 40° to a thick sirup. Five cc. of absolute alcohol was then added and the mixture shaken until all of the sirup had gone into solution. It was then seeded from an impure batch of α-ethylglucoside made according to the method described by Fischer,[16] and put in the ice box. After twenty-four hours, granular crystals had separated and were filtered. The yield was 60% of the theoretical. The glucoside was recrystallized from dry acetone to constant melting point and rotation. The final melting point was 114.6°.

Optical Rotation.—0.1402 g. in 25 cc. of water solution in a 2-dm. tube gave $\alpha = 1.705°$; $[\alpha]_D^{28}$ 152.01°.

Summary

The alpha and beta forms of ethyl-*d*-glucoside and their tetraacetates have been prepared in pure condition and their rotations measured. The results closely confirm Hudson's second rule of isorotation when they are compared with other substances of the glucoside series. A test of the first rule of isorotation, made by comparing certain of them with the rotation of a substance of the maltose series (β-ethylmaltoside heptaacetate) also shows confirmation.

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[16] Fischer, *Ber.*, **28,** 1154 (1895).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

RING–CHAIN ISOMERISM IN THE ACETATES OF GALACTOSE OXIME

BY M. L. WOLFROM, ALVA THOMPSON AND L. W. GEORGES

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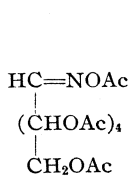
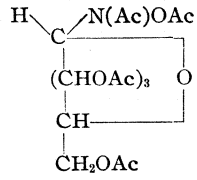
Isomerism of the ring–chain type has been studied[1] in two hexaacetates of glucose oxime and we now wish to report an extension of this study to the galactose series. Mild acetylation of the oxime of aldehydo-galactose pentaacetate yielded a hexaacetate (m. p. 145–146°; $[\alpha]_D$ + 23°, $CHCl_3$) which was distinctly different and was thus isomeric with that (m. p. 129–130°; $[\alpha]_D$ + 33°, $CHCl_3$) obtained by acetylation of galactose oxime under the conditions used by Behrend[2] for the acetylation of mutarotatory substances without change of structure. These two hexaacetates are represented by the formulas



Aldehydo-galactose oxime hexaacetate

I



α-Galactose oxime hexaacetate

II

The structure of compound I above is determined from its method of synthesis from aldehydo-galactose pentaacetate.[3] The ring structure of compound II is determined by its non-identity with compound I. The only other alternative is that these acetates are isomers of the *syn–anti* type. This may be excluded by the fact that the two substances are not directly interconvertible and also by the fact that this type of isomerism is not at all established in aliphatic aldoximes. The ring assignment (1,5) of formula II is arbitrary but the exact size of the ring is not pertinent in this work. Since galactose oxime (un-acetylated) exhibits mutarotation in the levo direction, the designation α is given to its acetate in accordance with the classification of Hudson.[4] In this respect the oxime of galactose differs from that of glucose, which mutarotates in the opposite sense.

The above work may also be used as proof of the existence of a ring structure in α-galactose oxime. This substance is thus similar to the

[1] M. L. Wolfrom and Alva Thompson, THIS JOURNAL, **53**, 622 (1931). In this communication we reported the synthesis of mannononitrile pentaacetate. This was also reported practically simultaneously by V. Deulofew, *J. Chem. Soc.*, 2602 (1930).

[2] R. Behrend and P. Roth, *Ann.*, **331**, 359 (1904); R. Behrend, *ibid.*, **353**, 109 (1907).

[3] M. L. Wolfrom, THIS JOURNAL, **52**, 2464 (1930).

[4] C. S. Hudson, *ibid.*, **31**, 66 (1909).

ammonia condensation product of galactose which has been assigned a ring structure by Levene[5] on the basis of its reactivity with nitrous acid. It differs from the hydrazones of galactose, which have been shown to be open chain or true hydrazones.[6] The same sugar may thus show a varying type of nitrogen condensation product.

Aldehydo-galactose pentaacetate was condensed with hydroxylamine in aqueous solution, in which this acetate exists as the aldehydrol. The resultant product was a monohydrate. Chloral hydrate likewise gives a hydrated oxime which has been formulated as $CCl_3CH(OH)NHOH$. In the case of the galactose compound the water was readily removed to produce the crystalline anhydrous substance. The practical identity of the molecular rotations in chloroform of the hydrated (13,500) and the anhydrous (13,800) galactose compounds is proof that the mole of water is not constitutional (primary valence) but is held by secondary valence forces. This may represent the first clear differentiation between a constitutional and non-constitutional hydrate and was made possible by the optical activity of the substances and by the solubility of the hydrate in a non-aqueous medium. A constitutional hydrate is exemplified by the aldehydrol of aldehydo-galactose pentaacetate ($[\alpha]_D$ + 23°, $CHCl_3$) which has a rotation widely different from its anhydrous form ($[\alpha]_D$ −25°, $CHCl_3$). A hydrated sugar acetate not containing a free carbonyl group is unusual, but recently Haworth and Hickinbottom[7] have reported a monohydrate of a partially acetylated non-reducing sugar, neotrehalose heptaacetate.

The one known form of galactose oxime was prepared by Rischbieth[8] and was the first crystalline sugar oxime obtained. Its mutarotation in water was noted by Jacobi,[9] but his constants have been considerably revised in this work. It is interesting to note that the aldehydo-galactose oxime acetates reverted to the ring form on alkaline de-acetylation.

All substances reported herein were obtained in pure crystalline form.

Experimental

Mutarotation of α-Galactose Oxime.—α-Galactose oxime was prepared according to the directions of Wohl[10] and was recrystallized from hot water. After one recrystallization the melting point of 176–178° (with decomposition) was obtained. This was unchanged by further recrystallization. In water solution at 25° the rotation shown was $[\alpha]_D$ +84° (extrapolated initial value) ⟶ +14.5° (final) (*c*, 1.014; α +0.58° (final); 4-dm. tube). The melting point and final rotation values obtained are in good agreement with the literature. Rischbieth[8] obtained the melting point 175–176° and Jacobi[9]

[5] P. A. Levene, *J. Biol. Chem.*, **24**, 59 (1916).

[6] M. L. Wolfrom and Clarence C. Christman, THIS JOURNAL, **53**, 3413 (1931).

[7] W. N. Haworth and W. J. Hickinbottom, *J. Chem. Soc.*, 2847 (1931).

[8] P. Rischbieth, *Ber.*, **20**, 2673 (1887).

[9] H. Jacobi, *ibid.*, **24**, 696 (1891).

[10] A. Wohl, *ibid.*, **30**, 3103 (1897).

recorded the rotation in water as $[\alpha]_D$ +20.7° (ten minutes) changing to $[\alpha]_D$ +14.7° (final) for a concentration of 5% by volume. We found a much higher value for the initial rotation although the mutarotation was in the same direction. From the solution concentration recorded by Jacobi, it seems probable that initial heating was performed to effect solution before taking the first reading.

α-Galactose Oxime Hexaacetate.—Five grams of α-galactose oxime was treated with 30 cc. of pyridine and 20 cc. of acetic anhydride. After standing overnight, the solution was poured into ice water, whereupon the acetate crystallized immediately; yield, 6.5 g. After two recrystallizations performed by dissolving in a rather large volume of warm ethanol, cooling to room temperature, and adding water to incipient opalescence, the melting point was 130°, unchanged by further recrystallization. The rotation in U. S. P.[11] chloroform of the recrystallized material was $[\alpha]_D^{25}$ +32.1° (*c*, 3.02, α +0.97°, 1-dm. tube). Further recrystallization gave the value $[\alpha]_D^{23}$ +33.7° (*c*, 3.470, α +1.17°, 1-dm. tube) in the same solvent. This value was unchanged over an eighteen-hour period. The substance crystallized in six-sided plates. It was very soluble in chloroform, methyl alcohol, acetone and benzene; soluble in ether and ethyl alcohol; sparingly soluble in petroleum ether and water on heating.

The same product was obtained by acetylating below room temperature, but in lower yield due to the insolubility of α-galactose oxime in the acetylating mixture. A mixture of 18 cc. of pyridine and 12 cc. of acetic anhydride was cooled to 0° and 3 g. of solid α-galactose oxime added. The mixture was shaken mechanically at 0° for several hours and then placed overnight in the ice box. At the end of that period a considerable portion of the oxime had not dissolved. The supernatant liquor was poured into 60 cc. of ice water. The product crystallized readily. It was filtered and washed with cold water; yield, 0.6 g. On one recrystallization from alcohol and water the melting point was 130–131° and showed no depression on admixture with material (m. p. 130°) obtained by room temperature acetylation.

Anal. Subs., 0.5060: 67.50 cc. of 0.1 *N* NaOH; subs., 0.3120: N_2, 11.5 cc. (746.1 mm., 31°). Calcd. for $C_6H_7O_6N(COCH_3)_6$: 13.4 cc. of 0.1 *N* NaOH per 100 mg.; N, 3.14. Found: 13.3 cc. 0.1 *N* NaOH; N, 3.88. The acetyl or saponification value was determined by distillation at constant volume with 15% phosphoric acid.

Aldehydo-galactose Oxime Pentaacetate Monohydrate.—Seven grams (1 mole) of aldehydo-galactose pentaacetate ethyl hemi-acetal was dissolved in 90 cc. of warm water, cooled to room temperature and a solid mixture of 3.5 g. of potassium acetate (2 mols) and 1.7 g. of hydroxylamine hydrochloride (1.5 mols) added to the solution and the mixture shaken until the added solids were dissolved. A heavy crystallization was immediately initiated on scratching the sides of the container. The crystals were removed by filtration and washed with cold water; yield, 4.5 g.; m. p. 104–106°; $[\alpha]_D^{29}$ +32.0° (*c*, 2.499; α +0.80°; 1-dm. tube; U. S. P. $CHCl_3$). After three recrystallizations from dilute alcohol, the melting point was 112–114° and the rotation was $[\alpha]_D^{29}$ +32.0° (*c*, 2.53; α +0.81°; 1-dm. tube; U. S. P. $CHCl_3$). This melting point was unchanged by further recrystallization. The substance showed no tendency to mutarotate in chloroform solution, thus differing from aldehydogalactose pentaacetate aldehydrol. The compound crystallized in lustrous, six-sided, diamond-shaped plates and was very soluble in chloroform and acetone, soluble in benzene and ether, moderately so in ethyl alcohol and warm water and was practically insoluble in petroleum ether.

Anal. Subs., 0.2394: CO_2, 0.4013; H_2O, 0.1290. Subs., 0.3196: 10.40 cc. N_2 (744 mm., 22°). Subs., 0.2601, 0.2000: 31.00, 23.30 cc. 0.1 *N* NaOH. Calcd. for $C_6H_8O_6N(COCH_3)_5 \cdot H_2O$: C, 45.36; H, 5.95; N, 3.28; 11.8 cc. 0.1 *N* NaOH per 100 mg. subs. Found: C, 45.71; H, 6.03; N, 3.60; 11.9, 11.7 cc. 0.1 *N* NaOH.

[11] United States Pharmacopoeia.

The substance lost the equivalent of one mole of water on heating over sulfuric acid to constant weight under reduced pressure at 96–97°.

Anal. Subs., 0.2424: loss in weight, 0.0103. Subs., 0.1580: loss in weight, 0.0067. Calcd.: H_2O, 4.25. Found: 4.25, 4.24.

De-acetylation of the hydrated substance yielded α-galactose oxime. Aldehydo-galactose oxime pentaacetate monohydrate (5 g.) was dissolved in 125 cc. of methanol and cooled in an ice–salt mixture. Dry ammonia gas was then passed through the solution for about forty minutes. The flask was placed in the ice box overnight and the next day was evaporated to dryness in a vacuum desiccator at room temperature. The acetamide formed in the reaction was extracted from the residue with cold methanol. The yield of the crude galactose oxime so obtained was 1.3 g. melting at 160–165°. On one recrystallization from hot water the melting point was raised to 176–178°, which is the melting point of authentic α-galactose oxime. In water solution the rotation of the product was $[\alpha]_D^{26}$ +83° (extrapolated) ⟶ +14.1° (*c*, 1.134; α +0.16° (final); 1-dm. tube). The values previously found for α-galactose oxime were $[\alpha]_D$ +84° ⟶ 14.5°.

Aldehydo-galactose Oxime Pentaacetate.—This substance was prepared from the monohydrate by heating under reduced pressure over calcium chloride at 95–97°. Under these conditions the product did not fuse, the crystals merely appearing to lose their luster. On recrystallization from dry benzene the substance melted at 118–120°. The rotation in U. S. P. chloroform was $[\alpha]_D^{25}$ +34.0° (*c*, 4.994; α +1.70°; 1-dm. tube). Another sample gave the value $[\alpha]_D^{26}$ +34.0° (*c*, 5.146; α +1.75°; 1-dm. tube).

Anal. Subs., 0.2050, 0.1945: 25.2, 23.8 cc. 0.1 *N* NaOH. Calcd. for $C_6H_8O_6N(COCH_3)_5$: 12.35 cc. 0.1 *N* NaOH per 100 mg. subs. Found: 12.3, 12.2 cc. On recrystallization from hot water the monohydrate was reformed, as the following acetyl values show: subs., 0.2000, 0.1794: 23.9, 21.3 cc. 0.1 *N* NaOH. Calcd., 11.8 cc. per 100 mg. Found: 11.9, 11.9 cc.

Aldehydo-galactose Oxime Hexaacetate.—Five grams of aldehydo-galactose oxime pentaacetate monohydrate was added to a mixture of 15 cc. of acetic anhydride and 30 cc. of pyridine, previously cooled to 0°. After solution of the solid the solution was placed in the ice box for one hour. The mixture was then poured into water. The product crystallized immediately and was filtered and washed with water; yield, 3.8 g.; m. p. 144–145°. After one recrystallization performed by dissolving in alcohol and adding water, the substance melted at 146°. Another portion of the crude material was recrystallized four times from acetone, once from alcohol, and again from acetone. The melting point of the final product was then 144–146°. The original product crystallized from the water solution showed a rotation in U. S. P. chloroform solution of $[\alpha]_D^{27}$ +23.7° (*c*, 2.023; α +0.48°; 1-dm. tube) without mutarotation. The rotation of the purified product in the same solvent was $[\alpha]_D^{24}$ +22.5° (*c*, 4.00; α +0.91°; 1-dm. tube). The substance is very soluble in chloroform; soluble in acetone; slightly soluble in methyl and ethyl alcohol; practically insoluble in ether, benzene, water and petroleum ether. The solubilities were thus quite different from those of α-galactose oxime hexaacetate. A mixed melting point of the substance (m. p. 145–146°) with α-galactose oxime hexaacetate (m. p. 129–130°) was 138–143°.

Anal. Subs., 0.2628: 35.00 cc. 0.1 *N* NaOH. Subs., 0.3091: N_2, 9.72 cc. (744 mm., 23°). Calcd. for $C_6H_7O_6N(COCH_3)_6$: 13.4 cc. 0.1 *N* NaOH per 100 mg.; N, 3.13. Found: 13.3 cc.; N, 3.45. The acetyl or saponification value was determined by distillation at constant volume with 15% phosphoric acid.

This substance was de-acetylated in the manner recorded for the hydrated oxime pentaacetate and likewise produced α-galactose oxime. The melting point of the purified product was 177–178°, melting at 176–178° in admixture with authentic α-galactose oxime (m. p. 176–178°).

Summary

1. α-Galactose oxime hexaacetate and the hexaacetate and pentaacetate of aldehydo-galactose oxime have been synthesized in pure crystalline form.

2. It is shown that the two oxime hexaacetates above are isomers of the ring–open chain type.

3. The mole of water in the hydrate of aldehydo-galactose oxime pentaacetate has been shown to be held by non-constitutional or secondary valence forces.

4. Galactose oxime has been shown to possess a ring structure of the α-type.

5. The acetylated aldehydo-galactose oximes revert to the ring form on alkaline de-acetylation.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A POTENTIOMETRIC STUDY OF SCHOLL'S ANTHROXYL RADICALS

BY LOUIS F. FIESER AND WAI YUN YOUNG

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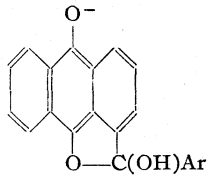
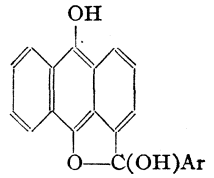
It is generally agreed that the primary oxidation products of all of the monatomic phenols are radicals having univalent oxygen atoms ("oxyls"). The radicals ordinarily are too unstable to have any but a transitory existence, for the free valence shifts from oxygen to carbon and the carbyl radical undergoes various secondary changes. In chlorophenanthrol Goldschmidt and Steigerwald[1] found a compound in which, probably because of the blocking of the positions ortho and para to the oxygen atom, this wandering of the free valence does not occur. Their phenanthroxyls, however, were not completely stable, but associated to form dimolecular peroxides. It remained for Scholl to discover a type of radical which does not manifest even this second kind of instability.[2] That his blue-violet aryl-hydroxyl-*peri*-hydrofurano-anthroxyls of the type of I are strictly monomeric may be due to the spatial characteristics of the anthracene



I



II

[1] Goldschmidt and Steigerwald, *Ann.*, **438**, 202 (1924).

[2] Scholl, *Ber.*, **64**, 1158 (1931).

molecule. Whatever the reason may be, it remains a fact that these remarkable compounds are as stable in the presence of aqueous solvents as many of the quinones, and it is a matter of considerable interest to apply to these compounds the potentiometric methods which have been so fruitful in the study of the oxidation products of the diatomic phenols.

It has been found that an anthroxyl radical in combination with its immediate reduction product (II) forms a reversible oxidation–reduction system having a characteristic and fairly reproducible normal potential. The system is not completely stable, electrode equilibrium is rather slow, and the potentials are not as clearly defined as they are in the case of the majority of quinone–hydroquinone systems; but there is no really essential deviation from the usual behavior.

In planning our experiments we hoped to obtain some information regarding the mode of formation of the radical, for on this point Scholl is not clear. The anthroxyl is formed on the reduction of the corresponding α-aroylanthraquinone, from which it differs by one hydrogen atom, and Scholl, in his first paper,[3] written at a time when the structure of the product was not yet established, considered that the radical is produced directly as the result of the addition of a single hydrogen atom to the quinone. In more recent work[4] the free radical has been prepared by heating the aroylanthrahydroquinone in an acidic medium, when it undergoes some still obscure process of disproportionation.

We prepared a solution of the α-aroylanthraquinone in alcoholic hydrochloric acid, reduced it catalytically at room temperature, and titrated the filtered solution electrometrically in an atmosphere of nitrogen with a solution of benzoquinone. When the titration was carried out very shortly after the reduction, there was obtained a curve (the lower curve in Fig. 1) which is clearly that of the anthraquinone–anthrahydroquinone system, for the slope is that of the two-hydrogen type of oxidation ($n = 2$) and the normal potential of 0.178 v. is very close to the value for anthraquinone itself ($E_0 = 0.154$ v.). Like most other quinones, the α-aroylanthraquinone thus adds two hydrogen atoms simultaneously, even on gentle reduction. When a titration was carried out with a portion of the same reduced solution after it had been allowed to stand for some time, or after it had been heated, there were two distinct portions of the titration curve. The first portion, shown as the lower part of the upper curve in Fig. 1, again had a slope corresponding to $n = 2$ and a mid-point potential of 0.178 v., but it was considerably shorter than that obtained with the fresher solution. It is evident that some of the α-aroylanthrahydroquinone present at the time of the first titration had disappeared on standing. The amount so lost is indicated on the chart by the distance, A, between the two end-points.

[3] Scholl, *Ber.*, **54**, 2376 (1921).

[4] Scholl and Hähle, *ibid.*, **56**, 1065 (1923).

The upper portion of the second curve is quite different. The slope corresponds more nearly to that to be expected in an oxidation which involves a single hydrogen atom ($n = 1$), and the average value of 0.361 v. found for the normal potential is considerably higher than that for the anthraquinone–anthrahydroquinone system. This part of the titration obviously represents the oxidation of the monatomic phenol, II, to the

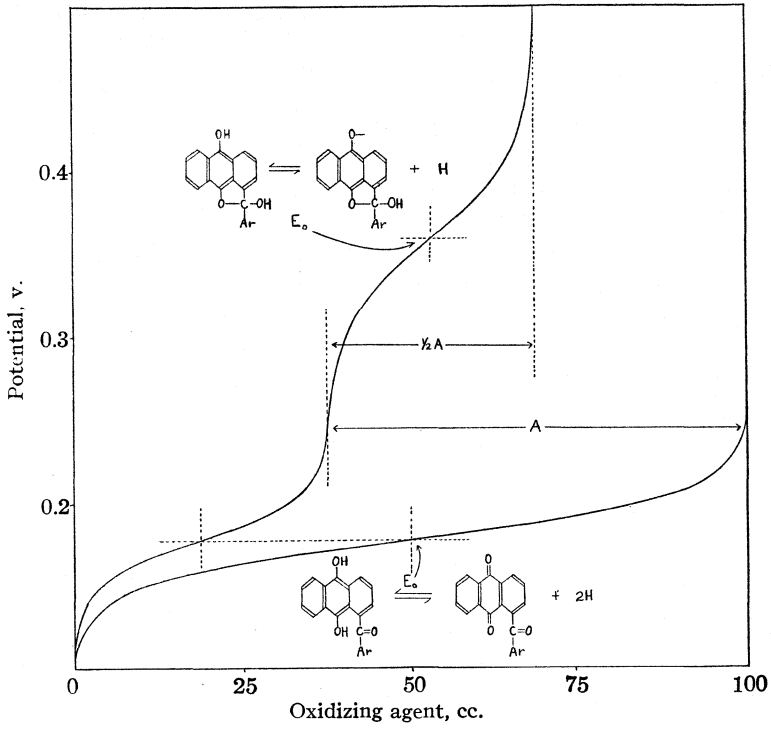
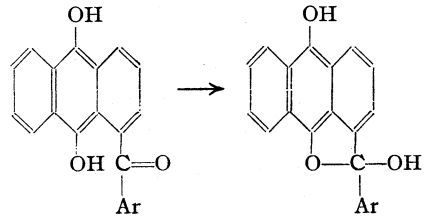


Fig. 1.

anthroxyl radical. It is of significance that the amount of oxidizing solution required for this second part of the titration was found to be approximately half of the quantity, A, which represents the amount of the anthrahydroquinone which disappeared between the first and the second experiment. Since one molecule of the phenol (II) is equivalent to one-



half molecule of the anthrahydroquinone, it is clear that the former substance is produced quantitatively from the latter. The aroylanthrahydroquinone evidently undergoes intramolecular addition of the hydroxyl group to the carbonyl group, the reaction being catalyzed by mineral acids.

If an oxidizing agent is added at this point the phenol is converted into the anthroxyl radical. In the absence of an oxidizing agent, and when heated, the phenol apparently disproportionates to give the radical and an unidentified reduction product.

The compounds included in our study were those obtained from α-benzoyl-, α-[*m*-xyloyl]- and α-[*p*-anisoyl]-anthraquinone. It was found that the potential of the radical system is influenced to only a negligible extent by substitution in the aryl group, and it thus appears unprofitable to pursue this line of investigation further. The interesting nitrogen-containing radicals described by Scholl[5] were also examined, but the potentials were so ill-defined that we can only say that these systems lie in approximately the same potential range as those of the oxyl radicals.

The potentials found for the systems containing the anthroxyl radicals are of course more certain than the values estimated[6] for a number of simply constituted oxyl radicals by an indirect and approximate method, and some comparison of the results is of interest, even though the compounds studied are of such different types that only a very rough comparison is possible. If the reductant (II) of Scholl's radical is regarded as a *p*-alkoxy-anthranol, then it should bear a relationship to anthrahydroquinone similar to that of *p*-methoxyphenol (E_0, 0.984 v.) to hydroquinone (E_0, 0.715 v.). From these figures, the first of which was determined by the indirect method, and from the potential of the anthraquinone–anthrahydroquinone system (E_0, 0.154 v.), Scholl's radical would be expected to form a system having a potential of 0.423 v. This places the system in approximately the right region, the value found being 0.361 v.

Experimental Part

A weighed sample of the aroylanthraquinone was dissolved in the boiling solvent (95% ethyl alcohol, 0.2 *N* in both hydrogen chloride and lithium chloride) and the solution was washed into a hydrogenation bottle, cooled and the total weight of the solution determined. On adding Adams' platinum oxide catalyst and shaking for a few minutes under a slight pressure of hydrogen, the yellow solution became reddish-brown in color. Approximately half of the solution was then forced under hydrogen pressure through a filter and into a titration vessel which had been previously swept free of oxygen by purified nitrogen. The titration vessel was painted black, for the free radical is very sensitive to the light. The vessel was connected to a hydrogen electrode containing some of the same buffer solution, and a titration was performed as rapidly as possible, the end-points of the two curves and the mid-point potentials being estimated graphically. At the end of the titration the weight of the solution taken in the experiment was

[5] Scholl, *Ber.*, **60**, 1236, 1685 (1927); **61**, 968 (1928).

[6] Fieser, THIS JOURNAL, **52**, 5204 (1930).

determined, the weights of the vessel and of the titrating solution being deducted from the total weight. In this way the fraction of the weighed sample which had been used was determined. A titration was then carried out with a second portion of the same original solution, after allowing time for the condensation reaction to take place.

The first titration could be carried out within a few minutes and the potentials were sharply defined and showed only a slight drift. In the second part of the titration the potential after each addition of reagent came to a condition of comparative rest only after several minutes and the final values could not be determined with great accuracy. A typical titration is given in Table I, and the deviations in the values in the last column for the quantity n from the theoretical value of 1.0 will illustrate the general uncertainty of the results which can be obtained in this part of the titration.

TABLE I

TITRATION OF α-[*m*-XYLOYL]-ANTHRAHYDROQUINONE WITH BENZOQUINONE SOLUTION

First curve			Second curve		
Oxid. soln., cc.	E, v.	n	Oxid. soln., cc.	E, v.	n
0.0	0.1162	...	20.0	0.313	...
1.0	.1405	2.0	20.5	.339	...
4.0	.1596	2.0	21.5	.350	1.4
6.0	.1665	1.9	22.5	.359	1.5
8.5	.1737	1.8	23.0	.363	...
10.5	.1792	2.4	24.0	.376	1.0
13.0	.1865	1.9	24.5	.382	1.2
15.0	.1938	1.8	25.0	.391	1.2
17.0	.2042	1.8	25.5	.405	1.2
19.0	.2252	1.8	26.0	.421	1.4
19.5	.2550	1.9	26.5	.520	...
End-point, 19.8 cc.; E_0, 0.178 v.			End-point, 26.2 cc.; E_0, 0.360 v.		

Table II gives a summary of the quantities of reagent consumed in two typical pairs of experiments, all reduced to a common basis. One portion (a) of Solution 1 was titrated fifteen minutes after the completion of the hydrogenation, and it was found to contain both the anthrahydroquinone, which consumed 27.5 cc. of reagent, and the anthranol, which required 5.1 cc. On the assumption that the latter substance requires one-half as much reagent as the former, the total reagent used, in terms of anthrahydroquinone equivalents, is 27.5 + 10.2 = 37.7 cc. This is very close to the amount (last column) calculated from the weight of sample taken and the concentration of the titrating solution. A second check is given by comparing the two titrations, *a* and *b*, on portions of the same

TABLE II

TITRATION OF 0.2 G. OF α-[*m*-XYLOYL]-ANTHRAHYDROQUINONE IN 160 G. OF SOLVENT WITH 0.0157 MOLAR BENZOQUINONE SOLUTION

		Volume of oxidizing solution, cc.					
	Time of standing,	First		Second		Equiv. total	
No.	min.	curve	Decrease	curve	Increase	Found	Calcd.
1a	15	27.5	6.8	5.1	3.3	37.7	37.6
1b	153	20.7		8.4		37.5	37.6
2a	13	28.0	5.8	4.2	3.2	36.4	37.6
2b	132	22.2		7.4		37.0	37.6

solution. After standing for the time specified, Solution 1b contained less of the anthrahydroquinone and more of the anthranol. The change in titer of the latter is approximately half that of the former.

A summary of the average values found for the normal potentials, or the potentials of the half-oxidized solutions against a hydrogen electrode in the same buffer solution at 25°, is given in Table III.

TABLE III

POTENTIALS (E_0) OF THE SYSTEMS FROM α-AROYLANTHRAQUINONES AND THE CORRESPONDING RADICALS

Aryl group	Quinone, v.	Radical, v.
Phenyl-	0.182	0.360
m-Xylyl-	.178	.361
p-Anisyl-	.178	.356

Summary

The free anthroxyl radicals discovered by R. Scholl form, with their reductants, fairly stable oxidation–reduction systems of definite, if not very accurately determinable, potential. In dilute acidic solution the reductant of the radical is formed by the intramolecular condensation of the corresponding α-aroylanthrahydroquinone.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PREPARATION AND GERMICIDAL PROPERTIES OF PARA-HYDROXYPHENYL ALKYL SULFIDES

BY C. M. SUTER AND HAROLD L. HANSEN

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Although many investigations of the germicidal properties of alkylated phenolic compounds[1] have been made, the available systematic information demonstrating the influence of alkyl groups not directly attached to the aromatic nucleus has been limited to the recent[1f,2] work on the alkoxyphenols. The present communication describes a study of a series of *p*-hydroxyphenyl *n*-alkyl sulfides, the alkyl group varying from methyl to *n*-hexyl. Since it has been shown by other workers[3] that the hydroxy-

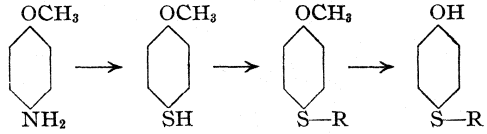
[1] Only some of the more recent articles can be listed here: (a) Johnson and Lane, THIS JOURNAL, **43**, 348 (1921); (b) Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926); (c) Talbot and Adams, *ibid.*, **49**, 2040 (1927); (d) Klarmann, *ibid.*, **48**, 791, 2358 (1926); (e) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930); (f) Read and Miller, THIS JOURNAL, **54**, 1195 (1932).

[2] Klarmann, Gatyas and Shternov, *ibid.*, **53**, 3397 (1931); **54**, 298, 1204 (1932).

[3] Hilbert and Johnson, *ibid.*, **51**, 1526 (1929); Dunning, Dunning and Drake, *ibid.*, **53**, 3466 (1931); Klarmann, Gates and Shternov, *ibid.*, **54**, 1204 (1932).

diphenyl sulfides are more potent germicides than the corresponding hydroxydiphenyl ethers, it was thought that the hydroxyphenyl alkyl sulfides would be more bactericidal than the corresponding oxygen compounds. The results have substantiated this surmise.

There are several procedures by which *p*-hydroxyphenyl alkyl sulfides have been synthesized.[4] The method developed for this work is outlined below.



The last step is of interest as it illustrates the relative inertness of the sulfide linkage toward hydrobromic acid. No trace of a thiol was ever noted among the reaction products. In two cases *p*-ethoxyphenyl alkyl sulfides were deëthylated but they gave somewhat lower yields of the desired phenols than the methoxy derivatives. An attempt to prepare *p*-hydroxyphenyl *n*-butyl sulfide by the action of diazotized *p*-aminophenol upon the sodium salt of butanethiol-1 was not successful.

Since the *p*-alkoxyphenyl alkyl sulfides were prepared in a pure state, a study of the value for the atomic refraction of sulfur in these compounds was made. It has been shown recently[5] that the value for thiol sulfur recommended by Price and Twiss[6] gives good results for two series of aliphatic thiols. The corresponding value for sulfide sulfur (7.97 for Na_D) is in only fair agreement with the refractive index for phenyl methyl sulfide and the presence of a methoxy group results in an exaltation which increases somewhat irregularly with the size of the alkyl group attached to the sulfur. These results are shown in Table I together with the boiling points of the samples used in the determinations.

TABLE I

Compound	B. p., °C.	mm.	d_4^{25}	n_D^{25}	MR_D Found	Calcd.	EM_D
$C_6H_5SCH_3$	58–60	6	1.0533	1.5832	39.40[7]	38.85	0.55
p-$CH_3OC_6H_4SH$	89–90	5	1.1313	1.5801	41.23	39.46	1.77
p-$CH_3OC_6H_4SCH_3$	99	4	1.1069	1.5764	46.12	44.16	1.96
p-$CH_3OC_6H_4SC_2H_5$	103	5	1.0674	1.5600	50.95	48.58	2.37
p-$CH_3OC_6H_4SC_3H_7$	110	5	1.0424	1.5545	56.07	53.00	3.07
p-$CH_3OC_6H_4SC_4H_9$	120	5	1.0303	1.5445	60.17	57.42	2.75
p-$CH_3OC_6H_4SC_5H_{11}$	127	5	1.0149	1.5380	64.64	61.84	2.80
p-$CH_3OC_6H_4SC_6H_{13}$	142	5	0.9975	1.5315	69.61	66.26	3.35
p-$C_2H_5OC_6H_4SCH_3$	98–100	5	1.0693	1.5618	52.58	48.58	4.00

[4] Leuckart, *J. prakt. Chem.*, [2] **41**, 192 (1890); Zincke and Ebel, *Ber.*, **47**, 1105 (1914).

[5] Ellis and Reid, THIS JOURNAL, **54**, 1674 (1932).

[6] Price and Twiss, *J. Chem. Soc.*, **101**, 1263 (1912).

The effect of the ethoxy group is very pronounced, the exaltation corresponding to a 50% increase in the value for the atomic refraction of sulfur. A study of the exaltations caused by a number of substituents in anisole and phenyl methyl sulfide has previously shown[7] the great susceptibility of sulfur to influences which cause optical exaltation.

The germicidal properties[8] of the *p*-hydroxyphenyl alkyl sulfides are at a maximum toward *B. typhosus* with the *n*-butyl and *n*-amyl compounds. The *n*-hexyl compound is probably the most effective in this series toward *Staph. aureus*, since its phenol coefficient is not much higher than that of the *n*-amyl derivative. In Table II is shown a summary of the results obtained together with the values for the corresponding oxygen compounds.[9]

TABLE II

Alkyl group	*B. typhosus* Sulfide	*B. typhosus* Ether	*Staph. aureus* Sulfide	*Staph. aureus* Ether
Methyl	5	1.0	4	0.8
Ethyl	12	1.5	12	1.5
n-Propyl	25	5.4	25	4.1
n-Butyl	75	14	60	9.3
n-Amyl	75	29	150	30
n-Hexyl	<40	18	200	100

The determinations of the phenol coefficients were made by diluting with water a solution of the sulfide in 20% alcohol (except *n*-hexyl where a 50% alcohol solution was used) to obtain the desired concentrations. The tests using *B. typhosus* were made at 20° in accordance with the Hygienic Laboratory method while those with *Staph. aureus* were made at 37.5°. The *n*-hexyl compound was too insoluble to determine its phenol coefficient toward *B. typhosus* except to note its ineffectiveness at a concentration corresponding to the value 40.

The study of various types of hydroxyphenyl alkyl sulfides is being continued in this Laboratory.

Experimental

p-Methoxythiophenol.—This was first prepared by Gattermann[10] by reduction of the corresponding sulfinic acid. In the present work it was prepared from *p*-anisidine by the Leuckart[11] reaction. The following conditions were found to be the most satisfactory. In a 5-liter 3-necked flask equipped with a mechanical stirrer, dropping funnel and outlet tube to the hood, was placed a solution of 300 g. (1.9 moles) of potassium ethyl xanthate dissolved in 700 cc. of water. To this solution, kept at 70 to 80°, was

[7] The value 39.44 is given by Brand and Kranz, *J. prakt. Chem.*, [2] **115**, 143 (1927).

[8] We are very much indebted to Dr. Oliver Kamm, scientific director, and Mr. H. C. Hamilton, pharmacologist, of Parke, Davis and Company for permission to include a report of the results of the pharmacological study of these compounds made by them.

[9] Klarmann, Gates and Shternov, THIS JOURNAL, **54**, 298 (1932).

[10] Gattermann, *Ber.*, **32**, 1147 (1899).

[11] Leuckart, *J. prakt. Chem.*, [2] **41**, 186 (1890).

added slowly with vigorous stirring a cold solution containing 123 g. (1 mole) of diazotized *p*-anisidine to which had been added enough sodium acetate to neutralize the free acid. Stirring and heating were continued for about an hour after the addition of the diazonium solution to complete the decomposition of the intermediate diazonium ethyl xanthate. The dark oil was removed from the cooled solution and the aqueous layer extracted with ether, the product obtained being combined with that first removed; this material was then refluxed for three hours with a solution of 115 g. of potassium hydroxide in 2 liters of 95% ethyl alcohol to which had been added 20 g. of glucose. The alcohol was removed by distillation until the residual volume was about 300 cc. This was acidified with cold dilute sulfuric acid, a few grams of zinc dust added, and the oily thiol removed by distillation with steam. The distillate was extracted with ether, the ether dried over calcium chloride, and the oil remaining after distillation of the ether was distilled under reduced pressure. The yield was 100 to 110 g. or 71 to 79% of the calculated amount of material boiling at 88–90° at 5 mm. pressure. The physical constants in Table I were determined on a redistilled sample boiling at 89–90° at 5 mm. pressure. The brown amorphous lead salt was prepared and analyzed.

Anal. Calcd. for $C_{14}H_{14}O_2S_2Pb$: Pb, 42.68. **Found:** Pb, 42.47.

***p*-Ethoxythiophenol.**—This has been made by Law and Johnson[12] by the Leuckart reaction. Following the procedure outlined for *p*-methoxythiophenol a 76% yield of material boiling at 102–104° under 4 mm. was obtained.

***p*-Alkoxyphenyl *n*-Alkyl Sulfides.**—The *p*-methoxyphenyl methyl sulfide[13] and *p*-ethoxyphenyl ethyl sulfide[14] have been prepared previously. The methyl and ethyl aryl sulfides were prepared here by the method of Gilman and Beaber[15] from the dialkyl sulfates and the thiol. For the other alkyl compounds the bromides were used. The following experiment is typical.

Preparation of *p*-Methoxyphenyl *n*-Propyl Sulfide.—To a solution of sodium ethylate made by dissolving 8 g. (0.35 mole) of sodium in 150 cc. of absolute ethyl alcohol, was added 42 g. (0.3 mole) of *p*-methoxythiophenol and 40 g. (excess) of *n*-propyl bromide. The mixture was refluxed for an hour, the alcohol removed by distillation and the residue poured into water. The yellow oil was extracted with ether, dried with sodium sulfate and distilled under reduced pressure. In Table III are given the yields obtained in the preparations and the boiling points and analyses of the sulfides prepared. The densities and refractive indices have been given in Table I.

TABLE III

Compound	Yield, %	B. p., °C.	Pressure, mm.	Sulfur, % Calcd.	Found
p-$CH_3OC_6H_4SCH_3$	90	99–100, m. p. 22–23	4	...	...
p-$CH_3OC_6H_4SC_2H_5$	93	103	5	19.06	19.33
p-$CH_3OC_6H_4SC_3H_7$	77	110–111	5	17.59	17.72
p-$CH_3OC_6H_4SC_4H_9$	87	119–122	5	16.33	16.41
p-$CH_3OC_6H_4SC_5H_{11}$	81	124–127	5	15.25	15.56
p-$CH_3OC_6H_4SC_6H_{13}$	87	138–141	5	14.29	14.19
p-$C_2H_5OC_6H_4SCH_3$	90	98–100, m. p. 19–20	5	19.06	19.30
p-$C_2H_5OC_6H_4SC_2H_5$	96	110–112	6	...	...

[12] Law and Johnson, THIS JOURNAL, **52**, 3625 (1930).

[13] Gattermann, *Ber.*, **32**, 1147 (1899).

[14] Kehrman and Sava, *ibid.*, **45**, 2895 (1912).

[15] Gilman and Beaber, THIS JOURNAL, **47**, 1449 (1925).

The boiling points of the compounds when refractionated have been given in Table I.

Three of the sulfides were converted into the corresponding sulfones by oxidation with 30% hydrogen peroxide in glacial acetic acid solution.[15] *p*-Methoxyphenyl methyl sulfone was recrystallized from hot water and melted at 119–120°.

Anal. Calcd. for $C_8H_{10}O_3S$: S, 17.22. Found: S, 17.23.

p-Methoxyphenyl ethyl sulfone, crystallized from dilute alcohol, melted at 55–56°.

Anal. Calcd. for $C_9H_{12}O_3S$: S, 16.01. Found: S, 16.18.

p-Ethoxyphenyl methyl sulfone crystallized from hot water in glistening white flakes which melted at 89–89.5°.

Anal. Calcd. for $C_9H_{12}O_3S$: S, 16.01. Found: S, 16.34.

Oxidation of *p*-ethoxyphenyl ethyl sulfide gave an oily material. Since the sulfones were prepared as convenient derivatives and this one was not suitable for identification purposes it was not further studied.

p-Hydroxyphenyl Alkyl Sulfides.—The alkoxy compounds were all dealkylated by a procedure based in part upon the methods used by Stoermer[16] and Semmler.[17] Details are given for the preparation of *p*-hydroxyphenyl methyl sulfide. The results for the whole series are given in tabular form in Table IV.

In a round-bottomed flask attached to a reflux condenser and supplied with an inlet tube for carbon dioxide were placed 5 g. of *p*-methoxyphenyl methyl sulfide, 40 cc. of glacial acetic acid and 15 cc. of 48% hydrobromic acid. A slow stream of carbon dioxide was passed through the mixture while it was heated at 120–130° in an oil-bath for three and one-half hours. The reaction mixture was poured onto ice, the acid neutralized with sodium carbonate and the phenol extracted with ether. The product was treated with sodium hydroxide to separate the phenol from any unchanged material, the alkaline solution acidified and the precipitate twice crystallized from petroleum ether (b. p. 60–90°). Included in Table IV are the approximate solubilities of the sulfides in 20% ethyl alcohol solutions.

TABLE IV

p-Hydroxyphenyl *n*-alkyl sulfide	Yield, %	M. p., °C. corr.	Sulfur, % Calcd.	Sulfur, % Found	Soly. in 20% g./100 cc.
Methyl[18]	55	83–84	22.87	23.00	1.0 (25°)
Ethyl[19]	59	39–41	...	...	0.4 (26°)
n-Propyl	54	33–33.5	19.06	19.23	.15 (25°)
n-Butyl	37	36–37	17.59	17.81	.1 (26°)
n-Amyl	42	55–56	16.34	16.54	.05 (30°)
n-Hexyl	26	58–59	15.26	15.35	.013 (25°)

Summary

A considerable number of sulfides have been prepared by alkylation of *p*-methoxy- and *p*-ethoxythiophenol. The atomic refraction of sulfur in these compounds is abnormally great.

A series of *p*-hydroxyphenyl alkyl sulfides has been prepared and the germicidal properties of these compounds are reported.

EVANSTON, ILLINOIS

[16] Stoermer, *Ber.*, **41**, 321 (1908).

[17] Semmler, *ibid.*, **41**, 1773 (1908).

[18] Zincke and Ebel, *Ber.*, **47**, 1105 (1914).

[19] This has been previously prepared by Leuckart, *Chem. Centr.*, [II] **1**, 758 (1890), by alkylation of *p*-hydroxythiophenol.

[COMMUNICATION NO. 100 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. XVII. FRIEDEL–CRAFTS SYNTHESES WITH THE POLYANHYDRIDES OF THE DIBASIC ACIDS

BY JULIAN W. HILL

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It has been shown that the polymeric anhydrides of aliphatic dibasic acids react smoothly and normally as acid anhydrides with aniline,[1] with phenol,[1a] with ammonia,[2] and with diethylamine.[2b] In each reaction three products are formed. The course of the reactions is shown by the following scheme, which does not consider the end groups of the polyanhydride

$$(\text{—OC(CH}_2)_n\text{CO—O—})_x + \text{RH} \longrightarrow \underset{\text{(a)}}{\frac{x}{4}\,\text{R—OC(CH}_2)_n\text{CO—R}} + \underset{\text{(b)}}{\frac{x}{2}\,\text{R—OC(CH}_2)_n\text{COOH}} + \underset{\text{(c)}}{\frac{x}{4}\,\text{HOOC(CH}_2)_n\text{COOH}}$$

where R is C_6H_5NH—, C_6H_5O—, NH_2— or $(C_2H_5)_2N$—

It has been demonstrated on theoretical grounds that the products of types (a), (b) and (c) should be formed in the molecular ratio of 1:2:1. This has been verified quantitatively in the aniline reaction.[1]

The dibasic acid polyanhydrides have now been found to react typically with benzene in the presence of anhydrous aluminum chloride to yield dibenzoyl alkane, ω-benzoyl fatty acid, and dibasic acid.

$$(\text{—OC(CH}_2)_n\text{CO—O})_x + \text{C}_6\text{H}_6 + (\text{AlCl}_3) \longrightarrow \frac{x}{4}\,\text{C}_6\text{H}_5\text{CO(CH}_2)_n\text{COC}_6\text{H}_5 + \frac{x}{2}\,\text{C}_6\text{H}_5\text{CO(CH}_2)_n\text{COOH} + \frac{x}{4}\,\text{HOOC(CH}_2)_n\text{COOH}$$

This reaction has been carried out with polymeric adipic and sebacic anhydrides and benzene. There is no reason to doubt that it is perfectly general and applicable to any polymeric dibasic anhydride and any suitable aromatic hydrocarbon.

This reaction is particularly interesting in providing a convenient method of synthesis for the ω-benzoyl fatty acids which have heretofore been prepared by more elaborate syntheses or in very low and uncertain yields as by-products in the Friedel–Crafts reaction of dibasic acid chlorides with aromatic hydrocarbons.[3]

Experimental Part

Friedel–Crafts Reaction between Adipic Polyanhydride and Benzene.—One hundred and forty-six grams (one mole) of adipic acid was refluxed with 400 cc. of acetic

[1] (a) Hill, THIS JOURNAL, **52**, 4110 (1930); (b) Hill and Carothers, *ibid.*, **54**, 1569 (1932).

[2] (a) Étaix, *Ann. chim.*, [7] **9**, 356 (1896); (b) Einhorn and Diesbach, *Ber.*, **39**, 1222 (1906).

[3] Auger, *Ann. chim.*, [6] **22**, 360 (1891); Étaix, *ibid.*, [7] **9**, 391 (1896).

anhydride for six hours. The excess acetic anhydride and the acetic acid formed in the reaction were removed by distillation *in vacuo* up to 120° bath temperature. The resulting polyanhydride[1a] was dissolved in 400 cc. of warm, dry benzene. Three hundred grams of anhydrous aluminum chloride was suspended in 1500 cc. of dry benzene contained in a 3-necked 3-liter flask fitted with a reflux condenser and a mechanical stirrer.

The anhydride solution was added with stirring over a period of one hour and the mixture allowed to stand overnight. The product was decomposed in ice and 250 cc. of concentrated hydrochloric acid added. The benzene layer was separated and extracted with dilute aqueous sodium hydroxide. The water phase deposited a small amount of crystals on standing which were identified after recrystallization from water as adipic acid by a mixed melting point determination.

The alkaline solution was acidified and the crystalline precipitate of ω-benzoylvaleric acid filtered off: weight dry, 78 g.; yield, 75%. The product was recrystallized from a benzene–petroleum ether mixture, m. p. 70–71°.[4]

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8. Found: C, 70.1; H, 6.7.

The extracted benzene was distilled to a small volume and chilled; 56.5 g. of dibenzoylbutane was obtained, yield 85%. Recrystallized from alcohol, it was slightly pink and melted at 105–106°.[5] It was identified by means of a mixed melting point determination with an authentic specimen.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found: C, 80.6; H, 7.0.

Friedel–Crafts Reaction between Sebacic Polyanhydride and Benzene.—One hundred and one grams (0.5 mole) of sebacic acid was refluxed with 300 cc. of acetic anhydride for five hours. The excess anhydride and the acetic acid formed were distilled off *in vacuo* up to 120°. The residual polyanhydride was dissolved in 250 cc. of warm dry benzene and added to 150 g. of anhydrous aluminum chloride suspended in 750 cc. of dry benzene as in the previous preparation. The products were worked up in the same way. The crude precipitated ω-benzoylnonanoic acid was extracted with hot water to remove sebacic acid. Fifteen grams of sebacic acid separated from the washings and was identified by a mixed melting point determination with a known sample. The ω-benzoylnonanoic acid weighed 50 g., a yield of 78%. Recrystallized from dilute alcohol, it melted at 77–78°.[6]

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.3; H, 8.4. Found: C, 73.3; H, 8.4.

The dibenzoyloctane was recovered from the benzene solution and weighed 35 g., a yield of 86%. Recrystallized from alcohol, it melted at 92–93°.[7]

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 82.0; H, 8.1. Found: C, 81.7; H, 8.1.

Summary

The polymeric anhydrides of adipic and sebacic acids react with benzene in the presence of anhydrous aluminum chloride to yield mixtures of the appropriate dibenzoyl alkane, ω-benzoyl fatty acid, and dibasic acid. The reaction is doubtless general.

WILMINGTON, DELAWARE

[4] Grateau, *Compt. rend.*, **191**, 947 (1930), gives 71°.

[5] Étaix, *Ann. chim.*, [7] **9**, 372 (1896), gives 102–103°.

[6] Auger, *ibid.*, [6] **22**, 364 (1891), gives 78–79°.

[7] Auger, *ibid.*, [6] **22**, 363 (1891), gives 88–89°.

NOTES

Bromophenacyl Esters of Organic Acids

By Hakon Lund and Tage Langvad

p-Bromophenacyl bromide has proved to be a useful reagent for the identification of organic acids. It is therefore of some value to know the properties of as large a number of esters as possible. As a contribution to the knowledge of such compounds we have prepared, carefully purified and analyzed a number of *p*-bromophenacyl esters. Usually the esters may be recrystallized from alcohol, but when they are very slightly soluble in this solvent glacial acetic acid is an excellent solvent for recrystallization.

The purified compounds were analyzed by micro-determination of bromine using the method of Pregl except that the bromine in the solution obtained after the combustion was titrated instead of being determined gravimetrically. 0.05 *N* silver nitrate and 0.05 *N* ammonium thiocyanate in microburets were used. The accuracy is about 0.4% and equals that of the gravimetric method, but the titration is much more convenient. If chlorine is present, a correction for dissolved silver chloride has to be applied. When the solution to be titrated is about 50 cc., this correction amounts to 0.027 cc., which is to be added to the volume of silver nitrate used. The solubility of silver chloride is considerably higher in this solution than in pure water. When chlorine is absent it is unnecessary to filter the solution from silver bromide.

The esters of adipic, *m*-nitrocinnamic, and *p*-nitrocinnamic acids are very slightly soluble in alcohol and were therefore recrystallized from glacial acetic acid.

From pyruvic and malonic acids no ester could be obtained.

p-Bromophenacyl Esters

(R means *p*-$BrC_6H_4COCH_2$)

Acid	Formula of ester	M. p. (corr.), °C.	Bromine, % Calcd.	Found
Tiglic	$CH_3CH{=}CH(CH_3)COOR$	67.9	26.9	27.0
Adipic	$(-CH_2CH_2COOR)_2$	152.6	29.6	29.5
Chloroacetic	$CH_2ClCOOR$	103.7	(1)[a]	
m-Hydroxybenzoic	HOC_6H_4COOR	176.1–176.4	24.4	24.5
p-Hydroxybenzoic	HOC_6H_4COOR	191.3–191.7	24.4	24.6
m-Nitrobenzoic	$NO_2C_6H_4COOR$	135.4	22.0	22.1
o-Chlorobenzoic	ClC_6H_4COOR	107.0	(2)[a]	
m-Nitrocinnamic	$NO_2C_6H_4CH{=}CHCOOR$	178.0	20.5	20.4
p-Nitrocinnamic	$NO_2C_6H_4CH{=}CHCOOR$	191.0	20.5	20.6
o-Methoxycinnamic	$CH_3OC_6H_4CH{=}CHCOOR$	145.0	21.4	21.3
o-Methoxy-allocinnamic	$CH_3OC_6H_4CH{=}CHCOOR$	97.5	21.4	21.46

[a] The analytical data are best expressed by calculation of the molecular weights based upon the titration results.

	Mol. wt. calcd.	Mol. wt. found
(1)	291.4	294.0
(2)	353.5	351.0

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RECEIVED MAY 16, 1932
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2-Chloro-5-methylfuran and 2-Methyl-5-nitrofuran

BY HENRY GILMAN AND GEORGE F. WRIGHT

The recent availability[1] of nuclear substituted 2-furfurals and the highly effective Wolff–Kischner[2] reduction for the conversion of an aldehyde to a methyl group combine to facilitate the allocation of substituents in the furan nucleus and so arrive at generalizations on furan nuclear orientation.

2-Chloro-5-methylfuran has been prepared by the hydrazine–sodium ethylate reduction[2] of 5-chloro-2-furfural. It is identical with the compound recently prepared by the decarboxylation of 5-chloro-2-methyl-3-furoic acid.[3a] The 2-chloro-5-methylfuran is of interest in connection with the rearrangement reactions of 2-furfuryl chloride,[3] particularly as they apply to rearrangements of organometallic compounds. The exclusion of the possibility of a dynamic isomerism of 2-chloro-5-methylfuran with 2-furfuryl chloride[3a] has been confirmed by us. There is an extraordinary difference in reactivity between a nuclear halogen furan like 3-iodofuran and a lateral halogen furan like furfuryl chloride. Studies with metals, leading to the formation of organometallic compounds, indicate that the former compound probably has the most inert iodine attached to a doubly bonded carbon, whereas the latter appears to have the most active chlorine attached to a carbon.[4] The exalted activity of chlorine in 2-furfuryl chloride is attributed by one of us (H. G.) to super-aromatic properties of the furan nucleus. Furfuryl fluoride should form a Grignard reagent with moderate ease, and this RMgF compound should undergo transformations of the kind shown by organometallic compounds containing magnesium, lithium, sodium, etc., when treated with reagents like formaldehyde and ethyl chlorocarbonate. In this connection, F. Breuer has

[1] Gilman and Wright, *Rec. trav. chim.*, **50**, 833 (1931) (for 5-chloro-2-furfural); THIS JOURNAL, **52**, 2550, 4165 (1930) (for 5-nitro-2-furfural); *ibid.*, **52**, 1170 (1930), (for 5-bromo-2-furfural).

[2] Wolff, *Ann.*, **394**, 86 (1912); Kischner, *J. Russ. Phys.-Chem. Soc.*, **43**, 1563 (1912); [*Chem. Abstracts*, **6**, 1430 (1912)].

[3] (a) Scott and Johnson, THIS JOURNAL, **54**, 2549 (1932); Reichstein, *Ber.*, **63**, 749 (1930); Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930); Reichstein and Zschokke, *Helv. Chim. Acta*, **15**, 249 (1932).

[4] Direct measurements with potassium iodide show that the chlorine in furfuryl chloride is distinctly more active than that in benzyl chloride.

shown that 2-methylfuran reacts with ethylsodium or phenylsodium to give a furan-sodium compound which on carbonation yields 5-methyl-2-furoic acid. By analogy with a related reaction with toluene and the xylenes, it is possible that furfurylsodium is first formed and then undergoes a transformation like that observed in the reaction between furfuryl chloride and sodium cyanide.

2-Methyl-5-nitrofuran has been prepared by the Wolff–Kischner[2] reduction of 5-nitro-2-furfural. It is identical with the methylnitrofuran prepared both by the nitration of 2-methylfuran and the nitration with accompanying decarboxylation of 5-methyl-2-furoic acid.[5] The identity of these methylnitrofurans has a two-fold significance from the viewpoint of orientation in the furan nucleus. First, it definitely establishes that an α- or 2-substituted furan, irrespective as to whether it is an ortho–para or meta orienting group in benzene types, orients to the other α- or the 5-position. This is evident when one recalls that the nitrofuroic acid obtained by nitration of furoic acid is identical with that obtained by the oxidation of the nitro-2-furfural resulting from the nitration of furfural. Second, the formation of 2-methyl-5-nitrofuran by the nitration of 2-methyl-5-furoic acid proves that the nitro group has taken the position originally occupied by the carboxyl group. This is of importance in the proof of structure of furan compounds because of the uncommon ease of decarboxylation of furoic acids and the accompanying possibility that the 5-methyl-2-furoic acid might have first nitrated and then lost carbon dioxide to give a methylnitrofuran having the nitro group in a position other than that occupied initially by the carboxyl group.

Although the position of the methyl group in 2-methyl-5-nitrofuran is known, it must be admitted that there is no unequivocal evidence for the position of the nitro group. This we are establishing, among several methods, by blocking the β-positions and by the synthesis of 3-nitrofuran, which from our present knowledge of β-substituted furans should give a relatively stable and diazotizable 3-aminofuran.

Experimental

To a solution of 65 g. (0.5 mole) of 5-chloro-2-furfural in 250 cc. of methyl alcohol, chilled in an ice-bath, was added at once 48 g. (0.96 mole) of hydrazine hydrate. After one hour, 56 g. (1 mole) of potassium hydroxide in pellet form was added without agitation, and at the end of twelve hours (spontaneous evolution of nitrogen having ceased) the mixture was distilled from the alkali. In working up the product in a customary manner there was obtained 21 g. or a 36.2% yield of 2-chloro-5-methylfuran: b. p. 110°, n_D^{20} 1.4619, d_4^{20} 1.180.

Anal. Calcd. for C_5H_5OCl: Cl, 30.44. Found: Cl, 30.66.

In accordance with other observations,[3a] the compound is relatively stable and after several months' standing in a refrigerator (without the addition of a stabilizer like

[5] Rinkes, *Rec. trav. chim.*, **49**, 1118 (1930).

hydroquinone) showed only slight decomposition. It does not react in ether with ordinary or activated magnesium. A vigorous reaction takes place with sodium, and this is being investigated. From other studies it appears that alkyl groups labilize furan nuclear halides as, for example, the β-iodine in 2,5-dimethyl-3-iodofuran.

In the reduction of 5-nitro-2-furfural, copper bronze in quinoline in place of potassium hydroxide was used for the decomposition of the hydrazone. The 2-methyl-5-nitrofuran was shown to be identical, by the method of mixed melting points, with an authentic specimen.[5] The copper bronze–quinoline procedure for removal of nitrogen is novel, we believe, and its application was indicated because of the marked sensitivity of α-nitrofurans to strong alkalies.

CONTRIBUTION FROM THE
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Phenanthrene-1-carboxylic Acid

BY LOUIS F. FIESER

Following the request of Dr. E. Mosettig for a sample of the above substance with which to compare an isomer isolated in the Virginia Laboratory,[1] this new phenanthrene derivative was prepared from the 1-sulfonic acid,[2] a small sample of which was still available.

Phenanthrene-1-nitrile, prepared from 1 g. of potassium phenanthrene-1-sulfonate and 2 g. of potassium ferrocyanide, was obtained in a pure condition (yield 0.4 g.) by distillation *in vacuo* and crystallization from alcohol. It formed stout, colorless needles melting at 128°.

Anal. Calcd. for $C_{15}H_9N$: C, 88.64; H, 4.47. Found: C, 88.50; H, 4.58.

Phenanthrenequinone-1-nitrile resulted from the oxidation of the phenanthrene derivative with chromic acid at 90°. It is sparingly soluble in glacial acetic acid and separates as fine, orange needles melting at 339°.

Anal. Calcd. for $C_{15}H_7O_2N$: C, 77.24; H, 3.03. Found: C, 77.30; H, 3.25.

Phenanthrene-1-carboxylic acid amide was obtained by boiling the corresponding nitrile with alcoholic alkali for two hours. It formed colorless plates, m. p. 284°, from dilute acetic acid.

Anal. Calcd. for $C_{15}H_{11}ON$: C, 81.41; H, 5.01. Found: C, 81.50; H, 5.26.

Phenanthrene-1-carboxylic Acid.—The amide is hydrolyzed only with difficulty. The reaction with alcoholic alkali was not complete even after heating for several hours at 160°. The acid is readily soluble in alcohol or benzene and crystallizes well from the former solvent as colorless needles melting at 232–233°.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54. Found: C, 81.22; H, 4.56.

The methyl ester, prepared with diazomethane, is very readily soluble even in cold organic solvents. Purified by distillation, it melted at 57°.

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RECEIVED JUNE 21, 1932
PUBLISHED OCTOBER 5, 1932

[1] Mosettig and van de Kamp, THIS JOURNAL, **54**, 3328 (1932).

[2] Fieser, *ibid.*, **51**, 2460 (1929).

COMMUNICATIONS TO THE EDITOR

THE RATE OF DISSOCIATION OF NITROGEN TETROXIDE

Sir:

Recently Richards and Reid [THIS JOURNAL, **54,** 3014 (1932)] reported that they had obtained a definite value of the velocity constant of the N_2O_4 dissociation, using high-frequency sound waves up to 500 k. c. This value is, of course, calculated from their velocity of sound data by the use of Einstein's theoretical equations, which they felt justified in applying to their measurements since they observed no increase in the absorption coefficient with frequency.

Their observations are not in accord with a series of experiments just completed by the author which are being submitted for publication. Sound velocity measurements at 53.8 k. c. checked with those previously reported by Kistiakowsky and Richards, although high absorption made observation difficult, but above 100 k. c. no evidence of sound transmission could be obtained with the set-up employed, although sound up to 860 k. c. was used. This increasing absorption is in accord with the theoretical predictions of D. G. C. Luck [*Phys. Rev.*, **40,** 440 (1932)], who has extended Einstein's theory to real absorbing dissociating gases. Calculations made by the author from his equations show that velocity constants computed from Einstein's original equations may be as much as 20% too low.

RESEARCH LABORATORY OF INORGANIC CHEMISTRY CHARLES E. TEETER, JR.
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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RECEIVED JULY 30, 1932
PUBLISHED OCTOBER 5, 1932

QUANTUM THEORY OF THE DOUBLE BOND

Sir:

An understanding of the structure of C_2H_4 can be obtained by studying its formation from two CH_2 radicals. Electronic structures of these can be given in terms of molecular orbitals [molecular one-electron orbital wave functions, *cf.* R. S. Mulliken, *Phys. Rev.*, **40,** 55 and **41,** 49 (1932)] similar to the atomic orbitals $1s$, $2s$, $2p$ commonly used in the quantum theory in building up electron configurations to describe the structures of atoms. It can be shown that, in agreement with the chemical evidence, the energy should be a minimum if the two CH_2 come together in the same plane, a maximum if they come together with their planes at right angles. An analogous result holds for other molecules with double bonds.

These results apply to the normal state of such molecules, but for certain excited states, probably including the upper levels of the ordinary ultraviolet absorption bands, it can be shown to be probable that the energy is a maximum for the plane arrangement, a minimum for an ar-

rangement with the planes of the two CR′R″ groups at 90°. Hence after a molecule has absorbed ultraviolet light, its two parts should undergo a spontaneous rotation with respect to each other, which can carry it from *cis* to *trans* or *vice versa*. Olson has already discussed possibilities somewhat similar to this [*Trans. Faraday Soc.*, **27**, 69 (1931)]. Details will be given in an article in the *Physical Review*.

The present quantum theory of the double bond is similar to that of Hückel [*Z. Physik*, **60**, 423 (1930)] but goes farther. As compared with the theory of Pauling and Slater [THIS JOURNAL, **53**, 1367 (1931), and *Phys. Rev.*, **37**, 481 (1931)] it appears to make closer contact with chemical and photochemical facts.

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ROBERT S. MULLIKEN

RECEIVED AUGUST 6, 1932
PUBLISHED OCTOBER 5, 1932

REACTIONS BETWEEN HYDRIODIC ACID AND HIGHLY INSOLUBLE COMPOUNDS

Sir:

Recently the writer published an account of the action of concentrated hydriodic acid on stannic oxide [THIS JOURNAL, **54**, 3240 (1932)]. Experiments made subsequent to the observations recorded in this paper have demonstrated that this acid reacts readily with numerous other compounds of very low solubility, including many of those not attacked by hydrochloric acid, nitric acid or aqua regia. A number of these reactions are apparently new. Some illustrative examples follow.

The alkaline earth sulfates are attacked and reduced by hot concentrated hydriodic acid with the evolution of hydrogen sulfide, sulfur dioxide or both, and the liberation of iodine, resulting in a solution of the corresponding iodides. Likewise anhydrous chromium sulfate is reduced and dissolved by this acid. Sublimed chromic chloride and bromide are rapidly dissolved by the warm concentrated acid. Lead sulfate and fused lead chromate readily dissolve in the cold concentrated acid. The first is transposed into lead iodide, which then dissolves in the excess acid to form a complex which appears to be iodoplumbous acid. In the case of the chromate the same reaction occurs accompanied by the reduction of the chromium to the tervalent state. The insoluble halides of silver are also transposed and dissolved by the cold concentrated acid, the complex forming in this case being an iodoargentic acid. Certain more complex insoluble compounds such as copper ferrocyanide are readily attacked and dissolved in a series of complicated reactions.

Many of these reactions are not only of interest in themselves but they

hold some promise of useful analytical application in the separation and identification of members of the group of highly insoluble compounds. The writer hopes to have the privilege of publishing a more detailed account of these reactions at some future date.

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EARLE R. CALEY

RECEIVED AUGUST 17, 1932
PUBLISHED OCTOBER 5, 1932

GERMICIDAL ACTIVITY OF ALKYL SULFUR ETHERS

Sir:

A problem interesting various investigators during recent years in the field of antiseptics has been the effect on the activity of phenol germicides of variations in substituting groups. Johnson and Lane [THIS JOURNAL, **43,** 348 (1921)], and Dohme, Cox and Miller [*ibid.*, **48,** 1688 (1926)] pointed out that alkyl resorcinols become progressively more active as the length of an alkyl side chain increases. Hilbert and Johnson [THIS JOURNAL, **51,** 1534 (1929)] showed that the activity of the three hydroxy diphenyl sulfides increased in the order: ortho, meta, para. The authors [*ibid.*, **54,** 1195 (1932)] discussed the effect of alkyl chains substituted into the phenol nucleus, stating that position isomerism is of slight importance but that variations in the chain are of greatest importance.

It seemed of interest to compare certain sulfur containing phenols with those previously studied. Methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, isopropyl, isobutyl, isoamyl and benzyl thio ethers of phenol of the general formula RSC_6H_4OH have been prepared.

As in the case of the alkylresorcinols, alkyl phenols and alkyl ethers of hydroquinone [Ref. 4 and Klarmann, Gatyas and Shternov, THIS JOURNAL, **54,** 298 (1932)], the germicidal activity of these alkyl sulfur ethers increases with increase in the size of the alkyl group. They show, however, a higher activity for a given alkyl group and reach the maximum with the amyl derivative. An increase in the temperature at which the bacteriological examination is made raises this maximum to higher members of the series. The iso-alkyl ethers have lower phenol coefficients than the corresponding normal alkyl derivatives.

The O-ethers of thiophenol are probably much less active than the corresponding S-ethers of phenol.

A complete report of this work will be published in the near future.

CHEMICAL LABORATORIES
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ELLIS MILLER
R. R. READ

RECEIVED AUGUST 18, 1932
PUBLISHED OCTOBER 5, 1932

THE CONCENTRATION AT WHICH HEATS OF DILUTION ARE MEASURED IN THE CALORIMETRIC METHOD

Sir:

In a series of excellent experimental papers, E. Lange and A. L. Robinson and their collaborators [for a summary of their work to 1931, see E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931)] have greatly improved the precision with which heats of dilution can be measured and have recorded results at much higher dilution than previous investigators. Unfortunately, their method of standardizing their data to the reference state of infinite dilution is open to a misunderstanding in respect to the concentration for which the heat of dilution has been actually measured which appears to be quite widespread.

They dilute a volume of solution at a given initial concentration with a measured amount of water to a readily computed final concentration and measure the heat evolved in the process. Thus

$$\frac{\mathrm{NaCl} + n_1\,\mathrm{H_2O}}{0.01\,m} + x\mathrm{H_2O} = \frac{\mathrm{NaCl} + (n_1 + x)\,\mathrm{H_2O}}{0.0005\,m}$$

$$\Delta H = \bar{L}_2(0.0005\,m) + (n_1 + x)\bar{L}_1 - \bar{L}_2(0.01\,m) - n_1\bar{L}_1\,(0.01)$$

These so called intermediate changes in heat content when calculated to one mole of salt are designated in Lange's notation as $V_{(c\text{ initial }c\text{ final})}$. Each dilution experiment thus gives two points on a curve, the initial and final concentrations. When a region of concentration is reached where these ΔH values become proportional to $\sqrt{c}$ (c = moles/liter), an extrapolation is made to $c = 0$ whereby these intermediate heats of dilution are interpreted as integral heats of dilution by addition of the quantity of V_c obtained by graphical extrapolation.

$$\frac{\mathrm{NaCl} + n_1\,\mathrm{H_2O}}{0.0005\,m} + (\infty - n_1)\,\mathrm{H_2O} = \frac{\mathrm{NaCl} + \infty\,\mathrm{H_2O}}{m = 0}$$

$$\Delta H = -\bar{L}_2(0.0005\,m) - n_1\bar{L}_1\,(0.0005) = V_c\,(\text{Lange's notation})$$

Lange and Robinson represent their results by curves in which the values for both the initial and final concentrations are plotted, thereby giving the impression that measurements of the heat of dilution have actually been made for the lower concentration. In fact, in their conclusions they state that the integral heats of dilution have been measured over a range which includes the lower concentration limits. [See, for example E. Lange and A. L. Robinson, THIS JOURNAL, **52**, 4218 (1930); H. Hammerschmid and A. L. Robinson, *ibid.*, **54**, 3120 (1932)]. That the measured values should refer only to the initial concentration and not to the final or any intermediate concentration is obvious when we recognize that, had the authors been able to measure the heat evolved by the addition of an infinite volume of water, all of the plotted points corresponding to the final concentrations would have vanished. All the data recorded in

their final tables, in the two papers referred to, below 0.0125 *m* (0.00625 *m* in the case of sodium bromide) should be designated as extrapolated and not as interpolated values. Although the values which they record for the final concentrations are very likely correct, it is, nevertheless, desirable to point out that they do not constitute measured values, but involve the acceptance of the validity of the Debye–Hückel theory. This theory is without doubt the best to employ at the present time, yet there have been examples in which specific individual characteristics have been obscured by its use at concentrations which, at the time, were thought to be sufficiently dilute for application.

DEPARTMENT OF CHEMISTRY
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V. K. LA MER
I. A. COWPERTHWAITE

RECEIVED AUGUST 23, 1932
PUBLISHED OCTOBER 5, 1932

THE OXYGEN VALENCE ANGLE AND THE STRUCTURE OF GLUCOSE AND RELATED COMPOUNDS

Sir:

During the last ten years an extensive series of investigations has been carried out on the synthesis and structure of various oxygen-bridged ring compounds from the point of view of elucidating the structure and properties of glucose and polysaccharides. During the progress of this work, it has become more and more evident that the assignment of the same tetrahedral angle to both the oxygen and carbon atoms is incorrect and that many of the anomalies found in the study of carbohydrate chemistry are due to the lack of recognition of this factor.

In the case of furanose and pyranose ring forms of the sugars this point has also been stressed by Haworth, Cox and other workers.

During the last three years a careful study has been made on the electric moments of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran (tetramethylene oxide) and tetrahydropyran (pentamethylene oxide), and the oxygen valence angles calculated in each case. These have been determined as follows.

OXYGEN VALENCE ANGLES IN CYCLIC ETHERS

Compound	Moment ($\times 10^{18}$)	Oxygen valence angle
Ethylene oxide	1.88	77°
Propylene oxide	1.88	65°[a]
		77°
Trimethylene oxide	2.01	102°
Tetrahydrofuran	1.71[a]	105°
		ca. 100°[a]
Tetrahydropyran	1.87	88°

[a] Smyth and Walls, THIS JOURNAL, **54**, 3230 (1932).

The "normal" oxygen valence angle has been determined from these measurements as 90 ± 5°. This value is the first experimental confirmation, by electric moment measurements, of the same angle suggested by the quantum mechanical considerations of Pauling. From these results it can be definitely shown that the pyranose ring of carbohydrates and related polysaccharides represents a "strainless" puckered ring system in which the carbon valence linkages are tetrahedral while the oxygen valence angle is approximately 90°. The pyranose ring has therefore a di-planar structure with all the carbon atoms in one plane and the oxygen atom in a different plane from the carbon atoms. On the other hand, the furanose ring structure of similar compounds represents a strained flat ring in which both the carbon and oxygen valence angles are distorted. The relative instability of furanose as compared with pyranose rings thus finds a satisfactory explanation. A full account of this work will be published in the near future.

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HAROLD HIBBERT
J. STANLEY ALLEN

RECEIVED SEPTEMBER 22, 1932
PUBLISHED OCTOBER 5, 1932

NICKEL BY THE RANEY PROCESS AS A CATALYST OF HYDROGENATION

Sir:

There is now available (Murray Raney, Chattanooga, Tennessee, U. S. Patent 1,628,190, May 19, 1927) a pure nickel catalyst which under some circumstances is preferable to the "nickel on kieselguhr" type of catalyst [Covert, Connor and Adkins, THIS JOURNAL, **54,** 1651 (1932)]. The Raney catalyst is prepared by alloying equal parts of nickel and aluminum and then dissolving out the latter with aqueous sodium hydroxide. Both the alloy and the metallic nickel suspended in water are commercially available. The latter is satisfactory for many hydrogenations but a more active catalyst may be prepared from the alloy by the following procedure. Three hundred grams of the finely ground nickel–aluminum alloy was added slowly (two or three hours) to a solution of 300 g. of sodium hydroxide (80%) in 1200 ml. of distilled water, contained in a 4-liter beaker surrounded by ice. The mixture was then heated on a hot-plate for four hours with occasional stirring at 115–120°. A further 400 ml. of a 19% solution of sodium hydroxide was added and the mixture kept at 115–120° for about three hours or until bubbles of hydrogen were no longer evolved, after which it was diluted to a volume of three liters. The clear solution of sodium aluminate was decanted, and the nickel washed by decantation six times, and then alternately by suspension and by washing on a Buchner filter with distilled water until the filtrate was neutral to litmus. The nickel was then washed three times with 95% ethanol and kept under

ethanol in glass-stoppered bottles. (Nickel prepared by this process is so reactive that it deoxygenated nitrobenzene, *o*- and *p*-nitrobenzene and *p*-nitrophenol with 38 to 50% yields of azo- and azoxybenzenes, when mixed with the nitro compounds in an open beaker.)

The outstanding characteristic of the Raney catalyst is its activity at low temperatures and pressures. For example, with a supported nickel catalyst, acetone did not undergo hydrogenation in any considerable amount much below 100°, while with the Raney catalyst, complete hydrogenation was obtained after 11.2 hours at 23° and 2 to 3 atmospheres' pressure. Similar hydrogenations were obtained with mesityl oxide and acetoacetic ester. Complete hydrogenations at room temperature but at 110 atmospheres' pressure were obtained with benzaldehyde, acetaldehyde, cinnamaldehyde, azobenzene and benzyl cyanide. In the case of all of these compounds hydrogenation proceeded to completion at pressures and (or) temperatures below those at which the supported catalyst was sufficiently active for the satisfactory hydrogenation of these compounds. Both catalysts are active against certain alkenes such as styrene at 23° and 2–5 atmospheres. The hydrogenation of aldol, furfural and the diethyl furfural acetal also proceeded at temperatures somewhat lower than have been observed with the supported catalyst. In the case of benzene, toluene, acetophenone, benzyl alcohol, ethyl benzoate, diethyl phthalate and pyridine the Raney catalyst was not active at markedly lower temperatures and pressures than was the supported catalyst. (The ratio of nickel to organic compound in the experiments referred to in this paragraph was in most instances approximately 1 to 15.)

A precise comparison of the activity of the Raney catalyst with the supported catalyst is impossible not only because they may show their optimum activity for a given compound in quite different temperature ranges but because there is no ratio of catalyst to hydrogen acceptor which would be fair to both catalysts. For example, 8 g. (occupying a volume of 4 ml.) of Raney catalyst was required for the hydrogenation at 23° of 74 ml. of acetone within 11.2 hours. An equivalent amount of nickel on the supported catalyst would have necessitated using 80 g. or *300 ml.* of the supported catalyst with *74 ml.* of acetone! If the Raney catalyst had been used in the same proportion as was nickel on kieselguhr (0.2 g. for 74 ml. of acetone), it would have been quite ineffective. The ratio of surface to weight of nickel is of course much higher for the supported than for the Raney catalyst so that comparisons of activities on the basis of weight of nickel in the catalyst are unduly unfavorable to the Raney catalyst.

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RECEIVED SEPTEMBER 22, 1932
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NEW BOOKS

The Adsorption of Gases by Solids. A General Discussion Held by The Faraday Society, January, 1932. Gurney and Jackson, 33 Paternoster Row, London, E. C. 4, England, 1932. iv + 320 pp. Illustrated. 15.5 × 25 cm. Price, 15/–.

This is a collection of some forty papers presented at a General Meeting of the Faraday Society at Oxford. The meeting arose on the initiative of Professor H. S. Taylor and he delivered the General Introduction. The papers were given in three sections, meeting in succession. The sections and the Speakers who delivered the Introductory Papers were as follows:

Section I. Experimental Methods. Introductory Paper by Eric K. Rideal.

Section II. Kinetics and Energetics of Gas Adsorption. Introductory Paper by Professor H. Freundlich.

Section III. Theories of the Adsorption of Gases. Introductory Paper by Professor M. Polanyi.

The definitive papers were presented by the leading investigators in this field from all over the world. They cover most of the modern work on the adsorption of gases and constitute practically a *vade mecum* of our present-day knowledge of this subject.

It is eminently fitting that this volume dealing with the adsorption of gases should be issued by the Faraday Society, and at this time, for in this field also Faraday displayed the same genius and prophetic insight that characterized his great experimental contribution to electromagnetism, the centenary of which has recently been so widely celebrated.

The book should be invaluable to all who are interested in the adsorption of gases.

ARTHUR B. LAMB

Théorie de la Quantification dans la Nouvelle Mécanique. (Theory of Quantization in the New Mechanics.) By LOUIS DE BROGLIE, Professor at the Sorbonne. Hermann et Cie, Éditeurs, 6, Rue de la Sorbonne, Paris, France, 1932. xxviii + 250 pp. 16 × 25 cm. Price, fr. 70.

The subject matter of this book is taken from a course of lectures given by Professor de Broglie in the first semester of 1929–1930 at the Institut Henri Poincaré and is a continuation of the ideas expressed in his earlier book. This one is meant to be complete in itself, however, and for that reason is prefaced by an historical introduction and discussion of the Bohr theory.

The first third of the book treats of the elementary theory of wave mechanics by the usual methods and shows how the various rotators and oscillators are quantized. The second part, which comprises the rest of the book, is called "The general theory of quantization in wave mechanics."

It is now well known that wave mechanics and matrix mechanics are two special cases of the same general theory only differing in the mathe-

matical apparatus. The proof of this is contained in the transformation theory which at the same time presented the general quantum mechanics that was required. The two special cases emphasize, respectively, the states of a system and its dynamical variables. The general theory, however, must be independent of these quantities, which are merely sets of numbers that represent the quantities of fundamental importance. This necessary invariance is enjoyed by the symbolic algebra of non-commutative numbers discovered by Dirac and has been the most popular method in the past. Its power and elegance cannot be questioned but there has always been a suspicion that it was not above reproach from the standpoint of mathematical rigor.

The transformation theory also has the required invariantive properties but in addition is known to be mathematically rigorous. It is essentially a geometrical theory and deals with the properties of certain linear operators in Hilbert space, which is a denumerable space with an infinite number of dimensions.

Professor de Broglie has chosen to use this method and develops the theory of unitary geometry along the same lines as that of Weyl in the first chapter of his celebrated book. He has, however, discussed it in a simpler way and in much greater detail and wherever possible has made use of the physical pictures of wave mechanics. The author's presentation is always clear and logical and the result is a very valuable statement of some of the most general theorems of quantum mechanics.

A book dealing with the fundamentals would not, of course, discuss perturbation theory. But it is to be hoped that Professor de Broglie's next book will deal with the problems of spin and relativistic invariance which have not been discussed here at all.

In a machine age, it would not seem necessary to have to cut all the pages of a book. There are no references to the literature, no index and the printing is rather poor. The price seems hardly low enough to make up for these defects.

G. M. MURPHY

The Theory of Electric and Magnetic Susceptibilities. By J. H. VAN VLECK, Professor of Theoretical Physics in the University of Wisconsin. Oxford University Press, 114 Fifth Ave., New York, 1932. xi + 384 pp. Illustrated. 16 × 24.5 cm. Price, $7.50.

This excellent treatise on the theory of electric and magnetic susceptibilities is written by the world's leading authority in this field. There is no similar modern theoretical treatment of the general subject existent. The author has to a considerable extent avoided the more specialized and elementary discussions given in Debye's and Smyth's books on electric moments and Stoner's book on magnetism and atomic structure. He has

solved the pedagogical problem presented by the existence of classical, old quantum theoretical, and quantum mechanical treatments of susceptibilities in a sensible and satisfactory way. Three of the thirteen chapters (I, II, IV) are devoted to classical foundations, the classical theory of the Langevin–Debye formula, and the classical theory of magnetic susceptibilities. The author opens the chapter on susceptibilities in the old quantum theory with the paragraph "To some readers it may seem like unburying the dead to devote a chapter to the old quantum theory. Everyone knows that the original quantum theory developed by Bohr in 1913 has been refined and in a certain sense replaced by the new quantum mechanics of Heisenberg, Schrödinger, Born and Dirac. However, there is perhaps no better field than that of electric and magnetic susceptibilities to illustrate the inadequacies of the old quantum theory and how they have been removed by the new mechanics. We shall merely summarize the results of applying the old theory, without giving any mathematical analysis. Also, we shall contrast descriptively with these results some of the outstanding features of the new quantum mechanics of susceptibilities, thereby giving a qualitative account of some of the new improvements which may perhaps satisfy some readers who do not wish to read the mathematics in the two following chapters." This discussion of the old quantum theory leads to the gradual development in the reader of an intuitive feeling for this field of theory, in which intuition is especially valuable. An excellent brief discussion of quantum mechanical foundations is given in Chapter VI, followed in VII by the quantum mechanical derivation of the Langevin–Debye formula. In accordance with the author's policy of introducing difficult theory only when unavoidable, electron spin is handled by the machinery of the semi-mechanical model (Pauli, Heisenberg, Jordan) rather than by the Dirac theory. The thorough and clear discussion of special applications of the theory of susceptibilities with extensive comparison with experimental results is given in five chapters, dealing with electric moments (III), dielectric constants and diamagnetic susceptibilities of atoms and monatomic ions (VIII), paramagnetism of free atoms and rare earth ions (IX), para- and diamagnetism of free molecules (X), and the paramagnetism of solids (XI). Two concluding chapters contain discussions of Heisenberg's theory of ferromagnetism, the magnetic susceptibility of free electrons (Pauli, Landau) with applications to metals, Kerr effect, Faraday effect and other relevant topics.

The book provides a nearly exhaustive survey of developments in this field up to the beginning of 1931. The method of correlating magnetic moments of molecules and complex ions with the nature of the chemical bonds involved, discovered early in 1931, is not mentioned. Mention of an interesting chemical application of magnetic data, the interpretation

ten years ago by G. N. Lewis of the observed variation in the partial molal paramagnetic susceptibility of solutions of oxygen in liquid nitrogen as due to the formation of diamagnetic O_4 molecules, is also omitted.

The book is characterized by clear exposition and interesting style, which, combined with the sound and reliable treatment, should make it a valuable text for an advanced course as well as the authoritative reference book in the field. Much of the text, especially the interpretation of experimental results, can be understood without a knowledge of quantum mechanics. The volume is handsomely printed, with pleasing typography and binding.

LINUS PAULING

The Kinetics of Homogeneous Gas Reactions. By LOUIS S. KASSEL, Ph.D., U. S. Bureau of Mines Experiment Station, Pittsburgh, Pa. American Chemical Society Monograph. Published by the Chemical Catalog Co., Inc., 419 Fourth Ave., New York. Price $6.50.

This is a book which must interest both students and workers in the field of gas reactions, and is, in the opinion of the reviewer, the best book on the subject which has thus far appeared.

It opens with a chapter which contains certain general propositions concerning the energy of activation, this being followed by one which gives a brief account of that portion of statistical mechanics needed for the subsequent development. Next there is a series of chapters on the theoretical side of the subject, one each on bimolecular, trimolecular, unimolecular and complex reactions. The first of these contains a brief but clear account of the recent developments of London, Eyring and Polanyi on the quantum mechanics of activation. The chapter on unimolecular reactions is based on the theory of activation by collision, the almost defunct radiation hypothesis being properly relegated to an appendix.

After this theoretical treatment comes a discussion of the experimental material. There is a chapter on second order reactions, including reactions involving free atoms, one on third and one on first order reactions, and two on complex reactions, including chain reactions, reactions in dilute flames, explosions involving branching chains and reactions in which the chains begin on the wall. The first three of these chapters include full discussions of practically all known simple reactions; in the last two, on complex reactions, the material is selected to illustrate the principles involved, and the treatment is in some instances quite brief, causing a slight loss in clarity.

As may be inferred from the arrangement of the material, the subject is treated from what is essentially a theoretical point of view. The theory being first developed, the experiments can be discussed with it in mind and their significance fully understood; nevertheless, the chapters on the experimental work are so written that the worker who is chiefly interested in the experimental results can find them readily enough. Indeed, there is a

wealth of material in these chapters which, for many purposes, will make reference to the original work unnecessary. A critical attitude is taken throughout; the viewpoint of the original author on a given subject is not necessarily accepted, and whenever it has seemed desirable to the author of the book, the results have been recalculated; when this has been done, it is clearly so stated in the text. An author who uses the critical method will necessarily be in disagreement with many of his readers; but the reviewer is convinced that in this particular instance the opinions of the author are, on the whole, quite sound.

The book is certainly one to be heartily recommended; it seems unfortunate that the high price will discourage many from purchasing it.

OSCAR K. RICE

Galvanische Elemente und Akkumulatoren. Darstellung der Theorie und Technik nebst Patentregister. (Treatise on Theory and Technics of Primary Cells and Storage Batteries with Index of Patents.) By PROFESSOR C. DRUCKER AND DR. A. FINKELSTEIN. Akademische Verlagsgesellschaft m. b. H., Margrafenstrasse 6, Leipzig C 1, Germany, 1932. vii + 425 pp. 140 figs. 17.5 × 24.5 cm. Price, RM. 34; bound, RM. 36.

This is a useful book that deals with both primary cells and storage batteries. It is written especially for the engineer and chemist engaged in the production and utilization of batteries, but the book should find wider use as a general reference book. The text covers 247 pages and is followed by a section of 168 pages listing German, English and American patents relating to batteries, with brief abstracts.

The first chapter traces the historical development of various types of batteries and serves as an introduction to the theoretical discussion of modern types in Chapter 2.

The major portion of the text is devoted to the materials used in making batteries, the methods employed in manufacturing them, and their electrical characteristics. General references to recent books are given at the beginning of several chapters and numerous patents are cited in the text.

Three chapters deal with the Leclanché type which is extensively used and popularly known as the "dry cell." Properties of natural ore (pyrolusite) and artificially prepared manganese dioxide are compared. Physical and chemical properties of zinc, carbon, graphite and materials for the electrolyte are discussed. Various types of machines used in making batteries are illustrated. Electrical characteristics, applications and tests are described.

The last three chapters deal in a similar manner with storage batteries, including both the acid and alkaline types.

Some errors in the text have been corrected (see unnumbered page following the subject index), but others have escaped in the proof reading. On

pages 46, 54 and 55 several errors in writing the ionic equations have occurred. The units of resistivity in Table 2, page 35, and Table 26, page 163, are inconsistent. In the former table an exponent has been omitted in the heading of the last column. The footnote on page 212 has no relation to the subject matter of Table 30.

The book contains much valuable information and should be helpful to those concerned with this subject.

GEORGE W. VINAL

Handbuch der anorganischen Chemie. (Handbook of Inorganic Chemistry.) Edited by R. ABEGG, FR. AUERBACH and I. KOPPEL. Vol. IV (Dritte Abteilung, zweiter Teil, B, Lieferung 2). Complex Cyanides of Di- and Trivalent Iron. Verlag von S. Hirzel, Königstrasse 2, Leipzig, Germany, 1932. iv + 210 pp. 19 figs. 18 × 25.5 cm. Price, RM. 24.

As Professor Koppel, the surviving editor of this Handbuch, points out, the complex cyanides of iron, which all contain iron in the anion, are closely related among themselves not only in properties and methods of formation but also in their reciprocal transformations. They exhibit, however, marked differences from the simple salts of iron where the iron functions as cation. For this reason, these compounds have been treated jointly in a separate volume.

This separate presentation is also justified by the extensive investigations which have been made of these compounds and the very considerable number of them that have been prepared. Indeed, an inspection shows that while a total of 396 pages has been devoted in the Handbuch to all the simple compounds of iron, this monograph solely on the complex cyanides of iron occupies some 212 pages. Even then a great deal of the information has been presented in a highly compact, but still very illuminating, fashion in tables and graphs.

This mode of treatment has the further advantage of making patent also the gaps and deficiencies in our knowledge, so that this volume should not only be a great convenience to those working in this field but should stimulate and suggest further investigations therein.

ARTHUR B. LAMB

An Introduction to Organic Chemistry. By IRA D. GARARD, Ph.D., Professor of Chemistry in the New Jersey College for Women, Rutgers University. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. ix + 296 pp. 15 figs. 15.5 × 23.5 cm. Price, $3.00.

This brief volume encompasses the theoretical and laboratory parts of a short course in organic chemistry. Two hundred and thirty-eight pages are devoted to text, and 36 to a laboratory manual introducing 28 well-chosen experiments. The diagrams are generally good and the style of the author, simple and lucid. A wise effort to correlate organic and in-

organic chemistry is apparent. Though but few errors in proof reading are noted, it is certainly regrettable to have homologous misspelled in the definition of that term. The author apparently does not admit the commonly recognized distinction between empirical and molecular formulas, and unnecessarily complicates matters by designating ordinary structural formulas as "semi-graphic." It is unfortunate that writers persist in conveying to students the idea that an asymmetric carbon atom, rather than an asymmetric molecule, is essential to optical activity. The older names are used throughout where the newer and more acceptable terms glycosides and alkoxides are to be expected. In such a brief though comprehensive text certain omissions are quite obviously demanded, but to omit all reference to Grignard reactions, and to malonic ester and to acetoacetic ester is almost equivalent to cutting off a dog's tail just behind his ears as far as an appreciation of organic syntheses is concerned. The author set himself a difficult task in preparing a brief text and he did surprisingly well with it. Where students' time is at a premium, and where laboratory assistance is not readily available, this book will serve excellently to introduce theoretical and experimental organic chemistry.

G. ALBERT HILL

BOOKS RECEIVED

August 15, 1932–September 15, 1932

WILDER D. BANCROFT. "Applied Colloid Chemistry. General Theory." Third edition. McGraw-Hill Book Company, Inc., 330 West 42d St., New York. 544 pp. $4.00.

FRANZ FISCHER, Editor. "Gesammelte Abhandlungen zur Kenntnis der Kohle." Vol. X, 1930. Verlag von Gebrüder Borntraeger, W 35 Schöneberger Ufer 12a, Berlin, Germany. 613 pp. RM. 56; bound, RM. 58.50.

D. D. KARVÉ AND G. D. ADVANI. "Model Essays in Organic Chemistry." Sind Juvenile Coöperative Society, 1873 Elphinstone St., Karachi, India. 300 pp. Rs. 5/-; Sh. 8/-, net.

GEORG KRÄNZLEIN. "Aluminiumchlorid in der organischen Chemie." Revised edition. Verlag Chemie G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 144 pp. RM. 12.

GUSTAV TAMMANN. "Lehrbuch der Metallkunde. Chemie und Physik der Metalle und ihrer Legierungen." Fourth, enlarged, edition. Verlag von Leopold Voss, Salomonstrasse 18B, Leipzig C 1, Germany. 536 pp. RM. 48; bound, RM. 49.50.

"Transactions of The Electrochemical Society." Volume LXI. Published by The Electrochemical Society, Inc., Office of the Secretary, Columbia University, New York City. 568 pp.

The Journal of the American Chemical Society

VOL. 54 NOVEMBER, 1932 No. 11

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

DIELECTRIC CONSTANTS OF SOME ORGANIC SOLVENT–WATER MIXTURES AT VARIOUS TEMPERATURES

BY GÖSTA ÅKERLÖF

RECEIVED APRIL 18, 1932 PUBLISHED NOVEMBER 5, 1932

Introduction.—In recent theories of the behavior of electrolytes in solution, the dielectric constant of the medium plays a very important role. Debye and Pauling[1] have discussed the various factors that influence the dielectric constant of the medium in the immediate neighborhood of an ion. They found that in very dilute solutions the dielectric constant of the pure solvent is the proper value to use for the so-called "limiting law." Furthermore, it has been shown that changes of the dielectric constant of the medium are closely connected with corresponding changes of the velocity of homogeneous reactions in solutions. An approach to a theoretical interpretation of the relation of these medium changes to the simultaneous changes in the velocity of certain catalyzed reactions has been given by Harned and Samaras.[2]

The measurement of the dielectric constant of conducting solutions is still very much a matter of controversy, and definite, reliable results seem as yet not to have been obtained. On the other hand, the measurement of the dielectric constant of a pure non-conducting solvent does not offer any particular difficulties and may be carried out according to a number of different methods. However, even the purest solvent has some conductivity, and the reliability of the measurement decreases rapidly with increasing conductance. Many solvents act as very weak acids or bases, showing large increases of the dissociation constant with increasing temperature and thus also giving less reliable data for their dielectric constant. Mixtures of solvents have sometimes, already at ordinary temperatures, a relatively high conductance, probably due to the medium effect of one solvent upon the dissociation constant of the other. Therefore it is important to select a method of measurement the results of which would be influenced as little as possible by the conductance of the solvent or the solvent mixture used.

[1] Debye and Pauling, THIS JOURNAL, **47**, 2129 (1925).

[2] Harned and Samaras, *ibid.*, **54**, 9 (1932).

Apparatus.—The measurements presented in this paper have been carried out according to the method given by Astin.[3] The maximum potential drop of an impressed electromotive force of constant frequency is measured across a conducting condenser in a resonance circuit with this condenser in series with a non-conducting condenser. At maximum the conductance of the first condenser cancels out in the expression for its capacity, which is a function of a number of terms that may be kept constant. Thus, the capacity of the conducting condenser may be measured directly from the change in the capacity of a standard condenser placed in parallel with it. A diagram of the entire system is shown in Fig. 1.

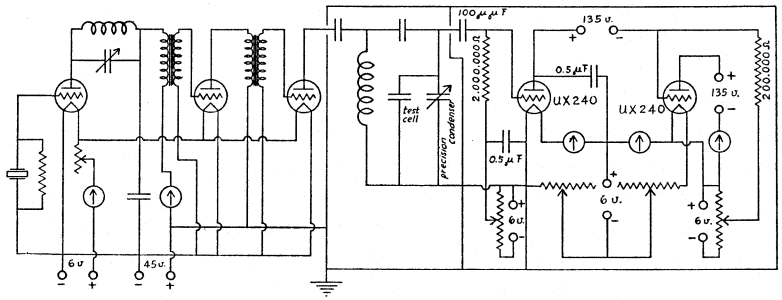

Fig. 1.—Wiring diagram for dielectric constant apparatus.

A General Radio high frequency piezo-electric oscillator, Type 375, was coupled to the measuring circuit through a small variable air condenser with a total capacity of about 100 micro-microfarads. The frequency of the oscillator was very near 2,000,000, corresponding to a wave length of 150 meters. A quartz plate with a frequency of 1,000,000 was also tried out, but it was found that the minimum on the vacuum tube voltmeter was somewhat sharper at the higher frequency. The oscillator was placed on a large shield above the shielded box containing the vacuum tube voltmeter and the measuring circuit, with which it was connected through a short antenna. The very loose coupling used by Astin between antenna and measuring circuit was found to be insufficient, but it was also found that an increase within the limits of the capacity of the small coupling condenser used did not change the value obtained for the capacity of the test condenser to any measurable extent.

The self-inductance in the measuring circuit had nine complete turns at a distance of 2 millimeters from each other and the diameter of the coil was 7 cm. The non-conducting condenser was a General Radio, Type 246-L, variable air condenser, which was set at a value of about 700 micro-microfarads. The standard condenser parallel to the test condenser was a General Radio, Type 222, precision condenser with a total capacity of 1500 micro-microfarads. The zero point of the apparatus with the test condenser out was adjusted in such a way that all readings on the precision condenser were obtained on the part of the scale where the capacity varied linearly with the setting. To remove the influence of body capacity, the precision condenser was turned from the outside of the shielding.

The construction of the vacuum tube voltmeter is clearly shown in Fig. 1 and further elaboration is unnecessary. The maximum potential drop was indicated by a

[3] Astin, *Phys. Rev.*, **34**, 300 (1929).

Weston model 322 quadruple range direct current microammeter. At lower temperatures, and using solvent mixtures that did not contain large amounts of water, the minimum observed on the microammeter was very sharp and it would have been possible to set the precision condenser with an accuracy of 1 part in 5000, if the backlash had not made this impossible. The backlash seemed to amount to about one division in the drum. At high temperatures and using solvent mixtures high in water content, the sharpness of the minimum decreased rapidly, and in some cases it was impossible to obtain good readings at temperatures over 80°. The various parts of the electrical circuit system were not temperature controlled, and therefore the zero point of the apparatus showed small irregular variations up and down, which made it necessary to redetermine this point for almost every other measurement. The errors due to the temperature variations of the circuits are very small and relatively unimportant.

The construction of the test condenser is shown in Fig. 2. The circular plates made of tantalum were 1 mm. thick, 5 cm. in diameter, and placed at a distance of about 2 mm. from each other, thus giving the empty condenser a capacity of about 10.2 micro-microfarads. For a measurement, the filled test condenser was suspended in the center of a large oil thermostat placed right beside the shielded box for the measuring circuit and the vacuum tube voltmeter. The holder for the test condenser was made of fiber and it was carried by two long fiber rods clamped to a horizontal metal bar above the thermostat. The lead from the measuring circuit to the test condenser was made as short as the conditions allowed.

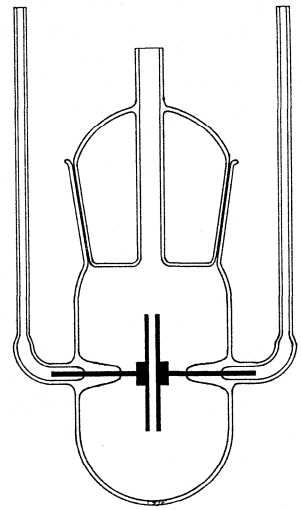

Fig. 2.—Test condenser.

At temperatures higher than that of the surroundings, the oil thermostat was regulated by a series of mercury thermoregulators set at different temperatures. At lower temperatures the viscosity of the oil increased so much that the stirring provided became insufficient and a close regulation with a cooling coil was made impossible. To obtain readings at 20° or lower, the oil was cooled by a stream of water through a long coil of 1-cm. copper tubing pressed flat against the sides of the thermostat. The cooling water lowered the temperature of the oil-bath very slowly to a few degrees below 20°. When the temperature had shown a variation of about 0.1° or less during one hour, the capacity of the test condenser immersed in the oil was determined. All readings below 20° were interpolated to be valid at this temperature. The oil-bath could be heated at the rate of about 1° temperature rise per minute by forcing high pressure steam through the cooling coil. When the desired temperature had been reached and properly regulated, about half an hour or more was allowed to elapse before the capacity of the test condenser was determined. It was found repeatedly that almost complete equilibrium was reached within fifteen minutes after the desired temperature had been attained.

The calibration of the apparatus was carried out using water as standard liquid. The dielectric constant of water over a large temperature range has recently been determined with great accuracy by Drake, Pierce and Dow[4] and Wyman,[5] according to two quite different methods. The values obtained for pure water according to the two methods agreed so closely that the error at 20° certainly must be considerably

[4] Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).

[5] Wyman, *ibid.*, **35**, 623 (1930).

less than 0.1%. Standardization of the apparatus described above with benzene, the usual procedure, would have given a very large probable error since both the capacity of the test condenser and the dielectric constant of benzene were relatively small. The close agreement between the values obtained by Wyman and those presented in this paper for the dielectric constant of water at various temperatures was regarded as a sufficient test of the reliability of the apparatus.

Materials.—It was considered undesirable to use any other organic solvents than those which could be obtained easily in a state of high purity, in large quantities, and at a comparatively low price. In order to obtain a sharp minimum on the microammeter, it was necessary to use solvents having a very small conductivity, and all impurities acting as electrolytes had to be removed carefully. Traces of non-conducting impurities did not seem to have any appreciable effect on the measurements, but great efforts were made to obtain the pure organic solvents used as free from water as possible.

(1) Water was obtained from a large Barnstead still. Its conductance at ordinary temperatures was less than 10^{-6} and good readings could be obtained up to 100°.

(2) Methyl alcohol, Baker's Analyzed, absolute and acetone free, was dried with sufficient sodium metal to take care of about 5% of water. The alcohol was slowly fractionated, rejecting the first and last 500 cc. from a batch of 5 liters.

(3) Ethyl alcohol, ordinary absolute alcohol, was dried with sufficient sodium metal to take care of about 5% of water and then slowly fractionated, rejecting the first liter. About ten liters was treated in one operation.

(4) *n*-Propyl alcohol, Eastman Kodak Co., was dried with sodium metal and then fractionated, rejecting the first 500 cc. A batch of about 5 liters was treated and approximately 500 cc. left undistilled.

(5) Isopropyl alcohol was obtained from Dr. A. S. Brown, who, with greatest care, had chemically purified, dried and fractionated a sample of about 2000 g.

(6) *Tert.*-butyl alcohol, Eastman Kodak Co., was dried with anhydrous magnesium sulfate and fractionated. The melting point was 24.0° and it did not rise any further after two fractionated freezings.

(7) Ethylene glycol, Eastman Kodak Co., was dried with burnt, pulverized lime for two days. Then the glycol was poured off and distilled in vacuum. The first 500 cc. was rejected and about 500 cc. left undistilled from a batch of about 3 liters.

(8) Glycerol, Baker's Analyzed, was boiled in vacuum during three to four hours with precipitated and carefully washed calcium carbonate. At first, water containing small amounts of glycerol distilled over. Then the pressure started to drop, and, when it had gone below one millimeter of mercury, the first 250 cc. was rejected. After collecting about 1500 cc., approximately one liter was left in the still. The distillate was absolutely colorless, with a hardly perceptible odor, and it had an exceedingly high viscosity.

(9) Acetone, Baker's Analyzed, was treated in batches of about three liters with a small amount of very concentrated phosphoric acid and immediately distilled, then dried with burnt powdered lime for a day, poured off and redistilled. Acetone, Eastman Kodak Co., from the bisulfite compound, dried with anhydrous sodium sulfate and redistilled, gave almost exactly the same value for the dielectric constant as the sample prepared from Baker's acetone.

The distilled solvents were stored in Pyrex bottles which, after cleaning, had been rinsed out several times with conductivity water and then dried in a small oven at a temperature of about 200°. Each one of the dried and redistilled organic solvents employed gave excellent readings at all temperatures used. Beside the measurements carried out with water mixtures of the solvents given above, a few results were obtained for solutions of mannitol and sucrose in water.

(10) Mannitol, Th. Schuchardt, Görlitz, Germany, was recrystallized four times from conductivity water and then dried in vacuum to constant weight.

(11) Sucrose, Kahlbaum, Germany, for calorimetric measurements, was used without further purification. It was impossible to obtain good readings at sugar concentrations up to 40% and at higher temperatures. The values given below for solutions in this range are interpolated from the measurements of Kockel[6] and recalculated to the value given in this paper for the dielectric constant of pure water at the particular temperature of the sugar solution.

Measurements and Results.—All organic solvent–water mixtures were made up by weight in amounts of about 300–400 g., with an average error in the concentration of the components less than 0.05%. The test condenser always was filled almost completely with the liquid to be used. At higher temperatures some solvent mixtures showed a more or less pronounced tendency to develop slight concentration gradients in the cell. This was counteracted by taking the cell out of the bath and by shaking it gently for two minutes about five to ten minutes before the measurement. The measurement itself required about ten minutes, approaching the minimum from both sides and taking the average of all readings. After a series of measurements had been completed for a given liquid, the test condenser was thoroughly cleaned and dried at a temperature of about 200°. It was found that the presence of the slightest trace of oil on the plates in the test condenser gave erroneous results. Therefore, the cell was cleaned when considered necessary with hot concentrated sulfuric acid and then the acid was washed away with boiling conductivity water. The temperature at which the measurements were carried out was recorded with a solid stem thermometer for total immersion calibrated against thermometers certified by the Bureau of Standards.

The results of the measurements with pure solvents are summarized in Table I. The data obtained for all solvent mixtures and solutions of

TABLE I

DIELECTRIC CONSTANT AT VARIOUS TEMPERATURES OF (1) METHYL, (2) ETHYL, (3) *n*-PROPYL, (4) ISOPROPYL, (5) ISOBUTYL, (6) *Tert.*-BUTYL ALCOHOL, (7) ETHYLENE GLYCOL, (8) GLYCEROL AND (9) ACETONE

Temp., °C.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
20	32.35	25.00	20.81	18.62	16.68	3.76	38.66	41.14	19.56
25	...	24.20	...	...	...	9.90	...	...	19.10
30	30.68	23.55	19.54	17.38	15.27	9.37	36.80	39.22	18.67
40	29.03	22.20	18.25	16.23	14.00	8.44	34.94	37.30	17.80
50	27.44	20.87	17.11	15.06	12.83	7.67	33.21	35.53	16.98
60	25.97	19.55	15.88	14.03	11.75	6.96	31.58	33.82	...
70	...	18.31	14.90	13.00	10.80	6.45	29.93	32.14	...
80	...	...	13.86	11.91	9.89	5.90	28.45	30.63	...
90	...	...	12.93	...	9.08	..	26.95	29.20	...
100	...	...	...	...	8.19	..	25.61	27.88	...

[6] Kockel, *Ann. Physik*, **77**, 417 (1925).

mannitol and sucrose are collected in Tables II to XI. The dielectric constant of pure water at 20° is set equal to 80.37 in accordance with the measurements of Wyman. The values given for solutions of sucrose up to 40 weight per cent. were interpolated from the measurements of Kockel as indicated above. Since most investigations of the behavior of solutions have been carried out at 25°, the data in Tables I to XI were carefully

TABLE II

DIELECTRIC CONSTANT OF METHYL ALCOHOL–WATER MIXTURES

Alcohol, wt. %	20°	30°	40°	50°	60°
0	80.37	76.73	73.12	69.85	66.62
10	75.84	72.37	68.90	65.66	62.77
20	71.02	67.48	64.13	61.06	58.24
30	66.01	62.71	59.53	56.59	53.94
40	61.24	58.06	54.82	52.17	49.52
50	56.53	53.47	50.40	47.82	45.28
60	51.53	48.58	45.64	43.22	41.22
70	46.46	43.63	41.04	38.81	36.68
80	41.46	38.98	36.66	34.62	32.74
90	36.80	34.62	32.56	30.67	28.91
100	32.35	30.68	29.03	27.44	25.97

TABLE III

DIELECTRIC CONSTANT OF ETHYL ALCOHOL–WATER MIXTURES

Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	74.60	67.86	64.53	61.49	55.70
20	68.66	62.41	59.22	56.40	50.81
30	62.63	56.73	53.79	51.04	45.88
40	56.49	51.08	48.36	45.80	40.93
50	50.38	45.30	42.92	40.66	36.51
60	44.67	40.02	37.72	35.66	31.82
70	39.14	34.88	32.86	30.87	27.30
80	33.89	29.83	28.10	26.31	23.20
90	29.03	25.64	24.08	22.51	19.80
100	25.00	22.20	20.87	19.55	...

TABLE IV

DIELECTRIC CONSTANT OF *n*-PROPYL ALCOHOL–WATER MIXTURES

Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	73.52	66.81	63.66	60.65	54.77
20	66.54	60.24	57.23	54.49	49.01
30	59.21	53.46	50.72	48.19	43.00
40	51.68	46.55	44.08	41.76	37.53
50	44.29	39.70	37.38	35.39	31.42
60	37.51	33.54	31.49	29.71	26.22
70	31.56	28.20	26.42	24.92	21.84
80	26.83	23.89	22.39	20.95	18.28
90	23.34	20.67	19.37	18.07	15.81
100	20.81	18.25	17.11	15.88	13.86

TABLE V

DIELECTRIC CONSTANT OF ISOPROPYL ALCOHOL–WATER MIXTURES

Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	73.11	66.33	63.12	60.24	54.83
20	65.72	59.56	56.61	53.87	49.01
30	58.40	52.71	50.18	47.58	43.13
40	51.07	45.86	43.54	41.35	37.31
50	43.68	39.16	37.03	35.05	31.49
60	36.28	32.45	30.67	28.90	25.67
70	29.57	26.30	24.85	23.34	20.67
80	24.44	21.63	20.26	19.03	16.70
90	20.95	18.48	17.11	16.02	13.83
100	18.62	16.23	15.06	14.03	11.91

TABLE VI

DIELECTRIC CONSTANT OF *tert.*-BUTYL ALCOHOL–WATER MIXTURES

Alcohol, wt. %	20°	40°	50°	60°	80°
0	80.37	73.12	69.85	66.62	60.58
10	71.75	64.91	61.84	58.83	52.87
20	62.93	56.77	53.82	50.87	45.14
30	54.17	48.33	45.44	42.96	38.47
40	45.38	40.01	37.35	34.93	30.59
50	36.59	32.16	29.80	27.80	24.24
60	28.91	25.02	23.01	21.30	18.41
70	22.30	19.00	17.41	16.29	13.94
80	17.23	14.60	13.44	12.51	10.45
90	12.97	10.93	10.00	9.36	7.66
100	...	8.44	7.67	6.96	5.90

TABLE VII

DIELECTRIC CONSTANT OF ETHYLENE GLYCOL–WATER MIXTURES

Glycol, wt. %	20°	40°	60°	80°	100°
0	80.37	73.12	66.62	60.58	55.10
10	77.49	70.29	63.92	58.02	...
20	74.60	67.52	61.20	55.36	...
30	71.59	64.51	58.37	52.59	...
40	68.40	61.56	55.48	49.81	...
50	64.92	58.25	52.30	46.75	...
60	61.08	54.53	48.75	43.68	39.13
70	56.30	50.17	44.98	40.19	35.94
80	50.64	45.45	40.72	36.36	32.52
90	44.91	40.43	36.35	32.58	29.27
100	38.66	34.94	31.58	28.45	25.61

TABLE VIII

DIELECTRIC CONSTANT OF GLYCEROL–WATER MIXTURES

Glycerol, wt. %	20°	40°	60°	80°	100°
0	80.37	73.12	66.62	60.58	55.10
10	77.55	70.41	63.98	58.31	...
20	74.72	67.70	61.56	56.01	...
30	71.77	64.87	58.97	53.65	...

TABLE VIII (*Concluded*)

Glycerol, wt. %	20°	40°	60°	80°	100°
40	68.76	62.03	56.24	51.17	...
50	65.63	59.55	53.36	48.52	...
60	62.03	55.48	50.17	45.39	41.08
70	57.06	51.41	46.33	41.90	38.07
80	52.27	46.92	42.32	38.30	34.70
90	46.98	42.26	38.19	34.47	31.34
100	41.14	37.30	33.82	30.63	27.88

TABLE IX

DIELECTRIC CONSTANT OF ACETONE–WATER MIXTURES

Acetone, wt. %	20°	25°	30°	40°	50°
0	80.37	78.54	76.73	73.12	69.85
10	74.84	73.02	71.37	68.07	65.01
20	68.58	66.98	65.34	62.28	59.45
30	62.48	61.04	59.47	56.77	54.17
40	56.00	54.60	53.23	50.82	48.52
50	49.52	48.22	46.99	44.81	42.81
60	42.93	41.80	40.75	38.86	37.04
70	36.51	35.70	34.63	33.03	31.44
80	30.33	29.62	28.74	27.50	26.20
90	24.61	23.96	23.38	22.32	21.26
100	19.56	19.10	18.67	17.80	16.98

TABLE X

DIELECTRIC CONSTANT OF PURE AQUEOUS SOLUTIONS OF MANNITOL

Temp., °C.	0 Wt. %	5 Wt. %	10 Wt. %	15 Wt. %	20 Wt. %
20	80.37	79.66	78.84	78.07	...
25	78.54	77.83	77.12	76.30	75.47
30	76.73	76.06	75.18	74.47	73.64
40	73.12	72.40	71.57	70.87	70.10
50	69.85	69.16	68.33	67.57	66.74
60	66.62	65.85	65.08	64.38	63.61

TABLE XI

DIELECTRIC CONSTANT OF PURE AQUEOUS SOLUTIONS OF CANE SUGAR BETWEEN 10–40 WT. % ACCORDING TO KOCKEL, 50–70 WT. % ACCORDING TO ÅKERLÖF

Temp., °C.	0 Wt. %	10 Wt. %	20 Wt. %	30 Wt. %	40 Wt. %	50 Wt. %	60 Wt. %	70 Wt. %
10	84.2	81.5	78.8	75.9	72.8	..	..	..
20	80.4	78.0	75.4	72.6	69.8	65.7	61.2	55.0
30	76.7	74.2	71.7	68.9	66.1	62.4	58.2	52.5
40	73.1	70.7	68.3	65.7	63.0	59.4	55.5	50.1
50	69.9	67.5	65.0	62.5	59.8	56.3	52.5	47.6
60	66.6	64.4	62.0	59.4	56.8	53.4	49.8	45.1
70	63.5	61.2	58.8	56.2	53.6	50.5	47.1	42.7
80	60.6	58.2	55.8	53.2	50.5	47.6	44.3	40.3
90	57.8	55.4	52.9	50.4	47.7	..	..	38.0
100	55.1	52.7	50.2	47.6	44.8	..	..	35.7

interpolated to this standard temperature. The result of this interpolation is summarized in Table XII.

TABLE XII

DIELECTRIC CONSTANT AT 25° OF (1) METHYL, (2) ETHYL, (3) *n*-PROPYL, (4) ISOPROPYL, (5) *Tert.*-BUTYL ALCOHOL, (6) ETHYLENE GLYCOL, (7) GLYCEROL, (8) ACETONE–WATER MIXTURES, (9) MANNITOL AND (10) CANE SUGAR SOLUTIONS

Wt. %	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0	78.5	78.5	78.5	78.5	78.5	78.5	78.5	78.5	78.5	78.5
10	74.1	72.8	71.8	71.4	70.0	75.6	75.7	73.0	77.1	76.3
20	69.2	67.0	64.9	64.1	61.3	72.8	72.9	67.0	75.5	73.6
30	64.3	61.1	57.7	56.9	52.6	69.8	70.0	61.0	..	70.9
40	59.6	55.0	50.3	49.7	43.9	66.6	67.1	54.6	..	67.9
50	54.9	49.0	43.0	42.5	35.4	63.2	64.0	48.2	..	64.2
60	50.1	43.4	36.4	35.3	27.9	59.4	60.0	41.8	..	59.9
70	45.0	38.0	30.7	28.7	21.4	54.7	55.6	35.7	..	54.2
80	40.1	32.8	26.1	23.7	16.5	49.3	50.6	29.6	..	..
90	35.7	28.1	22.7	20.3	12.4	43.7	45.5	24.0	..	..
100	31.5	24.3	20.1	18.0	9.9	37.7	40.1	19.1	..	..

Discussion of the Results.[7]—In Fig. 3 has been plotted the logarithm of the dielectric constant of the pure solvents indicated. Every curve has been drawn as a straight line and in all cases this gives, without any doubt, the best representation of the results, or, in mathematical form:

$$D = ae^{-bT} \qquad (1)$$

where a and b are empirical constants and T is absolute temperature. A simple relation of this kind has a great value for interpolation purposes and therefore is well worth testing over as large a temperature range as possible. There are, however, various difficulties connected with this problem. The dielectric constant is known for very few liquids with certainty over a large range of either high or low temperatures, and in the latter case it should also be observed that the dispersion range with decreasing temperature may extend to wave lengths of many meters. For methyl and ethyl alcohols the most reliable data obtained at low temperatures seem to be those of Abegg and Seitz[8] at infinite wave length. Older data for the dielectric constant of higher alcohols show already at ordinary temperatures considerable discrepancies with the results in this paper. Furthermore, as has been shown by the investigations of Mizushima, dispersion occurs at low temperatures for these alcohols at large wave lengths and an extrapolation to a static value is always somewhat uncertain. Therefore, older measurements at low temperatures are not directly comparable with the data in Table I. Instead, equation 1 has been tested using a number of measurements of Smyth and Morgan[9] for ethyl bromide and chlorobenzene from −92 to +126°, of Smyth and Stoops[10]

[7] To save space comparison with data in literature is omitted.

[8] Abegg and Seitz, *Z. physik. Chem.*, **29**, 242 (1899).

[9] Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).

[10] Smyth and Stoops, *ibid.*, **50**, 1883 (1928).

for 2,2-dimethylpentane from −120 to +80°. Measurements of the latter with other hydrocarbons give practically the same result. As the numerical values do not interest, only a graphical representation is shown in Fig. 4. The scale used for plotting the logarithm of the dielectric constant has been varied for the different compounds in such a way

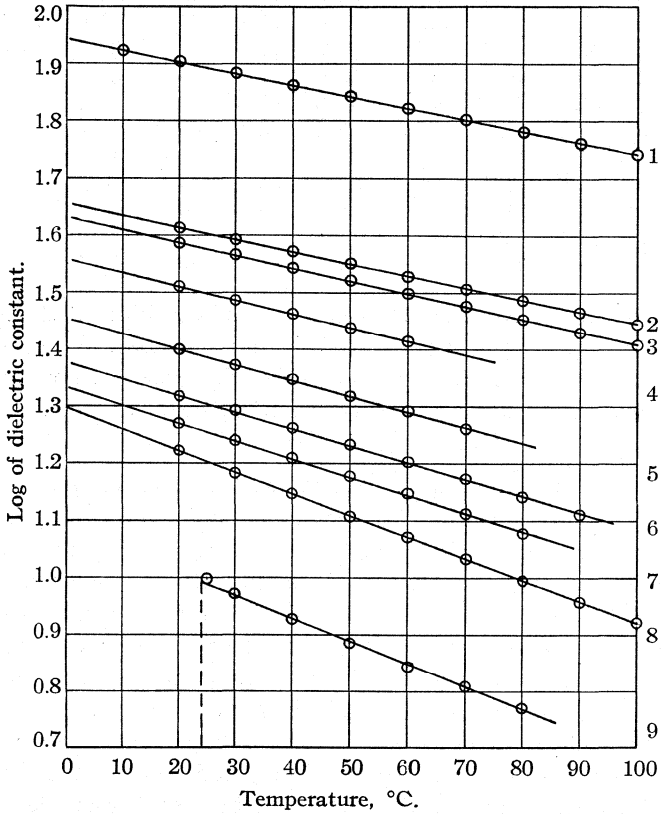

Fig. 3.—Curves for the logarithm of the dielectric constant of the pure solvents plotted against temperature. The curves represent (1) water, (2) glycerol, (3) ethylene glycol, (4) methyl, (5) ethyl, (6) *n*-propyl, (7) isopropyl, (8) isobutyl and (9) tertiary butyl alcohols.

as to give all lines a slope of the same order of magnitude. The variety of liquids represented in Fig. 4 is quite small, but every line seems to indicate that equation (1) is valid within the experimental errors over a temperature range of at least 150°. The constant b in equation (1) is a very important factor in the theory for heats of dilution. The integral heat of dilution is equal to the ionic electrical potential energy at the concentration given less that at infinite dilution multiplied by the factor

$(1 + T/D \cdot dD/dT)$, which is characteristic of the particular solvent used. Differentiation of equation (1) gives immediately

$$\frac{T}{D} \cdot \frac{dD}{dT} = -bT \qquad (2)$$

In the following tables, ten-logarithms have been used for the calculation of all values of log a and b. Before using the b values in equation (2), they should therefore be multiplied with the factor 2.3026.

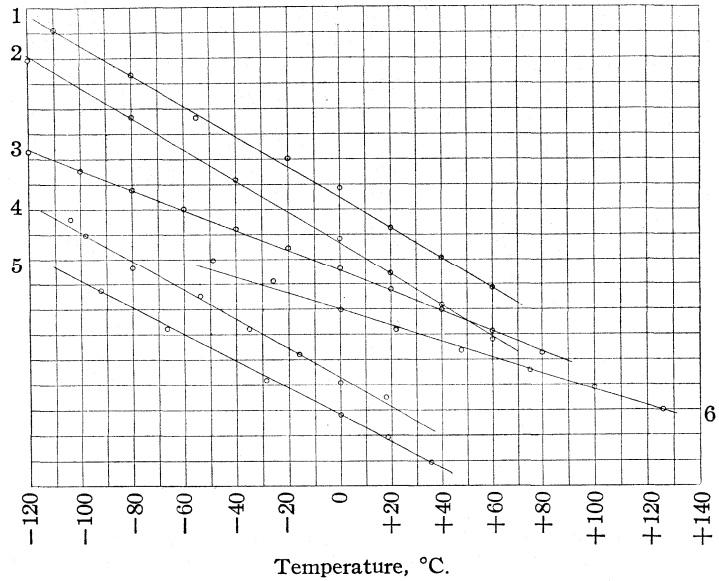

Fig. 4.—Curves for the logarithm of the dielectric constant of various compounds plotted against temperature. The lines represent (1) methyl, (2) ethyl alcohol, (3) 2,2-dimethylpentane, (4) dimethyl ether (according to measurements of Isnardi, *Cont. est. cienc. fís. mat.*, **3**, No. 53(1922)), (5) ethyl bromide and (6) chlorobenzene.

Using equation (1), graphical interpolation of the data in Table I gives the following expressions for the calculations of the dielectric constant of the pure solvents with varying temperature

(1)	Methyl alcohol	$\log D = 1.5099 - 0.00234\ (t - 20)$
(2)	Ethyl alcohol	$1.3979 - 0.00264\ (t - 20)$
(3)	*n*-Propyl alcohol	$1.3183 - 0.00293\ (t - 20)$
(4)	Isopropyl alcohol	$1.2700 - 0.00311\ (t - 20)$
(5)	Isobutyl alcohol	$1.2222 - 0.00386\ (t - 20)$
(6)	*Tert.*-butyl alcohol	$0.9870 - 0.00400\ (t - 25)$
(7)	Ethylene glycol	$1.5872 - 0.00224\ (t - 20)$
(8)	Glycerol	$1.6142 - 0.00212\ (t - 20)$
(9)	Acetone	$1.2914 - 0.00201\ (t - 20)$

If the variation of the dielectric constant of two pure solvents with temperature may be calculated from the expressions given above, it is reasonable to assume that the dielectric constant of any mixture of the two behaves in the same way. This has been found to be the case, and in Table XIII is given a summary of the constants derived for the equations for methyl, ethyl and *n*-propyl alcohols, in Table XIV for ethylene glycol, isopropyl and tertiary butyl alcohol–water mixtures. All constants are given with 20° as reference temperature, except in the case of pure tertiary butyl alcohol, as noted above.

TABLE XIII

CONSTANTS FOR CALCULATING THE DIELECTRIC CONSTANT OF METHYL, ETHYL AND *n*-PROPYL ALCOHOL–WATER MIXTURES WITH VARYING TEMPERATURES

Alcohol, wt. %	Methyl alcohol–water mixtures		Ethyl alcohol–water mixtures		*n*-Propyl alcohol–water mixtures	
	log *a*	*b*	log *a*	*b*	log *a*	*b*
0	1.9051	−0.00205	1.9051	−0.00205	1.9051	−0.00205
10	1.8799	− .00208	1.8727	− .00209	1.8664	− .00210
20	1.8505	− .00212	1.8367	− .00214	1.8231	− .00216
30	1.8190	− .00218	1.7968	− .00221	1.7724	− .00225
40	1.7865	− .00225	1.7520	− .00230	1.7133	− .00234
50	1.7513	− .00234	1.7024	− .00240	1.6455	− .00243
60	1.7120	− .00244	1.6500	− .00250	1.5740	− .00252
70	1.6658	− .00252	1.5926	− .00262	1.5000	− .00261
80	1.6160	− .00248	1.5300	− .00272	1.4300	− .00271
90	1.5648	− .00242	1.4625	− .00268	1.3710	− .00282
100	1.5099	− .00234	1.3979	− .00264	1.3183	− .00293

TABLE XIV

CONSTANTS FOR CALCULATING THE DIELECTRIC CONSTANTS OF ETHYLENE GLYCOL, ISOPROPYL AND *Tert.*-BUTYL ALCOHOL–WATER MIXTURES WITH VARYING TEMPERATURES

Alcohol, wt. %	Ethylene glycol–water mixtures		Isopropyl Alcohol–water mixtures		*Tert.*-butyl alcohol–water mixtures	
	log *a*	*b*	log *a*	*b*	log *a*	*b*
0	1.9051	−0.00205	1.9051	−0.00205	1.9051	−0.00205
10	1.8893	− .00210	1.8640	− .00208	1.8558	− .00216
20	1.8727	− .00215	1.8177	− .00213	1.7989	− .00230
30	1.8548	− .00222	1.7664	− .00220	1.7338	− .00250
40	1.8351	− .00230	1.7082	− .00228	1.6565	− .00274
50	1.8124	− .00237	1.6403	− .00238	1.5634	− .00298
60	1.7859	− .00240	1.5597	− .00249	1.4610	− .00322
70	1.7505	− .00242	1.4709	− .00262	1.3485	− .00340
80	1.7045	− .00238	1.3894	− .00277	1.2364	− .00360
90	1.6523	− .00231	1.3225	− .00294	1.1120	− .00380
100	1.5872	− .00224	1.2700	− .00311	0.9870[a]	− .00400

[a] Reference temperature for pure *tert.*-butyl alcohol 25°.

The molecular dielectric polarization P_{12} of a mixture of two compounds is given by the equation

$$P_{12} = \frac{D - 1}{D + 2} \frac{f_1 M_1 + f_2 M_2}{d} \qquad (3)$$

where f_1 and f_2 denote mole fractions, M_1 and M_2 molecular weights and d density of the mixture. Equation (3) is supposed to be used only for solu-

TABLE XV

DATA FOR THE POLARIZATION CURVE OF GLYCEROL–WATER MIXTURES AT 20° AND CONSTANTS FOR CALCULATING THE DIELECTRIC CONSTANT OF THESE MIXTURES WITH VARYING TEMPERATURES. MOLE FRACTION GIVEN FOR GLYCEROL

Glycerol, wt. %	log a	b	D	d	f	P_{12}
0	1.9051	−0.00205	80.37	0.9982	0.0000	17.40
10	1.8896	− .00207	77.55	1.0221	.0213	18.20
20	1.8734	− .00209	74.71	1.0470	.0466	19.68
30	1.8560	− .00211	71.78	1.0727	.0774	21.24
40	1.8373	− .00214	68.75	1.0995	.1154	23.14
50	1.8171	− .00217	65.63	1.1263	.1637	25.57
60	1.7890	− .00220	61.52	1.1533	.2269	28.77
70	1.7563	− .00220	57.05	1.1808	.3135	33.15
80	1.7154	− .00217	51.93	1.2079	.4391	39.68
90	1.6688	− .00214	46.65	1.2347	.6380	49.59
100	1.6142	− .00212	41.14	1.2609	1.0000	67.94

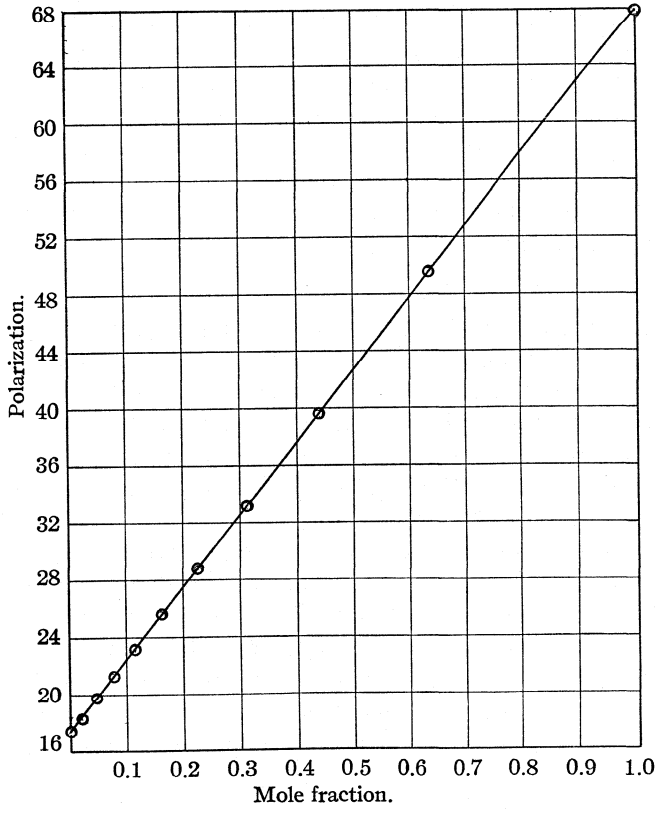

Fig. 5.—Curve for the dielectric polarization of glycerol–water mixtures at 20° according to equation (3).

tions of non-associated compounds in non-polar solvents. It has, however, been applied by Wyman to ethyl alcohol–water and by Graffunder and Heymann to ethyl alcohol and acetone–water or nitrobenzene mixtures. Both investigators found a linear variation of the polarization with the mole fraction of one of the compounds present. Glycerol is far more highly polar and has an enormously greater viscosity than either ethyl alcohol or acetone and a comparison of the polarization curve for glycerol–water mixtures with the straight lines found for the mixtures mentioned above has therefore some interest. In Table XV is given a summary of all the data necessary for the plotting of the polarization curve for glycerol–water mixtures. In the table are also included the constants to be employed for the calculation of the temperature variation of the dielectric constant of these mixtures.

The polarization data for glycerol–water mixtures are plotted in Fig. 5. The points all lie in a straight line, and thus we have obtained the same general result as previously found by Wyman and Graffunder and Heymann for other organic solvent–water mixtures. However, this result was partly to be expected since the mole fraction term in equation (3) varies approximately linearly and the dielectric constants of all the mixtures are high. The same holds true in the case of the mixtures measured by the investigators mentioned above. The calculation of the dielectric constant of alcohol–water mixtures from the known polarizations of the pure compounds would, assuming linear variation with the mole fraction, accordingly, give values of low accuracy.

Summary

Using a resonance method at a wave length of 150 meters, the dielectric constant at various temperatures has been measured for a series of water mixtures of the following organic solvents: (1) methyl, (2) ethyl, (3) *n*-propyl, (4) isopropyl, (5) tertiary butyl alcohol, (6) ethylene glycol, (7) glycerol and (8) acetone. The dielectric constants of a few pure aqueous solutions of mannitol and cane sugar have also been measured at various temperatures.

The results have been compared with corresponding data in the literature, and, in general, fairly good agreement has been found. In some instances a short discussion has been given of the results in order to indicate why the present data probably are nearer the true values than the older ones.

It has been found that the change with temperature of the dielectric constant of all the compounds employed for the measurements presented in this paper may be expressed with considerable accuracy by the equation

$$D = ae^{-bT}$$

where D is the dielectric constant, a and b are empirical constants, and T is temperature. The equation has also been tested using a number of series

of data in the literature. Straight line variation of the logarithm of the dielectric constant with temperature was generally found in every case over the entire range the measurements had been carried out.

Equations for the change with temperature of the dielectric constant of the pure solvents and the solvent–water mixtures have been obtained through large scale graphical interpolation. As a rule, the calculated values agree very well with the observed ones. A short discussion has been given of the polarization of glycerol–water mixtures.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 96]

7-IODO-8-HYDROXYQUINOLINE-5-SULFONIC ACID AS A REAGENT FOR THE COLORIMETRIC DETERMINATION OF FERRIC IRON

BY JOHN H. YOE

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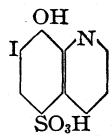
7-Iodo-8-hydroxyquinoline-5-sulfonic acid (I) dissolves in water to give a bright yellow solution which reacts with ferric ions, yielding blue to green colored solutions, the color and intensity varying with the iron concentration. The reaction is very sensitive and is best carried out in a solution acid to methyl orange paper. Ferrous ions give no color reaction and hence the reagent may be used to distinguish between ferrous and ferric iron. The color does not fade on standing, an advantage over the thiocyanate method.



I

Solutions

Standard Solutions of Various Ions.—Each standard solution was prepared from a good grade of salt, usually nitrate, chloride or sulfate, in the case of metallic ions, and from the potassium or sodium salt in the case of the non-metallic ions. Redistilled water was used (unless otherwise stated) and all solutions were kept in 30-ml. bottles that had been thoroughly cleaned and steamed out. Each bottle was fitted with a Pyrex glass dropper capped with a rubber stopper and nipple. Each dropper was calibrated, the capacities ranging from 18 to 28 drops per ml. The solutions were arranged according to the Periodic Chart and held in place on a wooden board, 45.5 cm. × 68.5 cm., in which were bored holes to carry the bottles. The concentration of the solutions was 400 mg. of the respective ion per liter, that is, 400 parts per million. Most of the solutions were aqueous, a few were in dilute acid (HCl, HNO_3 or H_2SO_4), and several were in concentrated acid.

In addition to the above solutions, more concentrated ones were prepared in the case of sodium, potassium, calcium and magnesium for use in preparing salt solutions for the determination of iron. These solutions contained 10 mg. of metallic ion per ml.

Standard Ferric Iron Solution.—A weighed quantity of pure ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, was dissolved in water, a few drops of concentrated sulfuric acid added and the iron oxidized by boiling with a little bromine. The excess bromine was expelled by boiling, the solution cooled to room temperature, transferred to

a volumetric flask, diluted to the mark and thoroughly mixed. Standard solutions containing 40 and 400 parts of Fe^{+++} per million, respectively, were prepared.

Reagent Solution.—Two-tenths gram of 7-iodo-8-hydroxy-quinoline-5-sulfonic acid dissolved in 100 ml. of water makes a satisfactory reagent solution.

The 7-iodo-8-hydroxyquinoline-5-sulfonic acid may be prepared according to Claus, German Patent 72,942, recorded in *Friedländer*, Vol. 3, page 964, and also in the *Jahresbericht der Chemischen Technologie*, 1894, page 625. Ten and twenty-five gram quantities of it may be purchased in a pure and crystalline form from G. D. Searle and Co., Chicago, Ill. The 7-iodo-8-hydroxyquinoline-5-sulfonic acid decomposes at 223° when heated in a capillary tube. Its aqueous solution is a bright yellow.

Procedure.—A preliminary procedure was carried out by placing a single drop of each of the standard solutions, respectively, in little glass cells (0.5 ml. capacity) used in P_H determinations according to the method of Brown.[1] These cells were lined up on a white glass plate which enabled rapid observation. No attention was paid to the acidity of the solution. Observations were repeated in the case of salts in acid solution. Measured quantities of these solutions were placed in small beakers, diluted with a few ml. of water and made weakly acid by partial neutralization with 6 *N* ammonium hydroxide. Each solution was transferred to a 50-ml. (210 mm. to mark) Nessler tube, 5 drops of iodohydroxyquinolinesulfonic acid solution added, the solution mixed, diluted to the 50-ml. mark with water, again mixed and then observed.

In observing the color reaction with ferric iron, a series of Nessler tubes was made up with varying concentration of the iron as follows. Measured quantities of standard ferric iron solution were transferred to Nessler tubes, 5 drops of iodohydroxyquinolinesulfonic acid solution added to each tube, the solutions mixed, diluted to the 50-ml. mark with water, again mixed and then observed. The observations are recorded in Table I.

TABLE I

Concn. of Fe^{+++}, parts per million	Remarks
"Blank," 5 drops reagent in 50 ml. water	Pale yellow
1 in 60	Not distinguishable from "blank"
1 in 30	Barely distinguishable from "blank"
1 in 15	Faint greenish tinge to the yellow solution
1 in 10	Faint greenish-yellow
1 in 7.5	Pale greenish-yellow
1 in 6	Pale greenish-yellow. Little more intense than the 1 in 7.5
1 in 3	Light yellowish-green. Much more intense than the 1 in 6
1 in 1.5	Bluish-green. Much more intense than the 1 in 3
8 in 1	Dark green. Four ml. of reagent used

Under the above conditions 1 part of ferric iron in 15 million parts of solution gives a faint greenish-yellow solution distinguishable from a "blank" containing only 5 drops of reagent and having a pale yellow color.

[1] Brown, *J. Lab. Clin. Med.*, **9**, 239–244 (1924).

With 1 part of iron in 10 million parts of solution a greenish-yellow is obtained which is easily distinguished from the blank. One part of iron in 1.5 million parts of solution gives a bright bluish-green color. Higher concentrations give green colored solutions, the intensity increasing with the concentration of iron. The color is very stable to light and hence it is not necessary to prepare the set of standards and the sample solution at the same time, as is necessary in the case of the thiocyanate method. The same set of standards may be used all day. The reaction is affected by strong acids and bases, both of which destroy the color.

Observations with Various Ions.—None of the following ions give color reactions with 7-iodo-8-hydroxyquinoline-5-sulfonic acid: Lithium (Li^+), sodium (Na^+), potassium (K^+), rubidium (Rb^+), cesium (Cs^+), copper (Cu^{++}), silver (Ag^+), gold (Au^{+++}), calcium (Ca^{++}), strontium (Sr^{++}), barium (Ba^{++}), beryllium (Be^{++}), magnesium (Mg^{++}), zinc (Zn^{++}), cadmium (Cd^{++}), mercury (Hg^+, Hg^{++}), boron (BO_3^{---}), aluminum (Al^{+++}), scandium (Sc^{+++}), yttrium (Y^{+++}), lanthanum (La^{+++}), cerium (Ce^{+++}), praseodymium (Pr^{+++}), neodymium (Nd^{+++}), samarium (Sm^{+++}), gadolinium (Gd^{+++}), dysprosium (Dy^{+++}), erbium (Er^{+++}), thulium (Tm^{+++}), ytterbium (Yb^{+++}), gallium (Ga^{+++}), indium (In^{+++}), thallium (Tl^{+++}), titanium (Ti^{++++}), zirconium (Zr^{++++}), hafnium (Hf^{++++}), thorium (Th^{++++}), germanium (Ge^{++++}), tin (Sn^{++}, Sn^{++++}), lead (Pb^{++}), vanadium (V^{++}), columbium (Cb^{++}), tantalum (Ta^{+++++}), phosphorus (PO_4^{---}), arsenic (As^{+++}), antimony (Sb^{+++}), bismuth (Bi^{+++}), chromium (Cr^{+++}), molybdenum,[2] tungsten (W^{++++++}), uranium (UO_2^{++}), sulfur (S^{--}), selenium,[3] tellurium,[4] manganese (Mn^{++}), rhenium,[5] fluorine (Fl^-), chlorine (Cl^-), bromine (Br^-), iodine (I^-), iron (Fe^{++}), cobalt (Co^{++}), nickel (Ni^{++}), ruthenium (Ru^{+++}), rhodium,[6] palladium (Pd^{++}), iridium (Ir^{++++}), platinum (Pt^{++++}).

Determination of Ferric Iron in Aqueous Solutions.—Measured quantities of solutions of various metallic salts (nitrates, chlorides or sulfates) were placed in 50-ml. Nessler tubes and to each tube was added a known amount of ferric iron. The solutions were diluted to approximately 5 ml.

[2] Metallic molybdenum was dissolved in *aqua regia* and the solution diluted with an equal volume of water.

[3] Selenium was dissolved in concd. nitric acid and the solution diluted to 3 *N* HNO_3.

[4] Tellurium was treated with *aqua regia* and the mixture evaporated to dryness. Concentrated nitric acid was added to the residue and the mixture evaporated to dryness. This treatment was repeated several times and the residue finally taken up in 3 *N* HNO_3.

[5] Rhenium was treated with *aqua regia* and the mixture evaporated to dryness. Concentrated nitric acid was added to the residue and the mixture evaporated to dryness. This treatment was repeated and the residue finally taken up in water.

[6] Rhodium was fused with potassium hydroxide and the fused mass dissolved in *aqua regia* and diluted 1:1 with water.

and made weakly acid[7] with sulfuric acid. Then 5 drops of the 7-iodo-8-hydroxyquinoline-5-sulfonic acid reagent was added to each, the solutions were mixed by gentle shaking, diluted with water to the mark and thoroughly mixed. The colors were then compared with a set of standard solutions prepared in a similar way by adding 5 drops of the reagent to measured quantities of ferric iron in approximately 5 ml. volume made weakly acid with sulfuric acid, and finally diluted to the 50-ml. mark. The results are tabulated in Table II. It should be noted that the reagent solution is *yellow* but changes to *green* upon reacting with ferric ions, the color varying from a faint greenish-yellow to dark green, depending upon the iron concentration.

TABLE II

ANALYTICAL RESULTS

	Concentration of ions, parts per million												Fe^{+++} found,
Soln.	Na^{+}	K^{+}	Ca^{++}	Mg^{++}	Co^{++}	Ni^{++}	Cu^{++}	Al^{+++}	Cr^{+++}	Sn^{++++}	Ti^{++++}	Fe^{+++}	p. p. m.
1	200	200										0.1	0.1
2	200	200	200	200								.1	.1
3	200	200										.7	.7
4	200	200	200	200								.7	.7
5	200	200	200	200								2.2	2.2[a]
6	200	200	200	200	3							0.7	0.7
7	200	200	200	200	8							.7	.6
8						3						.7	.5[b]
9					1.7	1.7						.7	.7
10							0.4					.7	.6
11							0.7					.7	.4[c]
12								4				.7	.7
13								8				.7	.6
14									0.3			.7	.7
15									1.5			.7	.6
16										1.7		.7	.7
17											1.7	.7	.7

[a] One ml. of reagent was used in Solution 5 and in the standards. [b] Tints do not match. The addition of three more drops of reagent gave a very good color match corresponding to Fe^{+++} 0.7 p. p. m. [c] Color bleached. Matching only approximate.

It will be noted that none of the colorless ions interfered with the color reaction nor did the colored ions interfere at the low concentrations used. Higher concentrations of the colored ions prevent accurate color matching. Cupric ions react with the reagent to give a white finely divided precipitate[8] and hence would interfere with the color comparison if present in amounts greater than a few tenths of a part per million parts of solution. How-

[7] Litmus paper was used at first and the acidity adjusted to a pale pink but in later experiments methyl orange paper has been employed and appears to permit a more uniform adjustment.

[8] The copper appears to be precipitated completely by the reagent. We are investigating this reaction to see whether it can be used to determine copper quantitatively.

ever, the ferric iron may be detected *qualitatively* in the presence of much higher concentrations of copper. For example, a small excess of reagent was added to a solution containing Fe^{+++} 8 p. p. m. and Cu^{++} 40 p. p. m. A white precipitate was formed which settled upon standing for a few minutes, giving a dark green supernatant solution showing the presence of ferric iron. Salts that easily hydrolyze, such as those of tin or titanium, interfere with the color matching unless their concentration is very low.

We desire to express our thanks to G. D. Searle and Co., Chicago, Ill., who furnished us with the 7-iodo-8-hydroxyquinoline-5-sulfonic acid used in this investigation. J. D. Riedel-E. deHaën A. G., Hannover, Germany, supplied a number of pure salts of the rare elements, for which we are very grateful.

Summary

7-Iodo-8-hydroxyquinoline-5-sulfonic acid is a very sensitive colorimetric reagent for ferric iron, its yellow aqueous solution changing to blue or green upon the addition of ferric ions. It gives no color reaction with ferrous ions nor with a large number of other ions. The reagent is sensitive to 1 part of ferric iron in 10 million parts of solution when the observation is made in a 50-ml. (210 mm. to mark) Nessler tube. The reaction is best carried out in a solution acid to methyl orange paper. The color is stable to light (an advantage over the thiocyanate method) but is destroyed by strong acids and bases. Salts that hydrolyze easily or yield colored ions should not be present unless in very low concentration.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

PHOTOCHEMICAL STUDIES. XV. GERMANE. SOME REMARKS ON THE DECOMPOSITION OF AMMONIA SENSITIZED BY MERCURY VAPOR

BY HENDRIK ROMEYN, JR., AND W. ALBERT NOYES, JR.

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The photochemistry of germane has not been investigated previously. It should be of interest because of the similarity between this compound and methane. Taylor and Hill[1] found the latter compound, in contrast to other saturated hydrocarbons, not to undergo reaction under the influence of excited mercury atoms. Bates[2] found also that excited cadmium atoms transferred their energy to methane without producing reaction. Bates[3] also investigated thoroughly the quenching of the resonance radiation of mercury by methane and found it to have an exceedingly

[1] Taylor and Hill, THIS JOURNAL, **51**, 2922 (1929).

[2] Bates, *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).

[3] Bates, THIS JOURNAL, **52**, 3825 (1930).

small effective cross section for quenching. He observed a peculiar effect of methane in producing increasing transparency of mercury vapor at pressures higher than forty or fifty millimeters. These properties and others show that methane is in many respects analogous to the noble gases.[4]

The absorption spectrum of methane in the Schumann region has been investigated by Leifson,[5] who found continuous absorption below 1800 Å. at high pressures and a series of bands below 1600 Å. at low pressures.

In studying the sensitized decomposition of germane it was desired to have some control reaction which would serve to determine the constancy of the intensity of resonance radiation. For this purpose the sensitized decomposition of ammonia was chosen. Both the sensitized and unsensitized decompositions of this gas have been investigated repeatedly.[6] This reaction proved not to be well adapted to the purpose at hand and it will be given only brief mention. Certain conclusions with regard to the mechanism of the sensitized reaction are, however, possible.

I. Experimental

The germane used in these experiments was prepared by the action of ammonium bromide on magnesium germanide in liquid ammonia solution.[7] It was purified by reaction with sodium in liquid ammonia to produce sodium germanyl ($NaGeH_3$), the germane being regenerated by causing the latter substance to react with ammonium bromide in liquid ammonia solution. In this way the higher hydrides of germanium are broken down. Final purification consisted in repeated fractional distillations with liquid air. To test the purity samples were decomposed thermally, leading to the reaction $GeH_4 = Ge + 2H_2$. For example, in one experiment the initial pressure of the germane was 0.1221 mm. and the final pressure of the hydrogen 0.2446 mm., calcd., 0.2442. The agreement with the theoretical is within experimental error, although if the impurity is assumed to be Ge_2H_6 the purity calculated from the figures is 99.7 mole per cent.

The ammonia was dried by sodium and purified by fractional distillation.

(a) Attempt to Obtain the Absorption Spectrum of Germane.—A condensed discharge through hydrogen at a pressure of a few millimeters served as a source of radiation.[8] A Hilger E3 spectrograph and plates sensitized either with Nujol or with a special sensitizing solution furnished by the Eastman Kodak Co. were used. Exposures were made in two tubes, one twenty centimeters in length and the other three hundred and fifty centimeters in length, at pressures varying from a few millimeters to approximately one atmosphere. Aside from a slight continuum at the short wave lengths which seemed to disappear upon further purification of the germane, no absorption was observed between 2130 and 7000 Å. As will be shown later it is possible,

[4] See Glockler, THIS JOURNAL, **48**, 2021 (1926).

[5] Leifson, *Astrophys. J.*, **63**, 73 (1926).

[6] For recent work on the unsensitized reaction see Wiig and Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932). This article contains references to earlier work on both types of reaction.

[7] E. Seaton Carney, Thesis, Brown University, 1928; G. K. Teal, Thesis, 1930. The authors wish to express their appreciation to Dr. Teal for preparing the germane used in these experiments.

[8] Chalonge and Lambray, *Rev. d'optique*, **8**, 332 (1929).

however, to obtain photochemical decomposition of germane by radiation transmitted by thin layers of quartz. It appears probable that germane does absorb at some place in the range of wave lengths between about 1800 and 2100 Å. Further studies with a vacuum grating will be made at a later date.

Two attempts yielding negative results were made to obtain the Raman spectrum of germane. Failure was caused undoubtedly by the fact that it was impossible to use sufficiently high pressures to give the requisite light scattering.

As a check on the method of obtaining absorption spectra the predissociation bands of ammonia were photographed.

(b) The Sensitized Decompositions of Germane and of Ammonia.—Customary technique was used for these studies. The mercury arc was a horizontal type operated with the mercury reservoirs under water. Two reaction vessels were placed above the lamp in such a way that one could be used as a control. The pressure of the mercury vapor was maintained constant by separating the reaction vessels from the rest of the apparatus by traps immersed in ice–water mixtures. Pressures below 0.2 mm. were read on ordinary McLeod gages. For runs at higher pressures a modified McLeod gage was used. In the case of ammonia the rate was determined by measuring the pressure of the gas uncondensed by liquid air. The vapor pressure of germane is not negligible at the temperature of liquid air and varies considerably between the boiling point of oxygen and the boiling point of nitrogen. Empirical corrections were made for the vapor pressure of germane, using the observed vapor pressure of the pure material at the beginning of a run.

Careful determinations were made to show that the sensitized reactions were not greatly complicated by the direct photochemical reactions. This was accomplished by removing the mercury vapor by means of a trap immersed in solid and liquid ammonia (−77°). In both cases not more than 5% of the observed rate could be ascribed to the unsensitized reaction.

(c) The Unsensitized Decomposition of Germane.—The radiation from the hydrogen discharge tube was used in these experiments. The discharge tube was waxed directly to the window of the reaction vessel, eliminating any air path and giving a thickness of quartz traversed by the radiation of less than one millimeter. Mercury vapor was removed as before by solid–liquid ammonia mixtures. In some experiments a second reaction vessel was placed so as to receive radiation which had traversed the first in order to ascertain the completeness of absorption. Results in the second vessel were always negative even with the first vessel evacuated due, undoubtedly, to the greater thickness of quartz traversed by the radiation.

These experiments on the unsensitized reaction are, therefore, very qualitative and serve merely to show that the general course of the reaction is not greatly different from that of the sensitized reaction.

II. Results

(a) The Photosensitized Decomposition of Germane.—Figure 1 shows the course of a typical reaction. The upper curve represents the total pressure and the lower curve the pressure of the gas uncondensed by liquid air corrected for the vapor pressure of germane and the cooling of the system. The latter pressure is due to the hydrogen formed during the reaction.

Several runs were carried to complete decomposition. One would predict from the equation $GeH_4 = Ge + 2H_2$ that the final pressure would be twice the initial pressure. This was never found to be the case, indicating an appreciable clean-up of hydrogen on the walls. Actually

the pressure at the end of the run averaged 1.81 times the initial pressure. Pumping out the hydrogen and flaming the walls led to an evolution of gas very closely equal to the amount cleaned up.

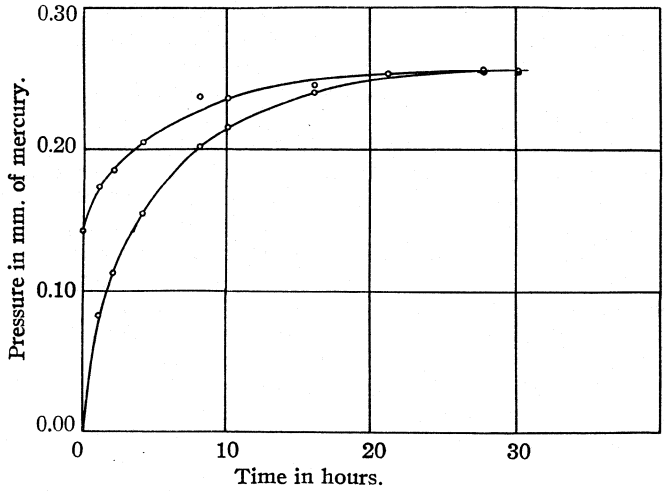

Fig. 1.—Photosensitized decomposition of germanium hydride.

If P_1 is the initial pressure of germane, P_t the total pressure at time t, P_g the pressure of germane at time t and P_H the pressure of hydrogen at time t, we may write

$$P_g = P_t - P_H \quad (1)$$

If the fraction of the hydrogen cleaned up by the walls is assumed to be constant during a run we may write

$$P_H = 1.81(P_1 - P_g) \quad (2)$$

Hence

$$P_g = (1.81P_1 - P_t)/0.81 \quad (3)$$

and

$$P_H/(P_t - P_1) = 2.23$$

Table I shows data illustrating the validity of this relationship.

TABLE I

PHOTOSENSITIZED DECOMPOSITION OF GERMANE

Time, hrs.	P_t, mm.	P_H, mm.	$P_H/(P_t - P_1)$
0	0.1413	0.0000	..
1	.1718	.0701	2.30
2	.1846	.1000	2.30
4	.2040	.1425	2.27
8	(.2370) (?)	.1896	1.98
10	.2360	.2034	2.15
16	.2441	.2257	2.19
30	.2544	.2560	2.26
		Av.	2.21

The average value of this ratio found for all runs is 2.25 and this figure will be used.

The dependence of the rate of decomposition on the pressure of the germane was investigated over a range of pressures from 0.01 mm. to several

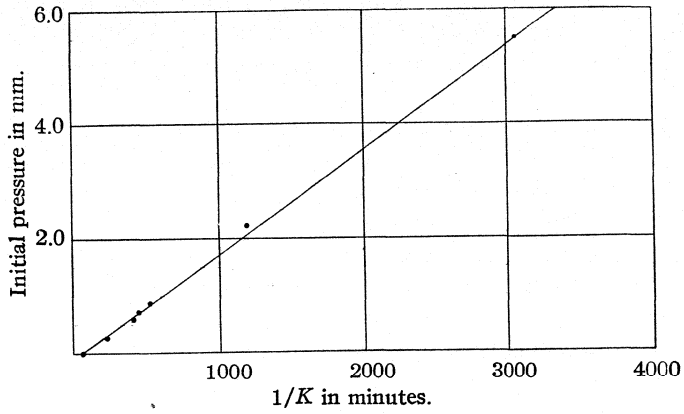

Fig. 2.

millimeters. In a given run it was sometimes difficult to decide definitely whether the data fitted best a first or second order equation. When constants at various pressures were compared the constants for both types

TABLE II

RATE OF PHOTOSENSITIZED DECOMPOSITION OF GERMANE

Time, hrs.	Pressure of germane, mm.	K (first order), hrs.$^{-1}$	K (second order), mm.$^{-1}$ hrs.$^{-1}$
0	0.1413		
		0.24	2.2
2	.1036		
		.17	2.2
4	.0878		
		.16	4.2
10	.0245		
		.15	16.1
21	.0046		
	.....		
0	.0560		
		.052	227.4
1.02	.0496		
		.042	207
2.03	.0449		
		.038	207
3.03	.0411		
		.035	207
4.08	.0377		

were found to vary markedly with pressure, although those for the first order equation varied less than the others. Figure 2 shows a plot of the reciprocal of the first order constant against the pressure of the germane at the beginning of the run. A similar plot for the second order constants gave a hyperbolic curve. It seems necessary to conclude, therefore, that a mechanism leading to a first order equation as a limiting case is most nearly applicable. Table II shows calculations of the two constants for two runs.

The deposit of germanium on the walls of the cell gradually decreased the amount of light transmitted. In making intercomparisons in a series of runs it became necessary to use some standard of comparison. This was done by alternating runs at different pressures and under different conditions with runs made at a standard pressure. In what follows corrections have been made where necessary for varying light intensity. Intercomparisons were made usually by means of short runs in order to reduce error due to variation in light intensity to a minimum.

The variation of reaction rate with temperature was investigated, although high temperatures were impossible due to thermal decomposition of the germane. Table III gives a summary of results on two runs.

TABLE III

VARIATION OF RATE OF SENSITIZED DECOMPOSITION OF GERMANE WITH TEMPERATURE

Temperature, °C.	93	28
Initial pressure of germane, mm.	0.2121	0.1998
K, hrs.$^{-1}$	0.012	0.017

There is, therefore, no marked dependence on temperature.

The effect of added gases was investigated, as shown in Table IV.

TABLE IV

EFFECT OF ADDED GASES ON THE RATE OF SENSITIZED DECOMPOSITION OF GERMANE

Added gas	Pressure of added gas, mm.	Initial pressure of germane, mm.	K, hrs.$^{-1}$
H_2	0.0916	0.0943	0.044
..	....	.0937	.045
N_2	0.2092	.1095	.051
..	....	.1182	.052

Thus neither hydrogen nor nitrogen affects the rate of decomposition markedly.

(b) The Direct Photochemical Decomposition of Germane.—In these experiments the same phenomenon of hydrogen clean-up was observed. Since the radiation was not strictly monochromatic, only an approximate rate equation may be given. This should be of the form

$$-dP_g/dt = aI(1 - e^{-kP_g}) \qquad (4)$$

which upon integration gives

$$aI(t_2 - t_1) = P_{g_1} - P_{g_2} + (1/k) \log (e^{-kP_{g_1}} - 1)/(e^{-kP_{g_2}} - 1) \quad (5)$$

From several runs an average value of k was found to be 12 if the pressure is expressed in millimeters. This value, even though it has no definite significance due to the fact that the radiation was not monochromatic, indicates a high absorption of the effective radiation even for a tube of the length used. It should be possible to evaluate aI from one time interval for a given run and calculate a theoretical curve. Direct calculation of pressures from equation (5) is rather laborious, so that a theoretical curve was plotted and comparison made between experimental values and values read from the curve. Table V shows the results of such a calculation for one run.

TABLE V

RATE OF DIRECT PHOTOCHEMICAL DECOMPOSITION OF GERMANE

Time, min.	Total pressure observed, mm.	Total pressure calcd., eq. (5), mm.
0	0.0517	0.0517
10	.0661	.0671
15	.0762	.0769
20	.0822	.0826
25	.0896	.0905

(c) **The Sensitized Decomposition of Ammonia.**—Figure 3 shows typical curves of pressure of gas uncondensed by liquid air against time for the sensitized decomposition of ammonia. All runs show a rather rapid initial rate followed by a decided falling off.

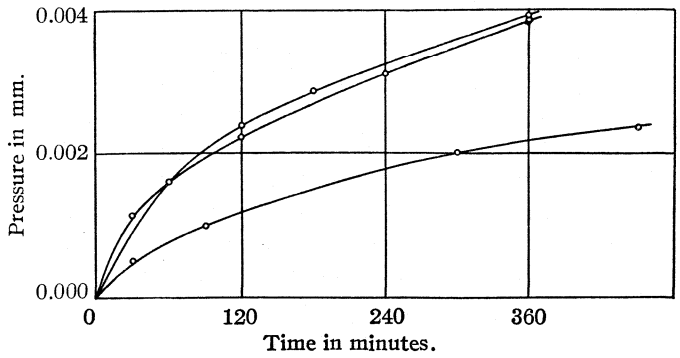

Fig. 3.—Photosensitized decomposition of ammonia.

III. Discussion of Results

(a) **Germane.**—The heat of dissociation of the germanium–hydrogen bond is not known. Mulliken[9] has summarized recently data derivable from band spectrum analysis for a large number of molecules. Inspection

[9] Mulliken, *Rev. Modern Physics*, **4**, 1 (1932).

of data on hydrides indicates that the energy of dissociation of the GeH molecule will probably correspond to about 2 electron volts with a large uncertainty (probably at least a volt). The presence of three more hydrogen atoms in the germane molecule may be expected to modify somewhat the energy of dissociation of the germanium hydrogen bond, but we may accept this figure tentatively as the energy required to produce the reaction $GeH_4 = GeH_3 + H$. In any case the removal of one hydrogen should require much less energy in germane than in methane.[10]

The energy which a 2^3P_1 mercury atom is capable of giving up on collision corresponds to 4.86 electron volts, whereas the long wave length limit of the ultraviolet absorption of germane corresponds to more than 6 electron volts. The direct and sensitized decompositions of germane seem in every way to be similar and to involve the primary process $GeH_4 = GeH_3 + H$. At least in the direct unsensitized reaction the GeH_3 radical must be formed in either a high energy level or with high kinetic energy. In fact there is ample energy absorbed to cause the ejection of more than one hydrogen atom by a species of Auger effect. In any case reactions of the type $GeH_3 = GeH + H_2$ could take place spontaneously since the heat of dissociation of hydrogen is probably about twice the heat of dissociation of the germanium–hydrogen bond.

The experiments in which hydrogen was added and others toward the end when the hydrogen was in large excess showed that this gas did not affect markedly the rate of reaction. As will be shown later the effect of hydrogen in quenching the fluorescence of mercury is probably much less than that of germane, so that any inhibiting effect to be expected from this source might be difficult to detect with certainty. The reaction $H + GeH_4 = H_2 + GeH_3$ should be energetically possible and may account for the fact that hydrogen is not proved definitely to be an inhibitor. The lack of effect of nitrogen probably means that 2^3P_1 and 2^3P_0 mercury atoms are equally effective in initiating the reaction and that diffusion processes do not play an important part in determining the rate. We may state, therefore, that the initial removal of a hydrogen atom from germane either by excited mercury or by another hydrogen atom is followed by a sequence of events so rapid as not to be decisive in determining the rate of reaction. In this manner the data may be accounted for quantitatively up to pressures of several millimeters. For higher pressures peculiar effects seem to be taking place which may be analogous to those found by Bates[3] for methane.

As shown above the rate of the unsensitized reaction is at least approximately proportional to the intensity of the absorbed radiation. For the sensitized reaction we may write

[10] Mecke, *Z. Elektrochem.*, **36**, 589 (1930), gives 5.4 electron volts for the reaction $CH_4 = CH_3 + H$. It seems probable that this figure is too high.

$$-dP_g/dt = Mk_1k_2IP_g/(k_2P_g + k_3P_H + k_4) \quad (6)$$

M = no. of germane molecules used up per molecule dissociated by collision with excited mercury

k_1I = rate of formation of excited mercury atoms

$k_2P_gP_m$ = rate at which excited mercury atoms are used up by collision with germane molecules

$k_3P_HP_m$ = rate at which excited mercury atoms are used up by collision with hydrogen molecules

k_4P_m = rate at which excited mercury atoms are used up by fluorescence

P_m = pressure of excited mercury atoms in the steady state

This equation ignores the reaction $H + GeH_4 = H_2 + GeH_3$ except as a possible secondary step. Integration of equation (6) after substitution for P_H from equation (2) gives

$$1/Mk_1k_2I[(k_2 - 1.81k_3)(P_1 - P_g) + (1.81k_3P_1 + k_4)\log(P_1/P_g)] = t \quad (7)$$

between the limits $t = 0$ and t, and P_1 and P_g. Since an appreciable fraction of the germane was decomposed in some of the runs shown graphically in Figure 2, it is necessary to use equation (7) to evaluate k_2. Values of this constant calculated in this manner show as good a constancy as could be expected and give for k_2 the value 4.7×10^7 if the unit of time is the second and the pressure is expressed in millimeters. The value of k_4 is assumed to be 9.7×10^6 sec.$^{-1}$ and that of k_3 to be 1.09×10^7 sec.$^{-1}$ mm.$^{-1}$.[11] It should now be possible to apply equation (7) to any run providing one point is used to calculate the quantity Mk_1I. Table VI shows how this equation applies to three runs. The bracketed pressures were used to calculate Mk_1I.

TABLE VI

APPLICABILITY OF COMPLETE RATE EQUATION TO THE DECOMPOSITION OF GERMANE

Time, min.	P(obs.)	P(calcd.)	Time, hrs.	P(obs.)	P(calcd.)	Time, min.	P(obs.)	P(calcd.)
0	0.0560	0.0560	0	0.1413	0.1413	0	0.2050	0.2050
61	.0605	.0612	1	.172	.159	30	.210	.208
122	.0645	.0650	2	.185	.173	60	.213	.213
182	.0677	.0681	4	.204	.196	90	.218	.217
245	.0708	[.0708]	10	.236	[.236]	120	.221	.221
			16	.244	.249	250	.237	[.237]
			21	.252	.253			

Equation (7) gives a fairly satisfactory representation of the course of the runs, probably as good as the data would warrant, although there are undoubtedly some factors which have not been included and which may be of importance. From the value of k_2 it should be possible to calculate an effective cross section for reaction between excited mercury atoms and germane molecules. This quantity may be defined as the square of the sum of the radii of the germane molecules and the excited mercury atoms.

[11] Calculated from the data of Zemansky, *Phys. Rev.*, **36**, 219, 919 (1930).

Obtained in this manner the effective cross section is very large (about 1.4×10^{-14} sq. cm.). The validity of this calculation may be open to question for a variety of reasons. Comparison of the rate of germane decomposition with that of ammonia leads to one of two conclusions: either the quantity M (number of molecules decomposing in a chain) is quite large (> 10) or the effective cross section for reaction is quite large. Equation (7) assumes the latter to be the case, although the quantity M is not determined as such. Definite decision between these two possibilities must be left for the future. It seems quite probable that both M and the cross section may be fairly large. The effective cross section for quenching by methane[3] is very much smaller than that found for germane as would be expected.

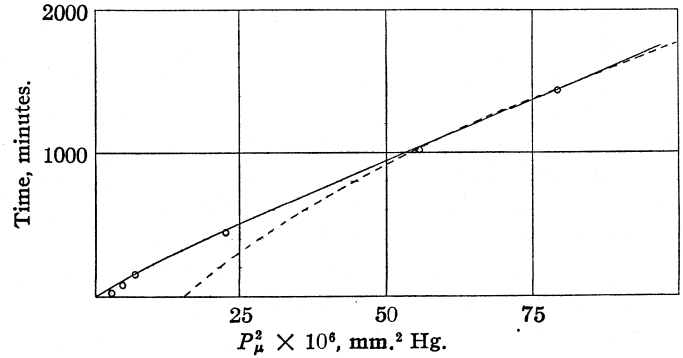

Fig. 4.—Solid curve is theoretical curve based on two methods of inhibition; lower curve assumes inhibition due to quenching only.

(b) Ammonia.—From the data of Zemansky[11] accurate values of the effective cross sections for quenching of ammonia, nitrogen and hydrogen are known. It should be possible to derive an equation for the rate of the sensitized decomposition of ammonia based on the assumption that the inhibiting effect of the hydrogen is due solely to its effectiveness in quenching the fluorescence of mercury. Using earlier and less satisfactory data on the quenching of fluorescence than now exist, Mitchell and Dickinson[12] have shown that hydrogen exhibits a larger inhibiting effect than could be accounted for by this mechanism. The equation derived in this manner is identical with equation (6) for germane. If the reaction $2NH_3 = N_2 + 3H_2$, which was found by Mitchell and Dickinson for the sensitized reaction[13] and by Wiig and Kistiakowsky for the unsensitized reaction, is assumed the equation may be integrated. Results of this type of equation are shown in Figure 4, in which the pressure of the gas uncondensed by

[12] Mitchell and Dickinson, THIS JOURNAL, **49**, 1478 (1927).

[13] Other workers have reported a higher percentage of hydrogen in the resulting gases than could be accounted for by this equation.

liquid air is plotted against the time. The dashed line is the theoretical curve for the equation analogous to equation (6). It was fitted arbitrarily to the two points shown in order to calculate a quantity proportional to the intensity.

It seems necessary to conclude, with Mitchell and Dickinson, that hydrogen exerts at least two inhibiting actions. Wiig and Kistiakowsky[6] have examined the entire question of the mechanism of this reaction. We do not feel justified, on the basis of the present experiments, in amplifying their discussion. It may be pointed out, however, that a satisfactory rate equation may be based on the following assumptions: (1) excited mercury atoms may lose their energy by collision with either ammonia or hydrogen molecules or by fluorescence; (2) the ammonia molecules are dissociated by collision with excited mercury; (3) one of the fragments produced may react either with ammonia to yield largely the final decomposition products (perhaps by a series of rapid steps) or with hydrogen to regenerate ammonia; (4) hydrogen atoms do not react with ammonia, but do combine with each other either by triple collision or on the walls. This mechanism leads to an equation of the type

$$-dt/dP_N = K_1 + K_2P_1/P_N + K_3/P_N + K_4P_1/P_N^2 \qquad (8)$$

where P_1 is the initial pressure of the ammonia and P_N is the pressure at time t. K_1, K_2, K_3 and K_4 are complex constants which are all inversely proportional to the light intensity. If the early stages of a run only are considered so that $\log (P_1/P_N)$ may be replaced by $(P_1/P_N - 1)$, equation (8) upon integration and collection of terms becomes

$$^1/_4K_1P_u^2 - P_u(A + t/2) + tP_1 = 0 \qquad (9)$$

where $2A = K_1P_1 + K_2P_1 + K_3 + K_4$ and P_u is the pressure of the gas uncondensed by liquid air. Having determined K_1 and A for any one run, it should be possible to fit this equation to any other run by using one point to calculate a coefficient depending on the light intensity by which both K_1 and A must be multiplied. For a complete solution of the equation the dependence of A on initial pressure must be determined, although the runs herein described were carried out mostly at approximately the same initial pressure. In Fig. 4 the solid curve is the theoretical curve for equation (9), the ratio between A and K_1 having been determined in an entirely different run.

Further details concerning the mechanism of the sensitized decomposition of ammonia would not seem to be of value at this point since from the method of deriving equation (8) several different steps might be postulated. In particular different behaviors for 2^3P_1 and 2^3P_0 mercury atoms may be postulated and a suitable equation derived. The temperature coefficient of this reaction seems to be exceedingly low. Several experiments were carried out at temperatures around 400° and in all

cases the rate of increase of pressure of gas uncondensed by liquid air was within the experimental error of that obtained at room temperature.

It may be possible, therefore, that the sensitized reaction has a different mechanism from that of the unsensitized reaction. Since molecules are known which show more than one predissociation region for a given band system,[14] there is no *a priori* reason for believing that dissociation always takes place after absorption of radiation in the predissociation region. Whether the probability of dissociation could be quite low if the predissociation bands are very diffuse is a question which cannot be answered unambiguously at present for molecules even as complex as those of ammonia, but one should expect at least a variation of quantum efficiency with wave length if this is the case. Wiig and Kistiakowsky[6] found no variation greater than the experimental error between 1962 and 2144 Å. We wish to emphasize merely, in agreement with these authors, that neither the direct nor the sensitized reaction is as yet completely understood. In particular, derivations of satisfactory rate equations for the latter may be based on several different mechanisms and there is as yet very little definite reason for preferring any single one.

Summary

1. Germane shows no absorption bands between 2100 and 7000 Å. Radiation transmitted by thin layers of quartz will, however, cause photochemical decomposition of this gas.

2. Both the sensitized and unsensitized photochemical decompositions of germane lead largely to the reaction $GeH_4 = Ge + 2H_2$. Part of the hydrogen does not appear in the gas phase and is probably removed by adsorption. The removal of one hydrogen atom from germane seems to be followed by a series of steps too rapid to be decisive in determining the rate.

3. Brief remarks on the sensitized decomposition of ammonia have been made. While a satisfactory rate equation may be obtained, it is not possible to choose unambiguously a definite mechanism for this reaction.

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[14] Christy and Naude, *Phys. Rev.*, **37**, 903 (1931).

[Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 321]

STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS. II. THE SEPARATION BY MEANS OF SODIUM HYDROXIDE AND SODIUM PEROXIDE

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Introduction.—As stated in the first paper of this series, the data here presented were collected during the course of an attempt to develop a system of qualitative analysis for the so-called common elements which would provide more quantitative information than that usually obtained.

The use of sodium hydroxide and sodium peroxide as a group reagent in a qualitative system seems to have been first suggested by Parr,[1] who used it to effect the separation of iron, manganese, nickel and cobalt from aluminum, chromium and zinc and it was later adopted by Noyes, Bray and Spear[2] in their system which included many of the less common elements. The process has also been used extensively in qualitative systems, and in quantitative methods for the separation of the individual elements of one of these groups from those of the other. Frequently in quantitative methods other oxidizing agents, such as bromine, chlorine or persulfate, are substituted for the peroxide but these are not as convenient as the peroxide or may introduce objectionable ions into the analysis.

Statements in the literature as to the effectiveness of these individual separations are somewhat incomplete and often not definite. Noyes, Bray and Spear state that: "The separation of the two groups by this process is entirely satisfactory, at any rate, from the standpoint of qualitative analysis, with the single exception that when 5 or 10 mg. of zinc are present this may be carried down completely when elements of the iron group (especially manganese) are present in large quantity." However, there appears to be a certain amount of distrust of the method which is perhaps explained by the statement of Hillebrand and Lundell:[3] "The use of sodium hydroxide for precipitations has not been in good repute among analysts because of the uncertain quality of the reagent and the slimy character of the solution and precipitate." It is explained, however, that the first objection is not as well founded today as in the past, that the difficulty in filtering about 5% solutions is not serious, and that: "In the hands of one of us (L.) the method has proved very satisfactory."

The confirmatory experiments and test analyses of Noyes, Bray and

[1] Parr, This Journal, **19**, 341 (1897).

[2] Noyes, Bray and Spear, *ibid.*, **30**, 484 (1908).

[3] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., 1929, p. 76.

Spear give quite complete information as to the qualitative value of the separation, as they perform it, in the detection of small amounts of an element in the presence of even large amounts of others; however, very meager systematic data seem to be available showing the completeness of the individual separations when considerable amounts of each element are present. Such data have been collected and are presented in this paper.

This study has been restricted to the common elements which may be found in the ammonium sulfide precipitate and therefore includes only the separation of iron, manganese, nickel and cobalt from aluminum, chromium and zinc. For more general statements concerning certain of the individual separations, as well as for references to the original literature, one is referred to Hillebrand and Lundell[3] and to Rüdisüle.[4]

Experimental Procedure

The separations have been carried out according to two general procedures. The first of these, called Procedure I, conforms closely to that given by A. A. Noyes[5] and by Noyes and Bray,[6] and more nearly represents the usual qualitative technique. It was as follows.

To a solution of the elements to be separated, containing 1–2 ml. of 6 *N* hydrochloric acid and having a volume of 30–40 ml., was added 6 *N* sodium hydroxide until the solution was alkaline to litmus, and then 5 g. of sodium peroxide. The sodium peroxide was sprinkled in very gradually and the mixture kept cold during the addition. Then the mixture was boiled until the sodium peroxide was decomposed, diluted to 60 ml. and filtered through hardened filters; in order to facilitate washing, two separate filters were used if the precipitate was bulky. The precipitate was washed with hot water until the washings no longer turned red litmus blue.

In Procedure II certain modifications were used which are recommended as giving more quantitative separations. It was as follows.

To a solution of the elements to be separated, containing 1–2 ml. of 6 *N* hydrochloric acid and having a volume of 15–20 ml., 6 *N* sodium hydroxide was added dropwise until the first permanent turbidity was produced. To this was added 20 ml. of 3% hydrogen peroxide and the resulting solution poured dropwise into 100 ml. of 5% sodium hydroxide which was kept just boiling during this addition. The mixture was then cooled and kept cool during the slow addition of 5 g. of sodium peroxide. Finally the mixture was boiled until the sodium peroxide was decomposed and then filtered, two separate papers being used in most cases. Hardened filters were not necessary in filtering these solutions. The precipitate was washed with 50 ml. of hot 5% sodium hydroxide and then with a hot 1% solution until no test for the soluble element being separated was obtained.

The slightly acid solution containing the hydrogen peroxide was poured into the hot sodium hydroxide solution since there appears to be general agreement that a better

[4] Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Max Drechsel, Bern.

[5] Noyes, "Qualitative Chemical Analysis," The Macmillan Company, New York, 1922, 9th ed., p. 95.

[6] Noyes and Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, 1927, pp. 164, 168.

separation results from this order of mixing.[7] Qualitative experiments also indicated that a more rapid and complete oxidation of chromium was obtained when hydrogen peroxide was present in the acid solution; when sodium peroxide was added to an alkaline solution, as in Procedure I, or upon adding an acid solution without peroxide to a hot sodium hydroxide solution, a precipitate which oxidized slowly was obtained. The acid solution could be added to a cold sodium peroxide solution; however, the preparation of a solution of sodium peroxide, even when it is kept cold, results in excessive loss of peroxide due to its decomposition. Furthermore, the precipitate produced upon addition of the acid solution to the hot hydroxide seemed more readily handled than that formed by precipitating in the cold and then heating.

In most of the experiments 250 mg. of the element to be precipitated was taken with 250 mg. of one of the soluble elements. The precipitate was then analyzed in order to determine the amount of the soluble element carried down. The results of these experiments, showing the amount of the soluble element carried down in each case, have been collected in Table I which is shown below. Observations and variations from the procedure outlined above are contained in the notes to the table. For the reason stated in the first paper of this series,[8] it is felt that significance should be given to the general magnitude, rather than the exact value, obtained in any individual experiment.

Methods of Analyzing the Precipitates.—The general methods used in analyzing the precipitates are here described. Changes or modifications in individual experiments are given in the notes which follow Table I.

The precipitates were in all cases dissolved in hot hydrochloric acid, sodium sulfite or hydrogen peroxide being used to help dissolve the manganese and cobalt precipitates.

The aluminum was recovered from the solution of the manganese precipitates by carefully neutralizing the boiling solution with ammonium hydroxide, avoiding an excess. The amount of aluminum in the precipitate thus obtained was estimated by comparing it with standard precipitates prepared under strictly similar conditions. The chromium in the manganese precipitate was recovered from the reduced hydrochloric acid solution by careful neutralization with ammonium hydroxide. The chromium hydroxide precipitate was dissolved and treated with sodium peroxide; any manganese dioxide present was filtered out and the chromate in the filtrate determined iodometrically. Zinc was recovered from the hydrochloric acid solution by fuming it with sulfuric acid, carefully neutralizing it, adding the proper excess of sulfuric acid and precipitating the zinc as sulfide. The precipitate was washed and introduced into an excess of ferric sulfate solution. The ferrous iron thus produced was titrated with standard permanganate solution.

After dissolving the ferric hydroxide precipitates in 6 *N* hydrochloric acid, the iron was removed by extraction with ether. The elements remaining in the aqueous solution were then estimated as indicated above.

The aluminum was recovered from the solution of the cobalt precipitates by carefully neutralizing the boiling solution with ammonium hydroxide;

[7] Ref. 4, Vol. V, pp. 96, 900, 1105; Ref. 3. p. 77.

[8] THIS JOURNAL, 54, 2219 (1932).

the precipitate thus obtained was dissolved, reprecipitated and compared with standards. The chromium, after reduction, was precipitated with ammonium hydroxide; this precipitate was dissolved and treated with sodium peroxide to remove the co-precipitated cobalt and to oxidize the chromium; after filtering out the cobalt oxide, the chromium was determined iodometrically. The zinc was recovered by precipitation as sulfide from a sulfuric acid solution. This precipitate was dissolved and treated with sodium peroxide to remove the co-precipitated cobalt. The zinc was again precipitated as the sulfide and determined as indicated above.

The aluminum in the hydrochloric acid solution of the nickel precipitates was recovered by carefully neutralizing with ammonium hydroxide; the aluminum hydroxide precipitate thus obtained was treated with sodium hydroxide and potassium persulfate to remove the nickel carried down, a final precipitation of the aluminum with ammonium hydroxide made, and this precipitate compared with standards. The chromium and zinc were recovered by the methods used in analyzing the solution containing cobalt.

TABLE I

THE SEPARATION OF MANGANESE, IRON, COBALT AND NICKEL FROM ALUMINUM, CHROMIUM AND ZINC BY PRECIPITATION WITH SODIUM HYDROXIDE AND PEROXIDE

In these experiments 250 mg. of one of the elements in the first column was precipitated from a solution containing 250 mg. of one of the elements listed at the top of one of the three major columns.

Element precipitated 250 mg. taken	Aluminum, 250 mg. taken Al found in ppt., mg.				Chromium, 250 mg. taken Cr found in ppt., mg.				Zinc, 250 mg. taken Zn found in ppt., mg.			
	Expt.	Method		Notes	Expt.	Method		Notes	Expt.	Method		Notes
Manganese	1	I	12–15	1, 2	3	I	50–70	3	29	I	65	6
	2	II	2–3		4	II	51	4, 5	5	II	60	6
					25	I	7	10				
Iron (ferric)	6	I	1–2	1, 2					9	I	103	7
	7	II	1–2		8	II	56		10	II	37	6
					24	I	37		32	II	47	
					24	I	0.2	10	33	II	46	
									34		67	11
									35		62	11
Cobalt	28	I	20–25		12	I	65–80	8	30	I	50	6
	11	II	12–15		13	I	65		16	II	88	6
					14	I	87	9				
					15	II	21					
					23	II	1	10				
Nickel	17	I	30–35		27	I	44		31	I	30	6
	18	II	30–40		19	II	42		21	II	25	
					22	II	0.5–1	10				

NOTES TO TABLE I

1. Only 125 mg. of aluminum was taken.

2. The aluminum was recovered from the precipitate by dissolving it in hydrochloric acid, repeating the sodium hydroxide–sodium peroxide treatment, acidifying this filtrate, making it just alkaline with ammonium hydroxide and comparing the aluminum hydroxide precipitate obtained with standards.

3. The chromium was recovered from the precipitate by dissolving it in hydro-

chloric acid, repeating the sodium hydroxide–sodium peroxide treatment, making this filtrate just acid with acetic acid and precipitating the chromate as lead chromate. The precipitate was matched with standards. Method uncertain due to retention of chromium in second precipitate and to uncertainty in matching the size of the precipitate of lead chromate.

4. The color of the solution indicated that the chromium was completely oxidized upon pouring the acid solution containing hydrogen peroxide into the sodium hydroxide.

5. Difficulty was had in washing the precipitate free of chromate.

6. Only 160 mg. of zinc was taken.

7. The zinc was estimated by precipitation as carbonate, dissolving this in an excess of standard acid and titrating back with standard base.

8. The chromium was estimated by repeating the sodium hydroxide–sodium peroxide treatment, precipitating the chromium in the second filtrate as lead chromate and matching the precipitate. See note 3.

9. The hydrochloric acid solution of the precipitate was evaporated, a large excess of 16 *N* nitric acid added, 4 g. of potassium chlorate slowly sprinkled in, and the solution boiled until the excess chlorate appeared to be decomposed. The solution was made alkaline with ammonium hydroxide, then just acid with acetic acid, and the chromate precipitated as lead chromate. This was filtered out, dissolved in hydrochloric acid and the chromate determined iodometrically.

10. The chromium was taken as potassium chromate and no hydrogen peroxide was added to the acid solution, otherwise a duplication of Expt. 19.

11. Duplicates of Expts. 32 and 33, except that the sodium hydroxide was added to the acid solution instead of the reverse order.

Discussion of the Data of Table I.—From the cases studied it would seem that, in general, the separations obtained by the two procedures are not strikingly different. To test the effectiveness of the method of adding the acid solution to the sodium hydroxide, Expts. 32–35 were carried out by Mr. Elvin Lien and Mr. James Radford. In all of these the conditions of Procedure II were duplicated, except that in Expts. 34 and 35 the 5% sodium hydroxide was added to the acid solution containing the hydrogen peroxide; this resulted in a definite increase in the zinc carried out. Where better separations are obtained by Procedure I, it seems probable that the higher concentration of sodium hydroxide at first obtained in that procedure is the deciding factor. It has been found in practice, however, that the results obtained in repeating the same separation by Procedure I vary more than do those by Procedure II.

More specifically, the separation of aluminum from manganese and iron can be made sufficiently complete for qualitative and for most quantitative work; with the amounts of each element here used, from 4 to 5% of the aluminum is left with the cobalt precipitate and from 12–14% with the nickel precipitate; this latter difficulty is generally recognized.[9,10]

The separation of chromium, beginning with chromic ion and using sodium peroxide as the oxidizing agent, is unsatisfactory in every case

[9] Ref. 4, Vol. V, p. 242.

[10] Ref. 3, pp. 77, 391.

regardless of method. That this is due to incomplete oxidation of the chromium by the peroxide is shown by Expts. 20–23, where, beginning with the chromium as chromate, satisfactory separations are obtained except in the case of manganese and there the co-precipitation is reduced from 20% to about 3%. We are indebted to Mr. Harrison Backus for the following experiments showing that only trivalent chromium is co-precipitated.

To 250 mg. of chromium and 250 mg. of nickel, as the chlorides, in 50 ml. of a solution containing 4 ml. of 6 *N* hydrochloric acid, was added 6 *N* sodium hydroxide until the first turbidity appeared, then 10 ml. of 3% hydrogen peroxide; this was slowly poured into a cold solution of 20 ml. of 6 *N* sodium hydroxide and 10 ml. of 3 *N* sodium carbonate to which had been added 1 g. of sodium peroxide. An additional gram of sodium peroxide was added during the mixing of the solution, then 3 g. more was slowly sprinkled in; finally, the mixture was boiled for three minutes after no more oxygen bubbles seemed to be evolved.

The precipitate was filtered out, washed thoroughly with hot water, dissolved in sulfuric acid and this solution made alkaline with ammonia; a precipitate of chromium hydroxide was obtained which was estimated to contain about 50 mg. of chromium. No test for chromate could be obtained in the solution. Further experiments showed that under the conditions of the above experiment chromium, when *alone*, was completely oxidized—the oxidation was slow in a cold solution, but proceeded rapidly when the mixture was heated. Also, it was found that when chromate was added to a nickel precipitate produced by sodium peroxide under the conditions of this experiment and this mixture then acidified with sulfuric acid, less than one milligram of the chromium was reduced, thus showing that the reduced chromium originally obtained could not have been due to peroxide held by the nickel precipitate. The adsorption of colloidal hydrous chromic oxide by precipitates of iron, manganese, cobalt and nickel frequently has been noted,[11] and it would be expected that the chromium thus held would be oxidized with difficulty. It is therefore recommended that chromium be oxidized to chromate in an acid solution before using the sodium hydroxide–sodium peroxide separation.

There is considerable evidence that alkaline solutions of chromate may be reduced by filter paper,[12,13,14] the effect apparently being dependent upon the quality of the paper, the temperature of the solution and the time of contact. To note the extent of this effect experiments were carried out by Mr. Backus in which solutions containing 250 mg. of chromium as chromate in 15 ml. of 4 *N* sodium hydroxide were heated to boiling and then filtered through four different types of paper filters—two qualitative papers of different price, a quantitative paper and a hardened paper. The solutions were kept hot and the rate of flow restricted so that the filtrations required from 6 to 10 minutes. There was no apparent color change of the solutions on the filters or in the filtrates. The filtrates were then acidified with sulfuric acid. There was produced in the filtrate from the cheaper qualitative paper a considerable precipitate of what appeared to be paper pulp; the filtrate from the other qualitative paper became slightly cloudy, while the other filtrates remained quite clear. The acid solutions were filtered and then made just alkaline with ammonium hydroxide. None of the solutions produced an observable precipitate. This indicates that the reduction of an alkaline chromate

[11] Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, p. 90.

[12] Jervis, *Chem. News*, **77**, 133 (1898).

[13] Allison, *ibid.*, **96**, 1 (1907).

[14] Mellor, "A Treatise on Quantitative Inorganic Analysis," Griffin, London, p. 477.

solution by filtration through paper filters is so small as to be inappreciable in its effect on qualitative or most quantitative separations.

The separation of zinc from the elements precipitated by sodium hydroxide is unsatisfatory in every case studied, from 10–50% of the zinc remaining in the precipitate.

Summary

An experimental study of the separation of manganese, iron, cobalt and nickel from aluminum, chromium and zinc by means of sodium hydroxide and sodium peroxide has been made.

With 250 mg. of each element present, from 1–3 mg. of aluminum remains with the manganese or the iron, from 12–15 mg. with the cobalt, and 30–40 mg. with the nickel.

The separation of trivalent chromium from these elements is unsatisfactory due to incomplete oxidation of the chromium. When the chromium is originally present as chromate, not over 1 mg. is carried down by any of the precipitates except manganese, where 7 mg. was co-precipitated.

The separation of zinc is unsatisfactory, from 10–40% of it being carried down with the precipitates.

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STUDIES OF VARIOUS METHODS FOR THE SEPARATION OF THE COMMON ELEMENTS INTO GROUPS. III. A NEW METHOD FOR THE SEPARATION OF ZINC, COBALT, NICKEL AND IRON FROM ALUMINUM, CHROMIUM AND MANGANESE

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Introduction

The two methods most frequently used in systems of qualitative analysis for dividing into sub-groups the elements found in the ammonium sulfide precipitate are: (1) the ammonium hydroxide precipitation, and (2) the sodium hydroxide–sodium peroxide treatment. The results of studies of these separations have been presented in the two preceding papers of this series,[1] and the data show that many of the individual separations obtained by either of these methods are so incomplete as to make their use unsatisfactory in a qualitative system in which it was desired to stress the quantitative information that could be obtained. Accordingly, other methods for separating these elements into groups were investigated.

[1] (a) Swift and Barton, THIS JOURNAL, 54, 2219 (1932); (b) Swift and Barton, *ibid.*, 54, 4155 (1932).

It had been found by Mr. F. N. Laird[2] that the well-known precipitation by ammonium sulfide from an ammonium tartrate solution provided exceptionally fine separations of iron and zinc from aluminum and chromium and later experiments showed that the separation of cobalt from either aluminum or chromium was equally satisfactory—these being separations which are surprisingly imperfect by either the ammonium hydroxide or sodium hydroxide–peroxide methods. However, there seems to be some uncertainty as to the complete precipitation of manganese and nickel; and, in addition, the removal of the tartrate from the filtrate by fuming with sulfuric and nitric acids and the resolution of the anhydrous chromic sulfate which formed proved so tedious and time-consuming that the method was considered as undesirable.

It is known that oxalate tends to form complex compounds with all of these elements and many of these compounds have been studied.[3] Very stable ions of the type $=M(C_2O_4)_3$ are formed with aluminum[4] and chromium[5] (as well as with ferric iron),[6] and ions, apparently somewhat less stable, of the type $=M(C_2O_4)_2$ are formed with manganese,[7] zinc,[8] nickel[9] and cobalt.[10] Although oxalate can be much more easily oxidized and removed from a solution, its use as a substitute for tartrate does not seem to have been adequately investigated. Carnot[11] states that the presence of a sufficient concentration of oxalate will prevent the precipitation of nickel by ammonium or sodium sulfide while under the same conditions cobalt is completely precipitated. It is also proposed that zinc be separated from nickel and cobalt by precipitation as sulfide from a weakly acid solution containing an excess of oxalate. No experimental data are given in support of the method and, as will be shown below, we have not been able to confirm the results reported.

Mr. Laird[2] had also found that moderate amounts of aluminum or chromium could be held in an ammoniacal solution if sufficient oxalate

[2] Laird, unpublished experiments carried out in this Laboratory.

[3] A review of these compounds with bibliographies will be found in Abegg and Auerbach, "Handbuch der anorganischen Chemie," S. Herzel, Leipzig, and in Gmelin-Kraut "Handbuch der anorganischen Chemie," Carl Winters, Heidelberg. Because of this only a few of the individual references will be given below.

[4] Plessy, *Compt. rend.*, **97**, 1033 (1887); Wahl, *Soc. Sci. Fennica, Commentations Phys.-Math.*, **4**, 1–9 (1927).

[5] Werner, *Ber.*, **45**, 865 (1912).

[6] Rieger, *Z. Electrochem.*, **7**, 871 (1901); Shäfer, *Z. anorg. Chem.*, **45**, 293 (1905); Scholz, *Wein. Monatsh.*, **29**, 439 (1908).

[7] Rüst, *Z. anal. Chem.*, **41**, 606 (1902); Hauser and Wirth, *J. prakt. Chem.*, [2] **79**, 358 (1909).

[8] Kunschert, *Z. anorg. Chem.*, **41**, 337 (1904).

[9] Rammelsberg, *Pogg. Ann.*, **95**, 198 (1855).

[10] Benedict, THIS JOURNAL, **28**, 171 (1906).

[11] Carnot, *Compt. rend.*, **166**, 329–333 (1918).

were present; however, it was later found that the precipitation of manganese as sulfide from such solutions was quite incomplete, as much as 50 mg. of manganese being present before a precipitate was obtained, also that in slightly acid solutions a precipitate of manganese oxalate was obtained. On neutralizing the solution with sodium hydrocarbonate, no precipitate of manganous oxalate formed when an excess of oxalate was present, and it was found possible to have even large amounts of manganese present without formation of a precipitate upon saturating the solution with hydrogen sulfide. These results seemed to warrant further investigation, and this paper presents experiments showing the results which may be obtained in precipitating zinc, nickel, cobalt and iron as sulfides from such solutions containing aluminum, chromium or manganese, and a study of some of the factors affecting these separations.

Experimental

Behavior of Manganese.—In order to study the conditions under which manganese could be kept in solution, the experiments recorded in Table I were performed. In these 70 millimoles of ammonium oxalate was added to a solution containing 30 millimoles of hydrochloric acid and the amount of manganese, as sulfate, shown in the second column. This amount of oxalate was found in preliminary experiments to

TABLE I

THE PRECIPITATION OF MANGANESE SULFIDE FROM HYDROCARBONATE SOLUTIONS CONTAINING OXALATE

Expt.	Manganese taken, mg.	Excess $NaHCO_3$ added, g.	Volume of solution, ml.	H_2S Treatment Time, min.	H_2S Treatment Temp., °C.	Mn precipitated as sulfide, mg.	Remarks
1	570	1	60	20	60–80	0	
2	570	2	60	45	60–80	182	No precipitate for 15 min.
3	570	3	60	45	60–80	250	No precipitate for 5 min.
4a	500	1	120	10	60–80	0	
4b	500	2*	120	15*	60–80	0	* 1 g. $NaHCO_3$ added to solution from 4a; treated with H_2S for 15 min. longer
4c	500	3*	120	10*	60–80	250	* 1 g. $NaHCO_3$ added to solution from 4b; treated with H_2S for 10 min. longer
5	500	1	120	30	70–90	0	After standing 4 days 11 mg. Mn had pptd.
6	500	2	120	30	70–90	0	Precipitate began to form slowly 10 min. after finish of H_2S treatment. After standing four days 133 mg. of Mn had precipitated
7	570	1	120	30	60–80	0	After standing 4 days 77 mg. Mn had pptd.
8	570	2	120	15	60–80	0	After 20 min. precipitate formed rapidly; after standing 4 days 130 mg. Mn had pptd.

TABLE I (*Concluded*)

Expt.	Manganese taken, mg.	Excess $NaHCO_3$ added, g.	Volume of solution, ml.	H_2S Treatment Time, min.	Temp., °C.	Mn precipitated as sulfide, mg.	Remarks
9	250	2	120	30	60–80	0	After standing 5 days 63 mg. Mn had pptd.
10	570	2	120	120	20	<1	93 mg. after standing 4 days
11	570	1	200	30	60–80	0	0.5 mg. after standing 2 days
12a	570	1	200	20	65	0	
12b	570	1	200	24 hrs.*	20	2–5	* Solution from (a) stood under pressure
12c	570	1	200	24 hrs.*	20	20	* Soln. from (b) stood with slow stream passing
12d	570	1	200	30*	60–70	51	Filtrate from (c). Very rapid stream of H_2S. Ppt. formed slowly
13	500	1	200	45	60–70	0	100 mg. pptd. after 5 days
14	570	2	200	30	60–80	0	57 mg. pptd. after 2 days
15a	570	2	200	20	60–70	0	
15b	570	2	200	24 hrs.*	20	0	* Solution from (a) stood under pressure
15c	570	2	200	24 hrs.*	20	15	* Soln. from (b) stood with slow stream passing
15d	570	2	200	30*	60–70	67	* Filtrate from (c), very rapid stream. Precipitate formed rapidly
16	500	2	200	20	60–70	1	Very rapid stream H_2S
				45	60–70	52	
17a	500	4	400	20	60–80	0	
17b	500	5*	400	10	60–80	Large ppt.	* 1 g. $NaHCO_3$ added to (a); treated with H_2S 10 min. longer

prevent the precipitation of even 500 milligrams of aluminum or chromium. The acid was nearly neutralized with ammonium hydroxide, solid sodium hydrocarbonate added in 0.1-g. portion until the solution was just neutral to litmus, and then the amount of sodium hydrocarbonate indicated in the third column of Table I was added in excess. It should be noted that 1 g. excess of the hydrocarbonate gives the solution a distinct alkaline reaction to litmus even after treatment with hydrogen sulfide. The solution was diluted to the volume indicated in the fourth column, then a rapid stream of hydrogen sulfide passed through it for the time indicated in the fifth column. The solution was maintained at the temperature shown in the sixth column. The amount of manganese in any precipitate obtained is given in the seventh column. The manganese was estimated by dissolving the sulfide precipitate with hydrochloric acid and reprecipitating the manganese as dioxide with sodium peroxide or by dissolving the sulfide precipitate with nitric acid and reprecipitating the manganese with chlorate; in either case the manganese dioxide precipitate was dissolved in an excess of potassium iodide and hydrochloric acid, and the iodine thus formed was titrated with standard thiosulfate solution.

Discussion of the Data of Table I.—It is seen from the data given that the precipitation of manganese sulfide from these solutions is dependent upon the excess of hydrocarbonate added, upon the volume of the solution, upon the time for which the hydrogen sulfide is passed, and, after this, upon the time for which the solution is allowed to stand. It is also apparent that with large quantities of manganese the separations attained may depend considerably upon maintaining a supersaturated solution. Other sulfide separations depending upon similar conditions are known. Thus the studies of Glixelli[12] and of Kolthoff and Pearson[13] show that the separation in acid solutions of the sulfides of the copper and tin group elements from zinc is due, at least in part, to the slow rate of precipitation of zinc sulfide. It would be expected that the precipitation of other sulfides from the solution would induce the precipitation of manganese sulfide. Although conclusive studies have not been made of this effect, it will be shown below that other sulfides can be precipitated and surprisingly sharp separations obtained from solutions which are probably supersaturated with respect to manganese sulfide; thus with 250 milligrams of each element present in a volume of 120–150 milliliters, the amount of manganese co-precipitated is insignificant even when the operations of precipitation and filtering extend over several hours.

A detailed study of the buffering action caused by the hydrocarbonate in these solutions has not been made. It is probable that on prolonged passage of hydrogen sulfide the carbon dioxide is quite completely swept out and the hydrocarbonate converted into hydrosulfide. Approximate calculations indicate that this conversion would result at no time in more than a two-fold change in the hydrogen-ion concentration of the solution; also that the sulfide-ion concentration would not be increased by more than about four-fold upon sweeping a solution, containing hydrocarbonate and saturated with both hydrogen sulfide and carbon dioxide, with hydrogen sulfide until the carbon dioxide has been removed and the hydrocarbonate converted into hydrosulfide.

The Precipitation of Zinc, Nickel, Cobalt and Iron as Sulfides from Oxalate Solutions.—Experiments showed that the precipitation of zinc from solutions having a volume of 120 ml. and containing 70 millimoles of ammonium oxalate and 30 millimoles of ammonium chloride was almost complete when the solution was just acid to litmus and that quantitative precipitation was obtained from neutral solutions. The zinc sulfide precipitated under these conditions was compact and readily filtered, while a precipitate from a solution containing an excess of 2 ml. of 6 *N* ammonium hydroxide was finely divided and difficult to filter.

[12] Glixelli, *Z. anorg. Chem.*, **55**, 297 (1907).

[13] Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

The precipitation of nickel from a slightly acid solution is quite incomplete and when the solution is just neutral to litmus the precipitate forms very slowly. However, from a solution containing 1 g. of sodium hydrocarbonate in excess the precipitation is fairly rapid, is complete, and, if the formation of disulfide is avoided, the precipitate is obtained in a coarse granular form that can be filtered and washed by decantation. The effect of the presence of disulfide is very pronounced. If ammonium sulfide containing only a small amount of disulfide is added or if during the treatment with hydrogen sulfide the solution is allowed to stand in contact with the air, the dark brownish colloidal solution, characteristic of nickel sulfide when it is precipitated by ammonium sulfide solution, is formed. This can be prevented by first boiling the solution to remove dissolved oxygen, then sweeping the flask with hydrogen sulfide and thereafter keeping a continuous flow of the gas through the mixture until precipitation is complete. Once formed this colloidal solution can sometimes be coagulated by very vigorous shaking of the stoppered flask or, this failing, by filtering out the coagulated portion of the precipitate, then making the filtrate distinctly acid to litmus, heating it almost to boiling and again shaking it. The precipitate thus coagulated, which usually contains less than 1 mg. of nickel, does not appreciably redissolve in the acid solution and can be readily filtered.

The precipitation of cobalt is complete, although slow, if the solution is made neutral to litmus with hydrocarbonate. With a 1-g. excess of sodium hydrocarbonate the precipitation is rapid and the precipitate is compact and easily filtered.

From 2 to 5 mg. of iron remain in a solution made neutral with hydrocarbonate. In solutions containing an excess of 1 g. of sodium hydrocarbonate the precipitate forms in a finely divided state and from 0.2–0.4 mg. may pass through the filter, giving the filtrate a greenish or even dark color. This is readily coagulated by shaking the solution, heating it, or passing in more hydrogen sulfide; with 2 g. of sodium hydrocarbonate precipitation is quite complete.

The Effect of Phosphate and of Alkaline Earth Elements.—Experiments showed that the presence of considerable phosphate caused manganese, but not aluminum or chromium, to precipitate. Alkaline earth elements would be more or less completely precipitated as oxalates. It is therefore necessary to remove phosphate and alkaline earth elements before applying this method as a general group separation.

Procedure for the Separation of the Zinc Group from the Aluminum Group.—From the above experiments it is indicated that from ammonium oxalate solutions containing a small concentration of sodium hydrocarbonate zinc, nickel, cobalt and iron (these elements will hereafter be designated the zinc group) can be precipitated as their sulfides and thus

separated from aluminum, chromium and manganese (these elements to be designated the aluminum group). Accordingly, two series of experiments were carried out to test the qualitative and quantitative value of this separation. The general procedure for these experiments was as follows.

To a solution containing 30 millimoles of hydrochloric acid and the elements to be separated in a volume of 100 ml., 6 *N* ammonium hydroxide was added until the solution was just acid to litmus or until any local precipitate which formed just redissolved. Ten grams (70 millimoles) of ammonium oxalate was added, the solution heated until the ammonium oxalate dissolved, cooled, and then solid sodium hydrocarbonate added, 0.1 g. at a time, until the solution was neutral to litmus, that is, turned both blue and red litmus to an intermediate purplish color. A rapid stream of hydrogen sulfide was passed through the solution for three to five minutes, then, while a slow stream of the gas was kept flowing, the mixture heated to 60–80°. The solution was tested with litmus (preferably without interrupting the flow of gas) and, if it had become acid, again neutralized with sodium hydrocarbonate, an excess of exactly 1.0 g. of the solid added, and hydrogen sulfide again passed through the solution for three to five minutes. This process was repeated until the solution remained slightly alkaline to litmus. In no case were more than three one-gram portions of the sodium hydrocarbonate required. It was found that when iron was present, or when nickel was present and disulfide had been allowed to form, the coagulation of the precipitate was facilitated by tightly closing the flask with a rubber stopper and vigorously shaking the hot mixture. The mixture was filtered immediately through a paper filter and the precipitate washed with a hot solution made by dissolving 1 g. of ammonium oxalate in 100 ml. of hot water and saturating it with hydrogen sulfide. When washing precipitates of iron sulfide it was found advantageous to add 0.5 g. of sodium hydrocarbonate to this wash solution before treating it with hydrogen sulfide.

The results of the qualitative tests obtained have been collected in Table II. In the experiments shown in that table an excess of one gram of sodium hydrocarbonate was provided in all of the experiments; where a large precipitate formed, it was necessary to add two or three one-gram portions. However, it is to be noted that there was never more than 1 g. of sodium hydrocarbonate in excess at any one time. Completeness of precipitation was tested for by adding more sodium hydrocarbonate and again treating the solution with hydrogen sulfide for a considerable length of time. The aluminum group elements in the filtrates were detected by evaporating it to a small volume, adding an excess of concentrated nitric acid, repeating the evaporation, then adding solid potassium chlorate and nitric acid until the oxalate was completely decomposed and any manganese precipitated

as the dioxide. This was filtered out and the filtrate made just alkaline with ammonia in order to precipitate the aluminum. The filtrate from this precipitate was made just acid with acetic acid and tested for chromium by addition of lead acetate. The zinc group precipitates were dissolved in hydrochloric and nitric acids, and the solutions made just alkaline with ammonia to precipitate the iron. An excess of sodium hydroxide was added to this filtrate, the ammonia boiled out, then sodium peroxide added and the mixture boiled until the peroxide was decomposed. The nickel and cobalt oxides were filtered out and hydrogen sulfide passed

TABLE II

THE QUALITATIVE SEPARATION OF THE ZINC GROUP FROM THE ALUMINUM GROUP

The solution contained 70 millimoles of oxalate, and an excess of approximately 1 g. of sodium hydrocarbonate was maintained.

Expt.	Elements taken, mg.	Elements found: Precipitate	Elements found: Filtrate	Notes
1	Zn 500	Zn		
	Al 1		Al	
	Cr 1		Cr	
	Mn 1		Mn	
2	Ni 500	Ni		No Ni found in filtrate
	Al 1		Al	Precipitate coagulated; easily filtered
	Cr 1		Cr	
	Mn 1		Mn	
3	Co 500	Co		
	Al 1		Al	
	Cr 1		Cr	
	Mn 1		Mn	
4	Fe* 500	Fe	Fe†	* Taken as $FeCl_3$; reduced by H_2S in slightly
	Al 1		Al	acid solution
	Cr 1		Cr	† 0.1 mg. Fe found in filtrate
	Mn 1		Mn	
5	Zn 1	Zn		No Al found in precipitate
	Ni 1	Ni		
	Co 1	Co	*	* Filtrate not analyzed
	Fe 1	Fe		
	Al 500			
6	Zn 1	Zn		No Cr found in precipitate
	Ni 1	Ni		† About 0.5 mg. Fe found
	Co 1	Co	*	* Filtrate not analyzed
	Fe 1	Fe†		
	Cr 500			
7	Zn 1	Zn		
	Ni 1	Ni		
	Co 1	Co		
	Fe 1	Fe		
	Mn 500	Mn*		* 5–6 mg. Mn found in precipitate

into the filtrate to test it for zinc. The sodium peroxide precipitate was dissolved in hydrochloric acid, the solution divided into equal portions and the cobaltinitrite test made for cobalt in one portion and the dimethylglyoxime test for nickel made on the other. Unless otherwise stated in the notes, the tests obtained indicated that no considerable fraction of the element had been lost in the separation.

The Quantitative Separation of the Elements of the Zinc and Aluminum Groups.—In order to ascertain the quantitative value of this method, especially when large amounts of each of the elements to be separated were present, the experiments collected in Table III were performed. The procedure was essentially that used in carrying out the qualitative experiments, except that varying amounts of ammonium oxalate and of the excess of hydrocarbonate were used; these are given in the third and fourth columns of the table. Other departures or variations are included in the column headed Remarks or in the Notes.

In each of these experiments 250 mg. of an element of the zinc group and 250 mg. of an element of the aluminum group were taken. The precipitate obtained was then analyzed to determine the amount of the soluble element which had been carried down; the results of these analyses are shown in the sixth column.

Methods of Analyzing the Precipitates.—As the amount of the aluminum group element found in the precipitate was in all cases small, these quantities were estimated by a comparison with a known quantity of that element after treating it by a similar process. When a negative test for one of these elements was obtained in a solution, the latter was then divided into equal portions and one milligram or less of the element being tested for added to one portion and the test then repeated. Care was taken always to ensure that any oxalate remaining in the sulfide precipitates was completely decomposed before applying the tests indicated below. The individual methods used are briefly outlined. The precipitates were usually dissolved in nitric acid containing potassium chlorate in order to destroy any oxalate present. Aluminum was precipitated from the acid solutions by very careful neutralization with ammonia. Iron, when present, was previously separated by two precipitations with sodium hydroxide. Blanks were made on the reagents used. Chromium was oxidized in the nitric acid solution by means of the potassium chlorate. This solution was neutralized with ammonia, made just acid with acetic acid and lead acetate added. Manganese was precipitated as dioxide by potassium chlorate or, more usually, the nitric acid solution treated with a large excess of sodium bismuthate.

The filtrates were tested for completeness of precipitation and the amount of the zinc group element found indicated under the column of remarks.

TABLE III

THE QUANTITATIVE SEPARATION OF THE ELEMENTS OF THE ZINC AND ALUMINUM GROUPS

Expt.	Elements taken (250 mg. of each)		Oxalate added (millimoles)	Excess of $NaHCO_3$ added, g.	Final volume, ml.	Found in precipitate, mg.		Remarks
1	Zn	Al	70	0[1]	120	Al	1	Precipitation started in an acid solution
2	Zn	Al	30	Note 2	100	Al	5	Precipitate difficult to filter and wash
3	Zn	Al	70	1[4]	130	Al	0.4–0.6	See note 3
4	Zn	Cr	57	0	120	Cr	0	
5	Zn	Mn	30	0	100	Mn	2	
6	Zn	Mn	70	2	400	Mn	0.5	
7	Zn	Mn	70	1	130	Mn	1[6]	Note 3
8	Ni	Al	57	1	125	Al	0	Ppt. slightly colloidal
9	Ni	Al	70	1	130	Al	0.8–1	Note 3
10	Ni	Cr	70	1	100	Cr	0	
11	Ni	Cr	70	1	130	Cr	0.1–0.6	Note 3
12	Ni	Mn	35	0	70	Mn	1	Ppt. colloidal, coagulated by shaking
13	Ni	Mn	70	1	130	Mn	0–0.2	Note 3
14	Co	Al	30	0	100	Al	0	Precipitate coagulated rapidly
15	Co	Al	70	1	130	Al	1–2	Note 3
16	Co	Cr	70	0	90	Cr	0.1	
17	Co	Cr	70	1	130	Cr	0	Note 3
18	Co	Mn	30	0	80	Mn	0	
19	Co	Mn	70	1	130	Mn	0.2–0.5	Note 3
20	Fe[5]	Al	70	1	100	Al	0.2	0.5 mg. Fe found in filtrate
21	Fe	Al	70	1	130	Al	1–2	Note 3
22	Fe[5]	Cr	70	1	120	Cr	0	0.3 mg. Fe found in filtrate
23	Fe	Cr	70	1	130	Cr	0–0.2	Note 3. 0.1–0.2 mg. Fe in filtrate
24	Fe[5]	Mn	70	1	100	Mn	2	No Fe found in filtrate
25	Fe	Mn	70	2	400	Mn	0	No Fe found in filtrate
26	Fe	Mn	70	1	130	Mn	0.3–0.4	Note 3. Filtrate stood 3 days; no MnS formed

NOTES

1. Where this value is zero the solution was made neutral to litmus with sodium hydrocarbonate, then tested during the precipitation and, if acid, again made just neutral by addition of sodium hydrocarbonate.

2. Two ml. of 6 *N* ammonium hydroxide was added in excess; no sodium hydrocarbonate.

3. Part of a group of experiments performed by a section of sophomore students in analytical chemistry. The procedure was provided in typed form and the separation carried out independently by the student. The sodium hydrocarbonate was added as a one formal solution; because of this the final volumes are somewhat uncertain. In most

cases the range in values for the amount of the aluminum group element found in the precipitate is that obtained from several experiments.

4. The solution was tested during precipitation, made neutral if acid, and a 1-g. excess of sodium hydrocarbonate added. This process was repeated until the solution remained neutral or, usually, slightly alkaline.

5. The iron was taken as ferric chloride and this reduced by hydrogen sulfide while the solution was slightly acid.

6. In an experiment in which the zinc sulfide precipitate was allowed to stand for three days before it was filtered 10 mg. of manganese was found in the precipitate.

Discussion.—An inspection of the data collected in Tables II and III shows that by this method of separation 1 mg. of any element of either group can be detected in the presence of even 500 mg. of any element of the other group. Also, by properly adjusting the conditions, less than 1 mg. of any element of either group will be carried into the other group even when large amounts of both are present.

The precipitates of the zinc group sulfides are usually quickly coagulated and much more readily filtered and washed than those obtained by the conventional ammonium sulfide precipitation, in fact, in most cases washing by decantation can be used. Experiment 2, Table III, shows that, even with oxalate present, if an excess of ammonium hydroxide is used, the zinc sulfide is difficult to handle. Iron, of the zinc group sulfides, shows the greatest tendency to pass into the filtrate. Unless a one-gram excess of the hydrocarbonate is present, this tendency is pronounced; with that excess the amount lost can be made negligible. The coagulation of the iron sulfide is slow and unless time is given for this the filtrate will appear dark colored. Experiments have shown that the original valence state of the iron has no apparent effect on the completeness of the precipitation. In Expts. 20, 22 and 24 the iron was reduced before neutralizing or adding oxalate, in Expts. 21, 22, 25 and 26 this treatment was omitted. Contrary to expectation manganese was not carried down in large amounts even when filtration of the zinc group sulfide was delayed or when the filtrate was allowed to stand for several days. This is probably due to the final concentration of hydrocarbonate being somewhat less than that indicated because of the formation of acid during precipitation of the zinc group sulfide. However, it is recommended that, where large amounts of manganese are probable, the sodium hydrocarbonate be limited to an excess of not more than 1 g. and the volume of the solution be increased to from 200–400 milliliters.

Summary

It has been found that zinc, nickel, cobalt and iron can be separated from aluminum, chromium and manganese by precipitation with hydrogen sulfide from a solution having a controlled excess of sodium hydro-

carbonate and sufficient oxalate to prevent the precipitation of the aluminum or chromium.

The behavior of these individual elements has been studied and the method is proposed for the qualitative separation of these elements into two groups, to be designated the Zinc Group and the Aluminum Group, respectively.

Experiments have shown that by this method 1 mg. of any element of one group can be separated from as much as 500 mg. of any element of the other group.

As a quantitative method it has been shown that 250 mg. of any element of the zinc group can be precipitated quantitatively from a solution containing 250 mg. of any element of the aluminum group and that less than 1 mg. of any element of the aluminum group will be carried out in the precipitate.

The sulfide precipitates obtained under these conditions are readily coagulated, filtered and washed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE MECHANISM OF HYDROLYSIS OF DIALKYLAMINOMETHYL ETHERS

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The aminomethyl ethers have been prepared by a modification of the method of McLeod and Robinson.[1]

$$CH_2O + ROH + R_2NH \xrightarrow{K_2CO_3} R_2N{-}CH_2{-}OR + H_2O \quad (1)$$

They are very rapidly hydrolyzed in dilute aqueous acid at room temperature, so that merely dissolving the ether in one equivalent or more of acid usually produces the reaction

$$R_2N{-}CH_2{-}OR + H^+ + H_2O \rightleftharpoons R_2NH_2^+ + CH_2O + ROH \quad (2)$$

Possible successive steps in the hydrolysis reaction may be represented as

$$R_2N{-}CH_2{-}OR + H^+ \longrightarrow R_2N^+H{-}CH_2{-}OR \quad (3)$$

$$R_2N^+H{-}CH_2{-}OR \begin{cases} \xrightarrow{H_2O} R_2N^+H{-}CH_2{-}OH + ROH \longrightarrow R_2N^+H_2 + CH_2O & (4a) \\ \longrightarrow R_2N^+{=}CH_2 + ROH & (4b) \end{cases}$$

or as an alternative

$$R_2N{-}CH_2OR \longrightarrow R_2N^+{=}CH_2 + OR^- \xrightarrow{H^+} R_2N^+{=}CH_2 + ROH \quad (5)$$

and

$$R_2N^+{=}CH_2 + OH^- \rightleftharpoons R_2N{-}CH_2OH \rightleftharpoons R_2NH + CH_2O \xrightleftharpoons{H^+} R_2N^+H_2 + CH_2O \quad (6)$$

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[1] McLeod and Robinson, *J. Chem. Soc.*, **119**, 1470 (1921).

There is no doubt that the separation of the alkoxyl group precedes rupture of the carbon–nitrogen attachment. It is less certain that ionization of alkoxylate ion is the primary step as represented in Equation (5); an argument in favor of this view will be presented.

A distinction is drawn between the ions, $R_2N^+{=}CH_2$ and $R_2N^+H{-}CH_2{-}OH$, although it is certain that the former is highly hydrated in solution. The latter ion is probably the cation of a very weak base. To the extent that it exists, it is presumed to be stable; the path for its dissociation into aldehyde and amine salt or into the iminium ion lies through the pseudo base, as represented in Equation (6). The iminium ion is usually not isolated in the case of these simple derivatives, either as the salt or as the base. It is proposed to show that it is an intermediate in the separation of the nitrogen and carbon atoms. The reaction thus takes the familiar form usually assigned to the pseudo bases of the pyridinium type.[2]

Robinson and Robinson[3] considered, and discarded the view that these amino ethers are a mixture of definite isomers

$$R_2N{-}CH_2{-}OR \rightleftharpoons CH_2{=}N^+R_2 + O^-R \qquad (7)$$

They preferred to represent the high reactivity to hydrolysis and to the Grignard reagent by the formula $CH_2\begin{cases}N^+R_2\\O^-R\end{cases}$. The nearest approach to an actual isolation of an iminium salt has been a platinum double salt, having a composition corresponding to the formula, $(CH_2Cl{-}NR_2H)_2PtCl_6$,[4] which could be simply the chloroamine chloroplatinate.

Stewart and Aston[5] measured the relative base strengths of the amino ethers in absolute alcohol, and considered that they were measuring the equilibrium of Equation (3). They prepared a hydrochloride in dry ether, which contained alcohol, presumably the simple hydrogen chloride addition product. In alcohol they observed nothing to indicate a dissociation of the alkoxyl group.

Preparation and Properties of N-Diethylmethylene Iminium Chloride.—Our first observance of the existence of the ion $CH_2{=}N^+R_2$ came in a study of diethylaminomethyl sulfonic acid, in its reaction with iodine solution.

$$CH_2\begin{cases}N^+R_2H\\SO_3^-\end{cases} + I_3^- + H_2O \xrightarrow{H^+} CH_2{=}N^+R_2 + SO_4^= + 3I^- + 3H^+ \qquad (8)$$

The reaction is relatively slow, being half over in from eight to ten minutes. The resulting solution uses up bisulfite ion instantaneously, so that formaldehyde is not a reaction product, since it reacts slowly with bisulfite at the hydrogen-ion concentrations used.

[2] Aston, THIS JOURNAL, **52**, 5254 (1930).

[3] Robinson and Robinson, *J. Chem. Soc.*, **123**, 532 (1923).

[4] Houben and Arnold, *Ber.*, **41**, 1575 (1908).

[5] Stewart and Aston, unpublished data.

$$CH_2{=}N^+R_2 + HSO_3^- \longrightarrow CH_2\begin{matrix}N^+R_2H \\ SO_3^-\end{matrix} \quad (9)$$

The presence of diethylammonium salts does not affect formaldehyde in this respect. Moreover, the sodium bisulfite addition product of formaldehyde in acid solution does not react at all with iodine, whereas the aminosulfonic acid reacts slowly at a rate independent of the iodine concentration. The cycle of reactions—slow iodine titration, sulfite addition, slow iodine titration—could be repeated at will, and quantitatively within one per cent. It thus appears that the product of the reaction with iodine is not formaldehyde and the secondary amine as such, but a compound of the two.

Excess of the iodine solution produced an oily precipitate which was collected in a separate experiment and washed with potassium iodide solution until the ratio of titratable iodine to nitrogen in the washings approached a constant value. The composition of the oil agrees with the formula, $CH_2I{-}NR_2I_4$, and suggests an association of iodide ion, or triiodide ion, with the iminium ion, and an additional association of iodine as amine periodide. This is the only evidence we now have of association of halogen ions with these iminium ions.[6]

The reactions of the iminium ion with bisulfite ion and with periodide ion furnish tools by which its presence in solution may be detected. When an α-aminomethyl ether is added drop by drop with vigorous stirring to one normal acid, the usual production of formaldehyde and amine salt is not observed. Instead, the solution has the same characteristics as the solution produced by adding iodine to the α-aminosulfonic acid. It reacts with bisulfite instantly to form the α-aminosulfonic acid, which in turn reacts with iodine at its characteristic rate. It is not the amino ether as such that reacts with the bisulfite ion, as the alcohol formed according to Equation (5) may be removed by vacuum distillation without affecting the reaction of the solution toward bisulfite.

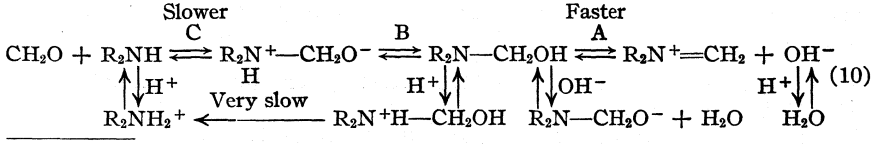
The validity of Equation (5) was further established by the actual isolation, in one instance, of a salt of the composition $CH_2{=}N(C_2H_5)_2{\cdot}Cl{\cdot}6H_2O$. N-Diethylaminomethyl isobutyl ether was rapidly neutralized

[6] The α-halogenoamines are usually unstable salts, of which the imido ester salts are examples, and are therefore to be considered as iminium salts. Pararosaniline color (pseudo) base in acid similarly forms a strong salt. If, however, the onium property of the nitrogen atom is completely neutralized by quaternary amine formation, a halogen in the alpha position is remarkably stabilized. For instance, iodomethyltrimethylammonium ion is difficult to hydrolyze, as are the alkoxymethyltrialkylammonium ions. The mobility of the halogen in the hypothetical halogenoamines is therefore dependent upon the capacity of the nitrogen to share its electron with the adjacent carbon, and the above association of iodide ion and iodine is evidence of both the weak salt-forming tendencies of iodide ion and the neutralization of the amine by periodide formation.

to the methyl orange end-point with 1 *N* hydrochloric acid, and the solution evaporated *in vacuo* over calcium chloride. The crystalline salt was kept for several weeks without decomposition except to form a tetrahydrate. Attempts to repeat the preparation failed, and yielded only formaldehyde and diethylammonium chloride. The one success was probably due to a fortuitous use of the right excess of acid, and illustrates the sensitiveness of these molecular systems.

Reactions with Alkali.—Equation (6) represents the reaction of hydroxide ion with the iminium ion, which appears to be instantaneous. Two simple experiments gave a clear idea of the equilibria concerned. A solution of amino ether in acid (iminium ion) was prepared, and one part neutralized to phenolphthalein, while another was made strongly alkaline. Each was then *rapidly* acidified. In the first case only about 15% of the original iminium ion was recovered, but in the second over 90% was found. A similar pair of experiments which differed in that the alkaline solutions were *slowly* acidified yielded, in both cases, a smaller amount of iminium ion, about five per cent. Identical results were obtained by starting with solutions of formaldehyde and diethylamine in equal molal ratio. The reaction is therefore strictly reversible. In dilute solution the amino alcohol corresponds at equilibrium to more than 80% of the theoretical.[7]

Discussion of Results.—Referring to Equation (10) below, slow addition of acid neutralizes the secondary amine and gradually shifts the equilibrium to the left, suggesting that diethylamine is a stronger base than the amino alcohol. Strong alkali shifts equilibria C and B to the right, the equilibrium A to the left. Experimentally, rapid acidification of this alkaline solution produces the iminium ion, which means either that the equilibrium A is more rapidly established than equilibrium C, resulting in loss of hydroxide ion rather than secondary amine, or that hydrogen ion first adds to form the ion, $R_2N^+H—CH_2—OH$, which then loses water rather than dialkylammonium ion. We are inclined to the first view, since the quaternization of the nitrogen, as mentioned in a footnote above, tends to stabilize negative groups in the alpha position.



[7] Henry, *Bull. Acad. Roy. Belgique*, [3] **28**, 370 (1894), claims to have isolated α-amino alcohols of the type $R_2N–CH_2–OH$ by the action of formaldehyde on secondary amines. His procedure normally leads to α-amino ether if alcohol is present, or to the methylenediamines if it is absent. He had no satisfactory criterion of purity and whereas it is believed that the simple amino alcohols exist in dilute aqueous solution, it is felt that any attempt to concentrate or dehydrate them results in the formation of methylene diamines or the diaminodimethyl ethers.

Step C is the rate determining step for the formation and molecular dissociation of the pseudo base. The conclusion is drawn that step A is much faster than steps B and C taken as successive reactions.

The chemistry of the substituted methylenediamines gives support to this mechanism. Attempts to quaternize them fail[8]

$$R_2N—CH_2NR_2 + RI \longrightarrow [R_2N—CH_2—N^+R_3 + I^-] \longrightarrow R_2N^+{=}CH_2 + R_3N + I^- \quad (11)$$

Solution in acid produces the iminium ion[9]

$$R_2N—CH_2—NR_2 + 2H^+ \longrightarrow R_2N^+{=}CH_2 + R_2M^+H_2 \quad (12)$$

The difficulty experienced in producing the iminium ion quantitatively from the amino ethers, methylenediamine or the polyiodide may be entirely due to a heterogeneity factor. The iminium ion is first formed in the boundary region between the acidic solution and the added amino ether; it can then pass to the acidic region and be metastable, or it can be subjected to alkali (or low acidity) in the adjoining region and be rapidly converted to amine and aldehyde.

Experimental Part

Preparation of Substituted Aminomethyl Ethers and Methylenediamines.—The method of McLeod and Robinson,[1,3] was modified in order to eliminate the presence of large amounts of excess formaldehyde in the crude product.

Diethylaminomethyl Methyl Ether.—Seventy-four grams of diethylamine was added to 34 g. of methyl alcohol; 30 g. of paraformaldehyde was added and the mixture placed under a reflux condenser. An ice-bath was kept in readiness as the reaction becomes quite vigorous and must be slowed down. When the reaction had ceased, anhydrous potassium carbonate was added and the whole allowed to stand overnight. The potassium carbonate was then filtered off by suction and the filtrate fractionated. A fraction distilling at 114–120° (755 mm.) was collected and dried with metallic sodium. Refractionation yielded 47 g. of a colorless, mobile liquid boiling at 115–115.8° (755 mm.). A sample of the product was dissolved in 10 cc. of ethyl alcohol and titrated with 0.1000 normal hydrochloric acid, using methyl orange as an indicator. An equivalent weight of 118.0 was obtained: calcd. for $C_6H_{15}ON$, 117.1; yield, 40%.

The same general method outlined above was used in the preparation of all the aminomethyl ethers listed below.

Diethylaminomethyl Ethyl Ether.—Seventy-three grams of diethylamine, 80 g. of ethyl alcohol (95%) and 30 g. of paraformaldehyde yielded 90 g. of a colorless, mobile liquid boiling at 132–134° (756 mm.). The equivalent weight was determined as 131.0: calcd. for $C_7H_{17}ON$, 131.1; yield, 69%.

[8] Litterschied, *Ann.*, **335**, 368 (1904), isolated the unstable dimethiodide of the furfuraldehyde derivative.

[9] Knoevenagel and Mercklin, *Ber.*, **37**, 4087 (1904), claimed to have prepared the dihydrochloride salt of the substituted methylenediamine. Attempts to repeat the preparation in dry alcoholic and ethereal chloride gave us only diethylamine hydrochloride. Ehrenberg, *J. prakt. Chem.*, **36**, 117 (1887), states that he was unable to obtain the dihydrochloride of the tetraethyl derivative, but did obtain the platinum double salt of the tetraisobutylmethylenediamine. We believe that we have shown that the substance he obtained has the structure $[CH_2{=}N(C_4H_9)_2]_2 \cdot PtCl_6$. See also Branch, THIS JOURNAL, **38**, 2466 (1916).

Diethylaminomethyl *n*-Butyl Ether.—Seventy-five grams of diethylamine, 95 g. of *n*-butyl alcohol and 30 g. of paraformaldehyde yielded 114 g. of a colorless, mobile liquid boiling at 172–173° (758 mm.). The equivalent weight was determined as 159.0: calcd. for $C_9H_{21}ON$, 159.2; yield, 72%.

Diethylaminomethyl *n*-Heptyl Ether.—Forty grams of diethylamine, 105 g. of *n*-heptyl alcohol and 15 g. of paraformaldehyde yielded a colorless liquid boiling at 112.5° (15 mm.). The equivalent weight was determined as 303.0: calcd. for $C_{12}H_{27}ON$, 201.2.

Di-*n*-propylaminomethyl *n*-Butyl Ether.—Sixty grams of di-*n*-propylamine, 74 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded 74 g. of a colorless, mobile liquid boiling at 87° (42 mm.). The equivalent weight was determined as 185.7: calcd. for $C_{11}H_{25}ON$, 187.2; yield, 79%.

Diisopropylaminomethyl *n*-Butyl Ether.—Ten grams of diisopropylamine, 14 g. of *n*-butyl alcohol and 2.9 g. of paraformaldehyde were mixed as already described. No attempt was made to purify the compound.

Di-*n*-butylaminomethyl *n*-Butyl Ether.—Seventy grams of di-*n*-butylamine, 74 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 116° (11 mm.).

Diisobutylaminomethyl *n*-Butyl Ether.—Seventy-five g. of diisobutylamine, 74 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded 88 g. of a colorless, mobile liquid boiling at 92° (5 mm.). The equivalent weight was determined as 213.5: calcd. for $C_{13}H_{29}ON$, 215.2; yield, 82%.

Di-*n*-amylaminomethyl *n*-Butyl Ether.—Eighty grams of di-*n*-amylamine, 70 g of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 128° (5 mm.).

Methylphenylaminomethyl *n*-Butyl Ether.—Fifty-five grams of methylaniline, 70 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde were mixed as already described. The mixture was fractionated under reduced pressure. Everything distilling over above 110° (10 mm.) was used.

Diallylaminomethyl *n*-Butyl Ether.—Fifty grams of diallylamine, 70 g. of *n*-butyl alcohol, and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 89° (11 mm.).

***n*-Butoxymethylpiperidine.**—Eighty grams of piperidine, 100 g. of *n*-butyl alcohol and 30 g. of paraformaldehyde yielded a colorless liquid boiling at 82° (5 mm.).

Dimethylaminomethyl *n*-Butyl Ether.—Twenty-five grams of dimethylamine, 70 g. of *n*-butyl alcohol and 15 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 128° (756 mm.). The equivalent weight was determined as 132.5: calcd. for $C_7H_{17}ON$, 131.1.

Tetraethylmethylenediamine.[10]—One hundred fifty grams of diethylamine and 30 g. of paraformaldehyde yielded a colorless, mobile liquid boiling at 166–167 (757 mm.); 128 g. of material was obtained. The equivalent weight was determined as 80.0: calcd. for $C_9H_{22}N_2$, 79.1.

3-β-Hydroxyethyloxazolidine.—Ten grams of diethanolamine, 14 g. of *n*-butyl alcohol and 2.8 g. of paraformaldehyde were mixed in an attempt to prepare diethanolaminomethyl *n*-butyl ether. Fractionation yielded a colorless viscous liquid boiling at 78° (2 mm.). The equivalent weight determined by titrating with *N*/10 hydrochloric acid was 119.5. The equivalent weight of the material was also determined by means of bisulfite and iodine, and found to be 65.3. The molecular weight, calculated for $C_5H_{11}NO_2$, is 117.1. Further purification was not attempted.

The Reaction between the Amino Ether or Methylenediamine and Paraformaldehyde.—Solid paraformaldehyde was stirred with a quantity of diethylaminomethyl-*n*-

[10] Ehrenberg, *J. prakt. Chem.*, **36**, 117 (1887).

butyl ether in a closed system for several days. Samples were withdrawn through a filter at intervals and the equivalent weight determined by acidic titration. The paraformaldehyde appeared to be practically insoluble as such. The amino ether added one mole of formaldehyde within ten days at 30°, after which the reaction proceeded much more slowly. The product was not investigated in detail, except to observe that it was high boiling and that its formation was to some extent reversible. It is probably a simple addition product such as diethylaminomethyl *n*-butoxymethyl ether.

In a similar way N-tetraethylmethylenediamine added formaldehyde. The reaction was practically complete in five days. Figure 1, in which the equivalent weight of the liquid phase of the reaction mixture is plotted against the time, illustrates this difference in rate. The formation of this type of addition product is the reason for avoiding the presence of excess formaldehyde during the preparations. On the other hand, in the preparation of the amino ether a large excess of diethylamine is to be avoided, since the N-tetraethylmethylenediamine will be formed and is difficult to separate by fractionation.

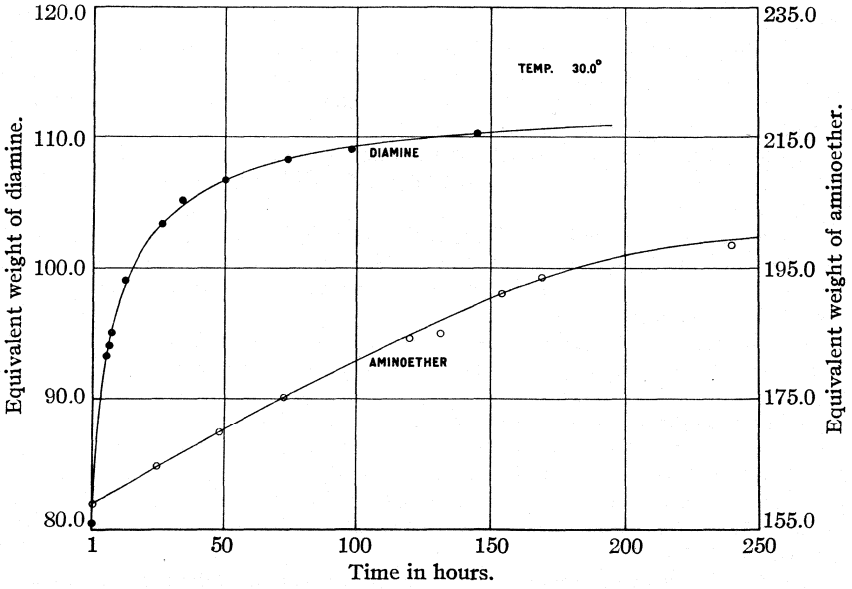


Fig. 1.—The addition of formaldehyde to the amino ether and methylenediamine, temp. 30°.

Preparation and Iodine Titration of Sodium-N-diethylaminomethyl Sulfonate.—Knoevenagel and Mercklin's method of preparation[11] was modified slightly. Solid formaldehyde sodium bisulfite was precipitated from a concentrated solution by alcohol and the dry salt redissolved in half its weight of water. Slightly in excess of one mole of liquid diethylamine was added slowly and the mixture placed in a desiccator. After a few hours standing the sample was dried *in vacuo* over calcium chloride. A weighed sample was dissolved in *N*/10 hydrochloric acid and the solution titrated with standard sodium hydroxide to the methyl orange end-point. The end-point was obscure; the indicated equivalent weight was 200 ± 5, the theoretical 189.1. A similarly prepared

[11] Knoevenagel and Mercklin, *Ber.*, **37**, 4087 (1904).

acid solution was titrated with iodine. From one to two per cent. (0.3 cc.) of the iodine was used up rapidly, the remainder (19.7 cc.) was used up slowly. The equivalent weight on the basis of the total iodine was 97 ± 1. The method of preparing the solution and its time of standing affected the results. The dry salt was stable for months.

The rate of the slow titration with iodine was ascertained to be first order in the aminosulfonate concentration and independent of the iodine concentration. It was markedly affected by temperature, slightly by changing ionic strength with small specific ion effects (retarded by iodide, increased by sulfate ion) and very slightly affected by changing hydrogen-ion concentration in the region of one-tenth normal. The usual plot, *log (reactant)* against *time*, was a straight line. In two identical experiments, except that in one the iodine was added in 1.0-cc. portions and the color allowed to fade, and in the other iodine was added drop by drop, keeping a barely perceptible color present (no starch), the specific rate constants at 25.0° were, respectively, 1.603×10^{-3} and 1.592×10^{-3} sec.$^{-1}$. After the completion of the reaction, a solution of sodium bisulfite equivalent to the iodine used in slow titration was added, and the titration repeated immediately after mixing. The same rate was observed as before for all the sulfite, within one per cent.

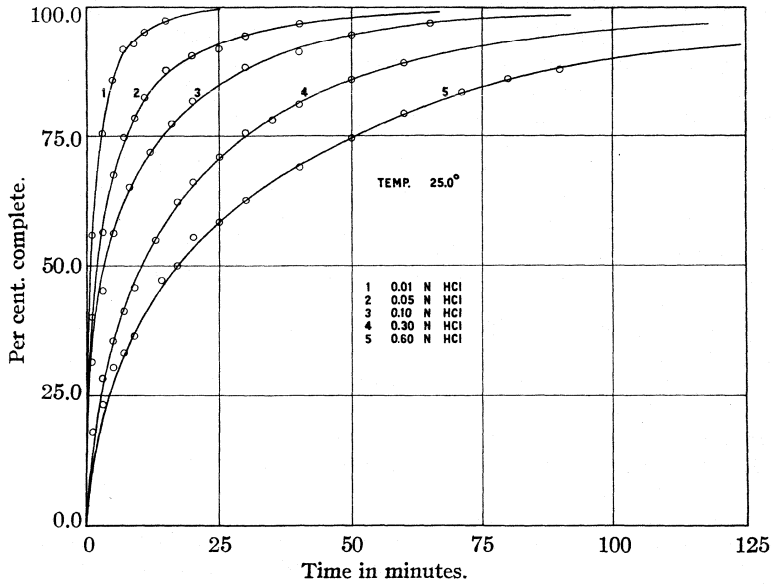


Fig. 2.—The addition of bisulfite ion (0.0366 *M*) and formaldehyde (0.0366 *M*).

Rate of Addition of Bisulfite to Formaldehyde as a Function of Hydrogen-Ion Concentration.—For control purposes the data plotted in Fig. 2 were obtained by adding aqueous formaldehyde and sodium bisulfite solutions to hydrochloric acid solutions, and following the disappearance of the ionized sulfite with iodine in extracted samples.

Formation of the Periodide, $CH_2{=}N^+R_2I_5$ or $CH_2(I_3)NR_2(I_2)$.—Addition of excess iodine to a solution of the iminium ion, preferably by oxidizing part of the iodide ion present by iodate ion, produces an oily precipitate of about the consistency of mercury. This was washed with aqueous potassium iodide solution until the ratio of nitrogen to iodine in the washings approached that ratio in the oil. The first washings contained

excess iodine. The periodide analyzed as follows: by the Carius method, using sugar as a reducing agent, 0.3790 g. gave 0.6201 g. of AgI, or 88.4% I; calculated for I—CH_2–$N(C_2H_5)_2I_4$, 88.1%. By Kjeldahl, 0.3580 g. gave 0.0072 g. N or 2.02%; calculated, 1.94%. Dissolved in 20 cc. of acidified alcohol (2.0 cc. 1.0 *N* HCl) and titrated with 0.1000 *N* thiosulfate, 0.3580 g. used 19.70 cc., an equivalent weight of 182; calculated, 180. To the resulting solution a known amount of sodium bisulfite solution was added, and after one minute the *excess* ionized sulfite was titrated rapidly; sulfite used up, 9.9×10^{-4} equivalents; calcd., 9.95×10^{-4} equivalents; d_{20}^{20} 2.81. Excess of iodide ion dissolves (or prevents the formation of) the polyiodide. The formulas assigned are arbitrary, but there is one good reason to prefer the second in comparison to the first above. On the basis of the first formula, the reactions of the iodine should not affect the iminium ion. However, great difficulty was experienced in regenerating that ion from the substance, particularly when the insoluble oil was shaken with aqueous solutions of iodide, sulfite or thiosulfite. In nearly every case most of the compound appeared as formaldehyde or formaldehyde bisulfite addition product. The solution in acidified alcohol, described above, sometimes failed to give a quantitative yield of the iminium ion. The most trustworthy procedure for analytical purposes involved solution of the oil in acidified alcohol and addition of excess bisulfite.

Preparation of a Solution of N-Diethylmethyleneiminium Salt.—Diethylaminomethyl isobutyl ether (0.4312 g.) was added dropwise with vigorous stirring to 3.00 cc. (0.29 cc. excess) of 1.0 *N* hydrochloric acid. To this solution 40.00 cc. of sodium bisulfite solution, equivalent to 64.00 cc. of 0.1000 *N* iodine, was added. Titration with iodine used 10.10 cc. of 0.1000 *N* iodine rapidly, to a fading end-point which could be measured to better than 0.1 cc. More iodine solution was then added until the end-point became permanent. This required about ninety minutes and used 53.7 cc. or a total of 63.8 cc. of iodine. The 0.2 cc. loss was probably due to the formation of formaldehyde bisulfite in small amount, which does not titrate with iodine in acid solution. Using the fading end-point as the proper measure of the amount of sulfite reacted, the equivalent weight of the amino ether to this reaction is 80.0. Toward direct titration with acid another sample gave an equivalent weight of 159.2. The production of the iminium ion was nearly quantitative.

Adding the original reagents in the inverse order, or not stirring so vigorously, or using 0.1 *N* acid, gave poorer yields.

Mechanism.—To show that after solution of the amino ether in acid the reactive species was the iminium ion, the following experiments were made: 0.00278 mole of the isobutyl ether was dissolved in 0.0035 equivalent to 1.0 *N* acid as before. The solution was evaporated *in vacuo* through a liquid-air trap to two-thirds its volume. The trap contained two liquid layers after warming, with the marked odor of isobutyl alcohol. The alcohol was taken up in benzene, the solution dried and the alcohol esterified with 2.0 cc. of acetic anhydride; 0.00197 equivalents of alcohol, amounting to a 65% yield, was found. The residue was treated with bisulfite (0.0060 equiv.) as before and the fading and permanent end-points to iodine noted. The slow titration involved 0.00557 equivalents of iodine or practically 100% yield of iminium ion. Hence the sulfite compound could not all have been formed from the ether directly. This result was obtained by avoiding too dilute solutions and allowing only two and one-half hours for the distillation.

An acidified solution of diethylammonium chloride, formaldehyde and bisulfite when titrated with iodine, gave no fading end-point and used the full amount of iodine solution expected on the basis of the sulfite present.

Isolation of the Crystalline Salt.—2.715 grams of the isobutyl ether derivative was titrated rapidly at room temperature to the methyl orange end-point with 1.00 *N*

hydrochloric acid. The solution was evaporated *in vacuo* over calcium chloride as rapidly as possible and yielded hygroscopic, white crystals. *Anal.:* 0.5500 g. in 0.10 *N* acid used 0.00478 equivalent of sulfite and produced by Kjeldahl 0.00242 equivalent of ammonia; equivalent weight to sulfite, 115, to Kjeldahl, 227.0; calcd. for $CH_2{=}N(C_2H_5)_2Cl{\cdot}6H_2O$, 229.5. The remainder of the preparation stood in the desiccator over calcium chloride for several weeks. A 0.1589-g. sample was dissolved in 0.1 *N* acid and 0.002340 equivalent of bisulfite added; iodine used up to the fading end-point was 0.00072 equivalent, to the permanent end-point 0.00162 equivalent. When treated by the Kjeldahl process, the sample gave 0.000828 equivalent of ammonia: equivalent weight, to sulfite, 98; to Kjeldahl, 192; calcd. for $CH_2{=}N(C_2H_5)_2Cl{\cdot}4H_2O$, 193.5. Another sample was allowed to stand longer in the presence of the excess sulfite to permit any free formaldehyde in the sample to react, as shown by failure subsequently to titrate completely all the bisulfite added. No evidence of any formaldehyde could be found. Since the remaining possible impurity, diethylammonium chloride, could not be present without throwing out the ratio of the two equivalent weights as determined above, it is presumed that water of crystallization is present. No further examination of the product was made. Repeated attempts to duplicate the preparation failed. Its original success was probably due to a fortuitous use of the proper amount of hydrochloric acid, since excess acid hastens the rate of hydrolysis to formaldehyde, while a basic solution produces a very rapid decomposition of the iminium ion to formaldehyde and secondary amine.

The Reaction between Formaldehyde and Diethylamine in Dilute Aqueous Solution.—These reagents could form the simple amino alcohol (pseudo base) by addition, or the methylenediamine derivative, or the iminium hydroxide.

$$CH_2O + R_2NH \rightleftharpoons CH_2(OH)NR_2 \rightleftharpoons CH_2{=}N^+R_2 + OH^- \quad (13)$$

$$CH_2{=}N^+R_2 + R_2NH \rightleftharpoons CH_2(NR_2)NR_2 + H^+ \quad (14)$$

Any one or all of these products upon *rapid* acidification could yield the substituted iminium ion. Slow acidification definitely produces only a trace of iminium ion. Acidification of the amine before adding formaldehyde permits no iminium ion to form; in fact, the latter is slowly hydrolyzed in acid at room temperature to the aldehyde and amine salt, so must be considered unstable in this medium. Since the iminium ion can be detected quantitatively by the sulfite reaction as explained above, some idea as to the molecular species present can be obtained. Table I describes a few experiments in which equal volumes (100 cc.) of amine and formaldehyde solutions were mixed, with and without the addition of acid or alkali. The last column gives the per cent. of total amine present, which is in the form of iminium ion after acidifying very rapidly. In the

TABLE I

THE REACTION BETWEEN FORMALDEHYDE AND DIETHYLAMINE

Expt.	Formaldehyde concn., m./l.	Diethylamine concn., m./l.	Acid or Base (6 *N*), cc.	Iminium ion, per cent. of total amine
1	0.18	0.4	5.7 (acid)	10
2	.18	.13	...	85
3	.20	.20	...	92
4	.20	.20	4.0 (base)	96

sample partly neutralized by acid (Expt. 1), the iminium ion formation corresponded to about 10% of the free amine present; in the others it approximates complete reaction. This indicates the formation of the amino alcohol or iminium base, since the diamine could yield as a maximum only 50% of iminium ion. This was further tested by freezing point determinations.

The freezing point lowering of a given 0.18 *M* formaldehyde solution was 0.311°. If the formaldehyde was not polymerized and formed a perfect solution, it would have been 0.334°. Anhydrous diethylamine was added sufficient to bring its concentration to 0.044 *M*. The freezing point lowering was then 0.316°. The amine concentration was raised to 0.126 *M;* and the freezing point lowering became 0.367°. Assuming 85% conversion of the amine to the amino alcohol, the freezing point lowering should have been 0.370°. These figures show qualitatively that one mole of addition product results, and together with the fact of 90% conversion to iminium ion in acid solution, point to the undissociated pseudo base, $CH_2(OH)NR_2$, as the main product. Equation (13) above best represents these facts, in which the first equilibrium is shifted to the left by acid and to the right by strong base. Action of acid upon the pseudo base leads first to the rapid formation of iminium ion, followed by the slower establishment of the equilibrium corresponding to the new alkalinity of the solution. If the addition of acid results in an acid solution, the metastable iminium ion is formed.

The Reaction between Aqueous Acid and Tetrasubstituted Methylenediamine.—The equivalent weight of freshly distilled, sodium-dry tetraethylmethylenediamine was determined as 80.0 by titration with *N*/10 hydrochloric acid; 0.3040 g. of this diamine was then added dropwise to 20.0 cc. of *N*/1 hydrochloric acid using a mechanical stirrer. Then 42.65 cc. of sodium bisulfite (equivalent to 39.10 cc. of 0.1008 normal iodine) and 2.0 cc. of starch solution were added and the solution immediately back-titrated with iodine; 3.05 cc. of 0.1008 normal iodine was added to the fading end-point and a total of 38.80 cc. of iodine to the permanent end-point. The equivalent weight of the diamine, on the basis of this titration, is 83.7. The equivalent weight calculated for $C_9H_{22}N_2$ is 79.1.

N-Diisobutylmethyleneiminium Chloroplatinate.—Diisobutylaminomethyl *n*-butyl ether was dissolved rapidly in a small excess of *N* hydrochloric acid, and chloroplatinic acid added. The light yellow precipitate was filtered off, washed with water and alcohol and dried in a desiccator. It melted with decomposition (heating started at room temperature) at 196–197° and 0.0579 g. gave 0.0161 g. of Pt: found, 27.8% Pt; calcd. for $[CH_2{=}N(C_4H_9)_2]_2.PtCl_6$, 28.2%. Ehrenberg[12] obtained a platinum salt from the corresponding diamine which decomposed at the same temperature and contained 28.35% Pt. He assigned to it the formula, $CH_2(N(C_4H_9)_2H)_2PtCl_6$, but it corresponds in all respects to the above substance, which cannot be of the structure assigned by Ehrenberg. Diisobutylammonium chloroplatinate melts at 212–213°, with decomposition and contains 29.21% platinum. It is the most probable impurity.

[12] Ehrenberg, *J. prakt. Chem.*, **36**, 117 (1887).

Summary

1. The preparation of a number of dialkylaminomethyl ethers is described.

2. The mechanism of their hydrolysis to formaldehyde, alcohol and secondary amine has been studied and the conclusion reached that it involves the primary formation of N-dialkylmethyleneiminium ion, which subsequently adds hydroxide ion to yield the amine and formaldehyde.

3. N-Diethylmethyleneiminium chloride, $(C_2H_5)_2N{=}CH_2Cl\cdot 6H_2O$ has been isolated. The platinum double salt, $(\text{iso-}C_4H_9)_2N{=}CH_2)_2PtCl_6$, has been prepared from the corresponding amino ether. It corresponds to the platinum double salt of Ehrenberg, prepared from tetraisobutylmethylene diamine.

4. The reaction between formaldehyde and diethylamine in dilute aqueous solution has been studied to confirm the mechanism of reaction of the amino ethers.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATE OF REACTION OF DISUBSTITUTED AMINOMETHYL SULFONIC ACIDS WITH IODINE

BY T. D. STEWART AND WILLIAM E. BRADLEY

RECEIVED JUNE 14, 1932 PUBLISHED NOVEMBER 5, 1932

The substituted aminomethyl sulfonic acids react with iodine in acid solution according to the equation

$$R_2N^+H{-}CH_2{-}SO_3^- + I_3^- \longrightarrow R_2N^+{=}CH_2 + SO_4^= + 3I^- + 3H^+$$

It has already been observed[1] that the reaction rate is independent of the iodine concentration, even for very low concentrations of iodine, and is first order with respect to the aminosulfonic acid. The rate is affected slightly by salts; the effect of increasing hydrogen-ion concentration up to about tenth normal is to decrease the rate; beyond that, up to one normal, there is but a small effect. At very low acidity the reaction is very fast and little or no iminium ion is formed.

The rate determining step appears to be the rate of ionization, represented as

$$R_2N^+H{-}CH_2{-}SO_3^- \underset{\text{(fast)}}{\overset{\text{(slow)}}{\rightleftharpoons}} R_2N^+{=}CH_2 + HSO_3^-$$

The free sulfite ion at equilibrium is less than one per cent. In fairly concentrated solutions some indication of the dissociation is found. The reaction would appear to lend itself peculiarly well therefore to a study

[1] Stewart and Bradley, THIS JOURNAL, 54, 4172 (1932), discuss this reaction and the evidence for the iminium ion.

of the effect of various substituents upon the reactivity of groups adjacent to the amino group.

Discussion of Results.—The experimental method is described in the next section. Under comparable conditions of ionic strength, acidity,

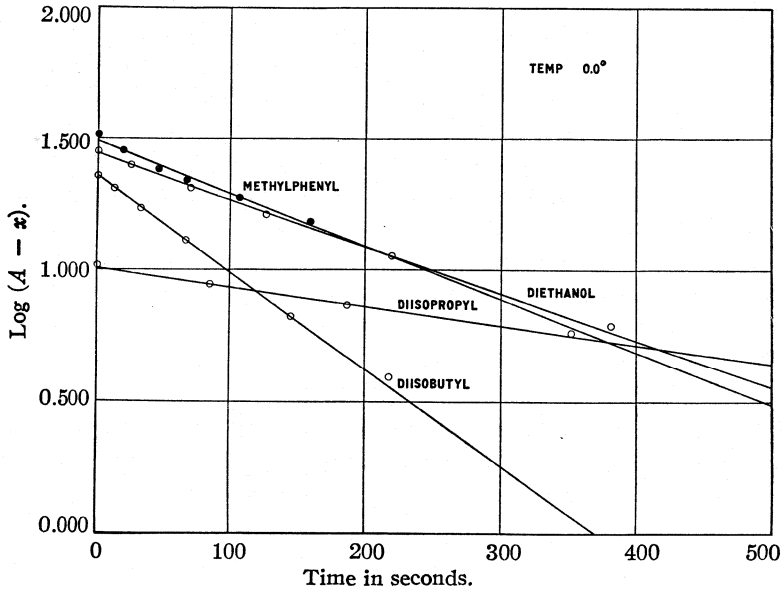


Fig. 1.—The reaction rate of disubstituted aminomethyl sulfonic acids (A) with iodine. $(A - x)$ is expressed in cc. of iodine solution.

and temperature, a number of derivatives have been studied, and the results given in Figs. 1–4 and Table I. The names in Table I and on the plots refer to the two nitrogen substituents in the reactant. At 20° the

TABLE I

THE REACTION RATES

Substituent groups	Specific rate constants ($sec.^{-1}$) 0.0°	20.0°	30.0°	40.0°
Dimethyl		0.000272	0.00103	
Diethyl		.000750	.00271	
Di-*n*-propyl		.00265	.00923 (I_2)	
			.00987 (Br_2)	
			.00978 (H_2O_2)	
Diisopropyl	0.00172			
Di-*n*-butyl			.00666	
Diisobutyl	.00845			
Di-*n*-amyl			.00195	
Diallyl			.00893	
N-Piperidyl			.000554	0.00196
Diethanol	.00424	.0488		
Methylphenyl	.00474	.0484		

rate increases in the following order of the substituents: N-piperidyl (1), dimethyl (1.6), di-*n*-amyl (3.0), diethyl (4.4), di-*n*-butyl (10), diallyl (14), di-*n*-propyl (15), diisopropyl (120), phenylmethyl (280), diethanol (290), diisobutyl (570).

The rate is the same for the three oxidizing agents tried, namely, iodine, bromine, and hydrogen peroxide. This indicates an activated state common to each reaction, which is best represented by an ionization. Attempts to obtain a deviation from a first order law by using extremely

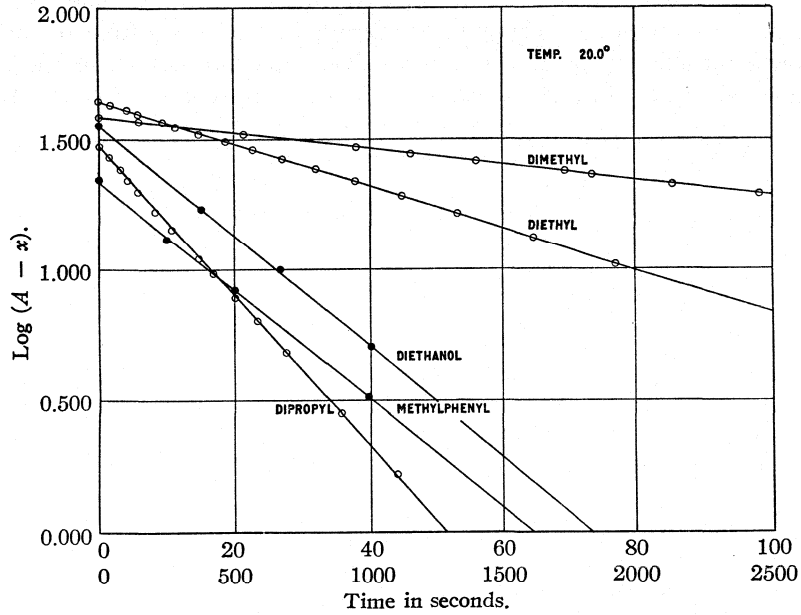


Fig. 2.—The reaction rate of disubstituted aminomethyl sulfonic acids (A) with iodine. $(A - x)$ is expressed in cc. of iodine solution.

low iodine concentrations failed. If, however, the reaction rate were observed by adding measured quantities of iodine solution, noting the time necessary to use up that amount, and then waiting before the addition of more iodine, aberrations in the rate were observed. After such a pause in the addition of iodine, a small but detectable amount of iodine would be used up instantly. This confirms the assumption of an actual ionization as the rate determining step.[2]

The heats of activation have been calculated in the usual way and listed in Table II. It is seen that except for the last two, the increasing order of reactivities at 20° is the inverse of the increasing order of activation energies. The last two substances are anomalous in another respect.

[2] The alternative explanation would be a slow hydrolysis to an amino alcohol, R_2NCH_2OH, followed by rapid iminium ion formation.

TABLE II

HEATS OF ACTIVATION

Compound	*E*, calcd.	Compound	*E*, calcd.
N-Piperidyl	23,830	Di-*n*-propyl	22,030
Dimethyl	23,470	Diethanol	19,440
Diethyl	22,680	Phenylmethyl	18,500

If the logarithm of the specific reaction rate constant is plotted against the activation energy, a good straight line is obtained involving the first four compounds of Table II; the last two fall off the line. The accuracy of the measurements warrants considering this as suggestive of an unknown variable in the rate which involves part but not all of the compounds studied. In fact, referring to the order of reactivity given above,

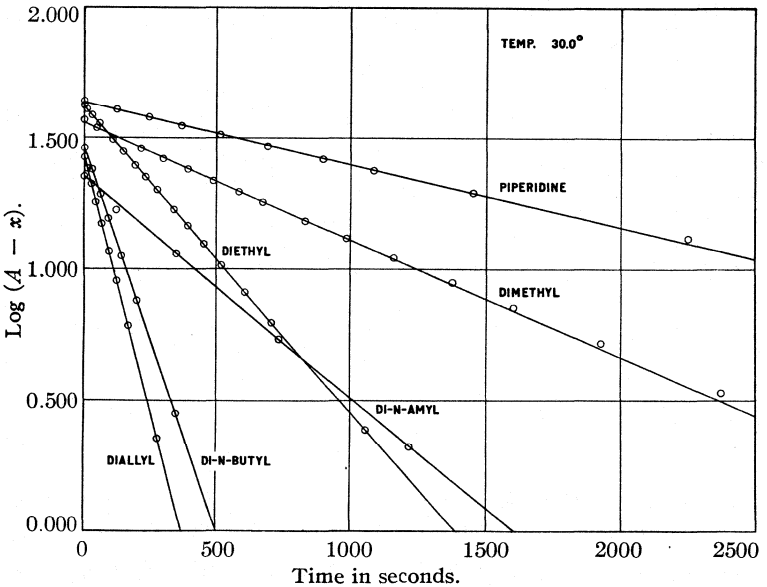


Fig. 3.—The reaction rate of disubstituted aminomethyl sulfonic acids (A) with iodine. $(A - x)$ is expressed in cc. of iodine solution.

the compounds seem to fall into two categories, those of high and those of low reactivity. Where the rates at 20° were not directly measured, or calculated from the measured activation energy, they were estimated by assuming the known activation energy of the substance having most closely the same reactivity.

The effect of the substituent groups in this reaction is probably exerted through the onium electron pair of the nitrogen atom and offers a valuable tool for the precise comparison of the effects of these groups upon chemical reactivity.

Experimental Part

Preparation of Materials.—Preparation of the amino ethers has already been described.[1] The aminosulfonic acids were prepared from the corresponding amino ethers by the reactions

$$R_2NCH_2OR + H^+ \longrightarrow R_2N^+{=}CH_2 + ROH$$

$$R_2N^+{=}CH_2 + HSO_3^- \longrightarrow R_2N{-}CH_2{-}SO_3^- \xrightarrow{H^+} R_2NH^+{-}CH_2{-}SO_3^-$$

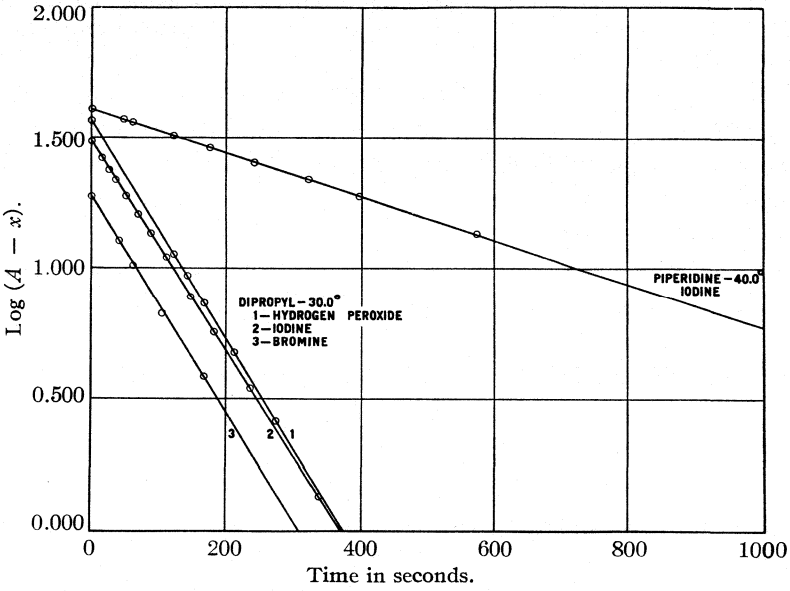


Fig. 4.—The reaction rate of disubstituted aminomethylsulfonic acids (A) with iodine, bromine and hydrogen peroxide. $(A - x)$ is expressed in cc. of iodine solution.

TABLE III

DIMETHYLAMINOMETHYL SULFONIC ACID

Temperature of thermostat, °C.	20.00
Weight of dimethylaminomethyl *n*-butyl ether, g.	0.2854
Cc. of 0.1008 normal $NaHSO_3$ added	48.50
Cc. of 0.1008 normal I_3^- added into fading range	8.05
Cc. of 0.1008 normal I_3^- to permanent end-point	46.52

Elapsed time, sec.	Equivalents of reactant (in cc. of I_3^-)	Elapsed time, sec.	Equivalents of reactant (in cc. of I_3^-)
0	38.47	1835	22.96
149	36.65	2138	21.12
283	35.15	2450	19.44
534	32.85	2792	17.74
945	29.39	3150	16.12
1152	27.79	3640	14.12
1402	25.97	4127	12.40
1734	23.85	5018	9.72
			0.0

Procedure.—A weighed sample of the disubstituted aminomethyl ether was added dropwise to 15.00 cc. of 1.00 *N* hydrochloric acid which was agitated by means of a mechanical stirrer. An excess of approximately 0.1 *N* sodium bisulfite and 2.0 cc. of starch solution was added and the solution placed in a thermostat. A sufficient amount of a solution of approximately 0.1 *N* iodine was added to use up any ionized sulfite present. When the solution had come to the temperature of the thermostat, the rate was determined by adding successive small portions of iodine solution and noting the time required for the starch color to fade in each case. The total amount of iodine required to reach the permanent end-point was determined by following the reaction to completion. A typical example is given in Table III. This and similar cases are plotted in Figs. 1, 2, 3 and 4.

Summary

The effect of various carbon groups upon the rates of ionization and heats of activation of disubstituted aminomethyl sulfonic acids has been studied.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

THE THERMAL DECOMPOSITION OF METHANE BY A CARBON FILAMENT[1]

BY H. H. STORCH[2]

RECEIVED JUNE 20, 1932 PUBLISHED NOVEMBER 5, 1932

The writer has published elsewhere a brief, critical review[3] of the literature on the pyrolysis of methane. The thermal decomposition of methane in an isothermal, static system has recently been studied by Kassel[4] at temperatures low enough (700–850°) so that rate measurements on the early stages of the reaction were feasible. The reaction was found to be a homogeneous one of first order with a heat of activation of about 79,000 calories.

The experiments described in the present paper were all conducted in carbon filament lamps, the objectives being to isolate some of the early products of the pyrolysis of methane by immersing the walls of the bulb in liquid nitrogen or oxygen, and to avoid loss of hydrogen such as occurs in experiments with quartz bulbs. An additional objective was to study the reaction on a carbon surface rather than on quartz or metal surfaces coated with carbon.

[1] Published with the permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Part of this work was presented at the meeting of the American Chemical Society at Buffalo, N. Y., in August, 1931.

[2] Principal physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

[3] "Physical Chemical Properties of Methane," U. S. Bureau of Mines Information Circular 6549, January, 1932.

[4] L. S. Kassel, THIS JOURNAL, **54**, 3949 (1932).

Preparation of Methane and Apparatus

The methane used in the experiments described in this paper was prepared by removal of ethane from Pittsburgh natural gas by adsorption on active charcoal. The gas thus obtained contained 95–98% methane, 2–5% nitrogen, and traces of ethane. The gas was then dried over phosphorus pentoxide, condensed by a bath of liquid nitrogen, and the solid methane repeatedly melted and frozen (the non-condensable gases being pumped off) until a constant vapor pressure (11 millimeters) was obtained. The methane was then allowed to vaporize into an evacuated 5-liter flask, the first and last thirds of the vapor being wasted. Such preparation yielded a gas which contained no detectable quantity of ethane, and only traces of nitrogen.

The reaction vessels consisted of 60-watt, 110-volt carbon filament lamps obtained from the General Electric Company. The filaments are made from cotton peptized with zinc chloride and subsequently washed and carbonized. They averaged 0.18 mm. in diameter and 24 cm. in length. In order to test the possible catalytic activity of the platinized inner leads, a number of specially constructed lamps containing tungsten inner leads were used. The latter gave practically the same results as the ordinary lamp. The lamps were sealed into a system containing an open arm manometer, a Töpler pump, a McLeod gage, a mercury diffusion vacuum pump and a 5-liter reservoir of methane. The mercury levels of the manometer were read with the aid of a Gaertner cathetometer. During the experiments the volume of the carbon filament lamp plus manometer was kept constant with the aid of a mercury leveling bulb attached to the bottom of the manometer.

The filaments were heated by storage battery current, the temperature being measured by a Leeds and Northrup optical pyrometer which had been calibrated by the U. S. Bureau of Standards. The measurement of the temperature by means of the resistance of the carbon filament was found to be impossible due to the variation of the resistance with the character and amount of the gas in the lamp, and to the deposition of small amounts of carbon on the filament.

Isolation of Early Products of the Pyrolysis.—The experiments listed in Table I were all conducted with the lamp completely immersed in a bath of liquid nitrogen contained in a transparent Dewar bulb. Accurate temperature measurements were not possible because of poor visibility through the boiling nitrogen, and hence no attempt was made to take any measurements of the reaction rate, the objective being the isolation of the primary reaction products.

TABLE I

PRIMARY PRODUCTS OF THE DECOMPOSITION OF METHANE BY A CARBON FILAMENT AT 1700°

	Pressure measurements			Analysis of product, %				
Expt.	Initial with bulb at room temperature, cm.	Final with bulb immersed in liquid nitrogen, cm.	Final with bulb at room temperature, cm.	CH_4	H_2	C_2H_6	Unsatd. hydrocarbons	Total time of expt., min.
15	39.29	5.20	41.22	62.6	13.6	20.3	3.4	17
16	33.76	3.52	34.65	55.0	16.4	25.0	3.5	28
17	40.88	3.20	41.74	73.4	11.1	13.8	1.8	14

It will be noted from Table I that the initial and final pressures measured with the bulb at room temperature were only 1 to 2 cm. apart, despite the

2 to 4 cm. (measured at liquid nitrogen temperature and therefore corresponding to 6 to 12 cm. at room temperature) of hydrogen generated. (Note: the vapor pressure of methane at liquid nitrogen temperatures is 1.1 cm. of mercury.) It is apparent therefore from stoichiometric considerations alone that since no carbon or tarry matter was formed, considerable quantities of ethane must have been produced. The gas analyses of Table I are calculated upon the assumption that ethane was the only saturated higher hydrocarbon present. A comparison of the hydrogen content with the percentages of ethane and unsaturated hydrocarbons indicates that the latter are largely ethylene.

The data of Table II were obtained in a manner similar to that of Table I, except that the methane and hydrogen were pumped off while the bulb was still immersed in liquid oxygen or nitrogen. The temperatures were more accurately estimated in these experiments, this being effected by a change in experimental conditions which will be described in a later paragraph.

TABLE II

COMBUSTION RATIOS OF SATURATED HYDROCARBON GAS FORMED IN THE PYROLYSIS OF METHANE BY A CARBON FILAMENT

			Analysis of residual gas after removal of $CH_4 + H_2$				
			Unsaturated hydrocarbons				
Expt.	Filament temp., °C.	Cooling liquid around bulb	Absorbed by 1.6 sp. gr. H_2SO_4, %	Absorbed by K_2HgI_4, %	Absorbed by fuming H_2SO_4, %	Satd. hydrocarbons (ethane), %	Combustion ratio obtained for saturated hydrocarbon
49	1700	N_2	..	..	14.4	85.6	1.240
51	2000	N_2	..	..	26.5	73.5	1.270
53	1700	O_2	..	..	50.2	49.8	1.246
60	1700	N_2	..	..	4.2	95.8	1.250
62	1457–1700	O_2	0.0	8.2	44.6	47.2	1.262
63	1457–1700	O_2	.3	7.9	38.5	53.3	1.256
64	1457–1570	O_2	.0	6.4[a]	14.2	79.4	1.251

[a] Absorbed by copper ammonium chloride.

An inspection of the data of Table II shows that the combustion ratios (contraction/carbon dioxide) for the saturated hydrocarbon are reasonably close to the theoretical for ethane, which is 1.250. It should also be noted that the unsaturated hydrocarbons appear to be largely ethylene. No confidence can, however, be placed in the figures for acetylene (absorption by K_2HgI_4), although it is probable that they are not more than 100% in error. Table II also shows that much larger amounts of unsaturates are formed when liquid oxygen instead of nitrogen is used.

Table III shows that very little if any excess hydrogen (and hence no carbon or tars) is produced during the pyrolysis in a bulb immersed in liquid oxygen or nitrogen. The 1.5% excess of experiment 62 is not significant considering the probable inaccuracy of the acetylene figure.

TABLE III

HYDROGEN BALANCE IN THE PYROLYSIS OF METHANE IN A CARBON FILAMENT LAMP IMMERSED IN LIQUID OXYGEN OR NITROGEN

Expt.	Analysis of product calculated on CH_4-free basis, % H_2	C_2H_6	C_2H_4	C_2H_2	Hydrogen excess, %	Filament temp., °C.	Cooling liquid around bulb
51	54.5	36.5	9.0	Trace	0.0	2000	N_2
62	60.3	18.8	17.7	3.2	1.5	1570–1700	O_2

The Order and Heat of Activation of the Decomposition Reaction.—To determine the effects of the pressure of methane and the filament temperature on the rate of the pyrolysis three series of experiments were made. In the first series the lamp was immersed in liquid oxygen, in the second in a bath of alcohol plus solid carbon dioxide, and in the third in an ice plus water-bath. These will be described in the order mentioned.

Experiments Using Bath at −183°.—It would, at first thought, seem possible to measure the hydrogen pressure due to the decomposition of methane by a carbon filament with the bulb immersed in liquid oxygen, so that all of the products of the reaction other than hydrogen were frozen out. It was, however, found that little change in pressure was obtained when the initial methane pressure was below its saturation value. Ethane, ethylene and acetylene were formed, and since the relative amounts of these varied considerably with the filament temperature and somewhat with the initial pressure of methane, it was not possible to interpret the small pressure changes without an analysis of the products. If an excess of methane was used so that the gas was always at saturation pressure by being in contact with solid methane, it was found that the ethane and ethylene formed during the pyrolysis markedly altered the equilibrium pressure of methane, so that any rate measurements made in the presence of solid methane could not be correlated with a definite pressure of methane.

The procedure finally adopted for the rate measurements may be briefly described as follows.

To the carbon filament lamp previously described was sealed a 15 by 3.8 cm. sight tube, the latter being concentric with the long axis of the lamp. This apparatus was placed in a 14 by 51 cm. Dewar tube, and connected with the rest of the apparatus (manometer, methane reservoir, etc.) by means of 3.2 mm. glass tubing. An optical pyrometer was mounted 25 cm. above the top of the sight tube, the telescope being placed inside a 5-cm. glass tube, the lower end of which was about 2.5 cm. below the top of the sight tube. Since the latter was kept immersed in liquid oxygen to within 1.4 cm. of the top, the 5-cm. tube dipped into the liquid oxygen. In this fashion moisture condensation on the top of the sight tube and on the telescope lens was effectively avoided. The total volume of the lamp plus the connections to the manometer, etc., was 515 cc. Of this volume about 475 cc. was immersed in liquid oxygen, approximately 10 cc. being contained in that portion of the sight tube above the bath level, and the remaining 30 cc. consisted of the volume of the connecting tubes to the rest of the apparatus.

Pure methane was admitted to the previously evacuated reaction vessel. After reading the initial pressure and the barometric pressure, the filament was ignited and

the temperature adjusted to the desired point by varying the resistances in circuit with the filament. The filament was then extinguished and the reaction vessel again evacuated and subsequently refilled with methane to the same pressure as that used to obtain the proper rheostat adjustments for the desired temperature. The filament was then again ignited, the operating pressure measured, and the time interval measured from the moment of ignition of the filament. During most of the time interval the filament was under constant observation and small adjustments of temperature were made when necessary. At the end of the time interval, the filament current was turned off, the final pressure measured, and the mixture of hydrogen and methane pumped off with a Töpler pump, its volume and hydrogen content being subsequently determined. The residual (ethane, ethylene and acetylene) mixture was permitted to accumulate for several experiments before being collected and analyzed. The results are given in Table IV.

TABLE IV

RATE OF DECOMPOSITION OF METHANE IN A CARBON FILAMENT LAMP IMMERSED IN LIQUID OXYGEN

Total volume of reaction vessel, 515 cc.

Expt.	Pressure measurements, cm. Initial	Operating	Final	Time of experiment, minutes	Rate of reaction: cc. (at 25° and 74 cm.) of hydrogen per minute	Rate of reaction per cm. of operating pressure × 100
		(a) Temperature, 1700°				
66A	0.50	0.83	0.50	2	0.65	78
66B	0.74	1.24	0.74	2	.95	77
65A	2.38	5.38	2.42	2	4.35	81
63C	3.24	6.34	3.31	3	5.40	85
62B	3.33	6.54	3.23	3	5.60	86
65B	4.29	8.80	4.55	2	7.75	88
65C	6.31	11.20	7.16	2	13.10	117
63G	6.01	11.59	7.44	2	26.80	231
66C	6.40	14.00	7.90	2	49.50	354
66D	6.21	16.85	9.15	2	50.50	300
66E	8.43	23.63	13.03	2	92.75	394
		(b) Temperature, 1570°				
63A	1.20	1.75	0.97	10	0.36	20.6
64A	1.20	2.10	1.18	5	.48	22.8
63B	3.37	6.43	3.26	5	2.98	41.4
62G	3.26	6.50	3.32	10	2.60	40.0
64C	5.37	8.57	5.41	2	3.85	45.0
64D	6.46	9.59	6.59	2	5.40	57.0
		(c) Temperature, 1457°				
64F	1.14	1.64	0.94	60	0.10	6.1
65D	2.28	4.22	2.32	20	.225	5.3
64E	3.13	6.35	3.17	10	.32	5.0
65E	4.28	7.30	4.48	10	.605	8.3
63H	6.12	8.32	6.08	20	.66	7.9

Before discussing the data of Table IV, it is desirable to indicate the composition of the higher hydrocarbons produced in the pyrolysis at various temperatures. This is done in Table IVd.

TABLE IVd

COMPOSITION OF HIGHER HYDROCARBONS PRODUCED IN THE PYROLYSIS OF METHANE BY A CARBON FILAMENT LAMP IMMERSED IN LIQUID OXYGEN

Temp. range, °C.	Operating pressure range, cm.	Average composition of hydrocarbon products, % C_2H_2	C_2H_4	Higher olefins	C_2H_6
1700	1–9	38.4	35.3	1.1	25.2
1700	11–23	68.7	25.7	0.9	4.7
1457–1500	2–10	6.4	14.2	...	79.4

In considering the data of Table IVa it should be noted that the rate constants for operating pressures greater than 9 cm. are not directly comparable with the others, for almost twice as much acetylene was produced in the 11–23 cm. range as in the 1–9 cm. The figures for the 11–23 cm. range should be divided by the factor 1.34 in order to be comparable with those for the lower pressures. This correction, however, does not affect materially the general trend of the constants, which indicate a first-order reaction in the low-pressure range, but this increases to almost second order in the 11–23 cm. range. The data of Tables IVb and IVc indicate an increase in the order of the reaction with increasing pressure.

With regard to the heat of activation of the reaction, the results at 1457 and 1570° are comparable, but neither of these are directly comparable with the 1700° data. The latter, in the 1–9 cm. pressure range, indicate that about 1.7 times as much hydrogen per mole of methane reacted was produced as compared with the 1457–1570° results. The data on the heats of activation are summarized in a later section which includes similar calculations from the data of Tables V and VI where solid carbon dioxide plus alcohol and ice plus water, respectively, were the cooling agents.

Experiments Using Bath at −78°.—In the experiments of Table V a mixture of ethyl alcohol and solid carbon dioxide was used as the cooling bath. Because of the frothing of this mixture it was found necessary to seal the 5-cm. tube containing the pyrometer telescope onto the 3.8-cm. sight tube of the reaction vessel with paraffin in order to maintain clear visibility. Since the reaction under these conditions proceeds almost completely to carbon and hydrogen, pressure measurements were a reliable index of the rate.

Table V also indicates a first-order reaction at the lower pressures with an increase toward second order at the higher pressures. In order to compare the rates of Table V with those of Table IV the pressure increases per minute per cm. operating pressure of Table V must be multiplied by a factor which will convert these pressure increases to cc. of hydrogen at 25° and 74 cm. pressure, and which will also take care of the differences in character of the products of Table IV as compared with Table V. This factor for the 1700° data of Table V is 11.3 for comparison with the 1–9 cm. range of Table IV, and 14.0 for comparison with the 11–23 cm. range. The

TABLE V

RATE OF DECOMPOSITION OF METHANE IN A CARBON FILAMENT LAMP IMMERSED IN AN ALCOHOL PLUS SOLID CARBON DIOXIDE BATH

Total volume of reaction vessel, 515 cc.

Expt.	Pressure measurements, cm. Initial	Operating	Final	Time of expt., minutes	Pressure increase per minute	Pressure increases/min per cm. Initial × 100	Operating × 100
		(a) Temperature, 1700°					
67A	1.51	2.20	1.87	3	0.120	7.96	5.47
67B	2.49	3.75	2.94	2	.225	9.03	6.00
67C	4.67	6.90	5.40	2	.365	7.80	5.27
67D	4.19	7.07	5.13	2	.470	11.17	6.12
67E	9.03	14.81	10.95	2	.960	10.65	6.50
67F	8.63	14.83	11.00	2	1.185	13.75	7.98
67G	16.64	32.47	22.81	2	3.085	18.53	9.50
		(b) Temperature, 1570°					
68A	0.76	0.99	0.90	10	0.014	1.84	1.42
68B	1.86	2.50	2.01	5	.030	1.61	1.20
68C	2.08	2.93	2.23	5	.030	1.44	1.02
68D	2.28	3.20	2.43	5	.032	1.40	1.00
68E	4.36	6.07	4.68	5	.064	1.47	1.05
68F	4.30	6.20	4.70	5	.080	1.85	1.28
68G	8.80	13.75	9.89	5	.218	2.48	1.58
68H	16.33	26.95	19.49	5	.632	3.87	2.34
68I	33.66	55.51	39.37	2	2.855	8.45	5.13
		(c) Temperature, 1457°					
69A	4.02	5.74	6.04	15	0.020	0.50	0.35
69B	8.47	13.03	9.13	15	.044	.52	.34
69C	8.87	13.45	9.52	15	.043	.49	.32
69D	16.36	26.27	17.43	5	.214	1.31	.80
69E	33.01	52.82	37.77	5	.952	2.88	1.80

factor for the 1457 and 1570° data of Table V is 6.7. Using these factors one notes that the 1457 and 1570° rates of Table V are 3 to 5 times smaller than those of Table IV, and that there is approximate agreement at 1700° in the 1–9 cm. range, whereas the rates of the 11–23 cm. range of Table V are smaller by a factor of about two. If, however, one compares operating concentrations instead of operating pressures of methane these differences are reduced by a factor of about 2.2, which results in fair agreement for the 1457° and the 11–23 cm. range at 1700° rates of the two tables. The 1–9 cm. rates at 1700° of Table V are now about 60% higher, and the 1570° rates about 50% smaller than those of Table IV. These differences are, however, within the limits of reproducibility of the data, and one can therefore say that there is approximate agreement between the rates of the pyrolysis of methane when conducted so that the primary products are rapidly removed and when the latter are permitted to react further so as to produce mainly carbon and hydrogen. This point is of considerable

importance for the agreement, although only approximate, indicates that the secondary reactions which ethane initiates are of minor importance in controlling the rate of the reaction in the presence of only small amounts of hydrogen. A later section will show that the secondary reactions become important when appreciable quantities of hydrogen are present.

Experiments with Bath at 0°.—The procedure and apparatus used with ice plus water as the fluid surrounding the reaction vessel were identical with those for liquid oxygen. The products of the reaction with the 0° bath were largely carbon and hydrogen. The results are given in Table VI.

TABLE VI

RATE OF DECOMPOSITION OF METHANE BY A CARBON FILAMENT LAMP IMMERSED IN AN ICE PLUS WATER BATH

Total volume of reaction vessel, 515 cc.

Expt.	Pressure measurements, cm. Initial	Operating	Final	Time of expt., minutes	Pressure increase per minute	Pressure increases per minute per cm. Initial × 100	per cm. Operating × 100
		(a) Temperature, 1700°					
70A	2.19	2.95	2.70	2	0.255	11.65	8.65
70B	4.27	5.97	5.15	2	.440	10.30	7.38
70C	4.37	6.07	5.40	2	.515	11.78	8.48
70D	8.32	12.25	10.95	2	1.315	15.80	10.73
		(b) Temperature, 1570°					
71A	1.56	2.02	1.80	5	0.048	3.08	2.37
71B	4.42	5.89	4.92	5	.10	2.26	1.70
71C	8.46	11.51	9.41	5	.19	2.25	1.65
71D	16.89	24.32	19.74	5	.57	3.38	2.34
71E	33.25	50.20	40.50	2	3.625	10.9	7.22
		(c) Temperature, 1457°					
72A	4.29	5.41	4.51	15	0.015	0.350	0.277
72B	4.26	5.51	4.54	15	.019	.446	.345
72C	8.61	11.22	9.07	15	.031	.360	.276
72D	16.40	21.93	16.76	5	.072	.433	.324
72E	33.62	45.36	36.27	5	.530	1.575	1.462

The data of Table VI also indicate a first-order reaction at the lower pressures, and an increase toward second order at the higher pressures. Upon comparing Tables V and VI it will be noted that there is fair (within about 25%) agreement at 1700 and 1457°, and at 1570° in the 11–50 cm. operating pressure range, whereas in the 2–6 cm. range the rates of Table VI are about twice those of Table V. If operating concentrations instead of pressures are compared (the factor between 0 and −78° is 1.4), the agreement is generally poorer, but except for the 2–6 cm. range at 1570° the rates agree within a factor of about 2.

Heat of Activation of the Reaction.—In order to facilitate the calculation of the heat of activation the rate data were plotted against the operat-

ing pressures using the data of Tables IV, V and VI. Extrapolation of the curves to very low pressures yielded the data given in Table VII. It should be noted that the 1700° rate resulting from the extrapolation of the data of Table IV must be divided by 1.7 so as to make this datum comparable with the rates at 1457 and 1570°. The nine heats of activation calculated from the extrapolated rate constants are also presented in Table VII.

TABLE VII

(A) EXTRAPOLATED RATE CONSTANTS × 100

Temp., °C.	Extrapolation of data from Table no. 4	5	6
1700	76.5/1.7	5.7	8.2
1570	22.0	1.1	1.8
1457	5.0	0.4	0.27

(B) HEATS OF ACTIVATION

Temp. intervals, °C.		Calories per mole of methane 4	5	6
1700–1570		40,900	91,350	84,050
1570–1457		83,000	56,700	108,000
1700–1457		60,750	74,050	95,700
	Averages	61,550	74,030	95,920

There appears to be a trend in the heat of activation in going from the liquid oxygen bath to the solid carbon dioxide plus alcohol and ice plus water baths. It is difficult to see any reason for expecting such a change in the heat of activation in view of the approximate agreement (within a factor of about two) of the rates of Tables IV, V and VI. Hence the writer is disposed to average all of the values of Table VII for the heat of activation. This yields 77,170 calories with an average deviation of 16,950 calories from the mean. The probable error of the mean is about 10,000 calories, and hence the heat of activation may be written as 77,170 ± 10,000 calories.

Effect of Hydrogen on the Rate.—If one accepts the mechanism of the thermal decomposition suggested by L. S. Kassel,[4] namely

$$CH_4 \rightleftharpoons CH_2 + H_2 \quad (1)$$

$$CH_2 + CH_4 \rightleftharpoons C_2H_6 \quad (2)$$

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \quad (3)$$

$$C_2H_4 \rightleftharpoons C_2H_2 + H_2 \quad (4)$$

$$C_2H_2 \longrightarrow 2C + H_2 \quad (5)$$

then the equation for the rate of generation of hydrogen is

$$\frac{d(H_2)}{dt} = \frac{a(CH_4)^2}{b(CH_4) + c(H_2) + d(H_2)^2 + e(H_2)^3} \quad (6)$$

where a, b, c, d and e are constants. Hence for experiments at constant pressure of methane, the rate at very low concentrations of hydrogen reduces to

$$\frac{d(H_2)}{dt} = \frac{K}{K' + K''(H)^2} \quad (7)$$

At higher pressures of hydrogen the square and cube of the hydrogen pressure will be the important terms in the denominator of equation (6).

Equation (7) indicates that a straight line should be obtained when the reciprocal of the rate of hydrogen generation at constant methane pressure is plotted against the hydrogen concentration. Such a straight line should extend for a distance corresponding to small values of (H_2). For higher values of the hydrogen concentration, equation (6) indicates that the curve should bend fairly sharply toward the axis on which the reciprocal of the rate is measured.

In Expts. 33 and 34 the methane pressure was held constant by attaching a small (10-cc.) bulb to a carbon filament lamp[5] and keeping the bulb immersed in liquid nitrogen. The lamp itself was at room temperature when the pressure readings were made at the end of each time interval. The 10-cc. bulb was several cm. off to one side of the lamp so that the cold nitrogen gas did not affect the temperature of the former appreciably. Under these conditions the products of the reaction were mainly carbon and hydrogen. The results are listed in Table VIII. The total volume of the reaction system in these experiments was 270 cc. and the room temperature 22 ± 3° (corrections were made for fluctuations in room temperature during each experiment).

TABLE VIII

DATA CONCERNING EFFECT OF HYDROGEN ON RATE

Total volume of reaction vessel, 270 cc.

Experiment No. 33 Temperature, 1570°		Experiment No. 34 Temperature, 1800°	
Pressure of hydrogen, cm.	Rate of pressure increase, cm./min.	Pressure of hydrogen, cm.	Rate of pressure increase cm./min.
0.06	0.02	0.085	0.17
.19	.014	.24	.13
.33	.014	.36	.12
.66	.009	.49	.07
1.15	.008	.68	.05
1.52	.0056	.92	.044
1.68	.0047	1.13	.038
1.82	.0040	1.38	.031
		1.67	.028
		2.01	.021
		2.48	.014

A plot of the data of Table VIII indicates that the data up to about 1 cm. pressure of hydrogen (H_2/CH_4 = about 0.9) do seem to form a straight line and that the curve swings upward very rapidly when the H_2/CH_4 ratio becomes greater than unity.

[5] Rate measurements with appreciable amounts of hydrogen present could not be made with the lamp completely immersed in liquid nitrogen, because the conduction of heat by the hydrogen raised the temperature of the solids (CH_4, C_2H_6, C_2H_4) and made the pressure of CH_4 uncertain.

Discussion

The increase in the apparent order of the decomposition of methane from first to about second with increase in methane pressure beyond about 8 cm. may conceivably be due to a large change in the temperature gradient in the immediate vicinity of the hot filament. Unfortunately it does not seem possible to obtain unequivocal criticisms of this possibility by a mathematical analysis of the flow of heat from the filament at various pressures of methane. The rate measurements made at pressures higher than about 8 cm. are generally not reproducible, whereas those below that pressure are readily reproduced within a factor of about 2.

The mechanism suggested by L. S. Kassel[4] accounts satisfactorily for the first order of the reaction when measurements are made at low concentrations of hydrogen and approximately constant $(H_2)/(CH_4)$ ratio, which is true of the data given in Tables IV, V and VI at methane pressures less than about 8 cm. This mechanism also predicts the shape of the curves obtained by plotting the data of Table VIII for the effect of hydrogen pressures on the rate.

Summary

The earliest product of the thermal decomposition of methane which has been isolated is shown to be ethane. In one experiment as much as 95% of the theoretical yield of ethane was obtained, by the decomposition of methane in a carbon filament lamp immersed in liquid nitrogen.

The thermal decomposition of methane by a carbon filament was found to be a first-order reaction at methane pressures from 1 to about 8 cm., the heat of activation being 77,170 ± 10,000 calories per mole. Above 8 cm. methane pressure the order increases to about second. Since no such increase is observed in isothermal static experiments, it seems probable that the increase is due to a rapid change in the temperature gradient in the immediate vicinity of the filament.

The influence of hydrogen on the rate of the decomposition was studied and the data obtained can be satisfactorily explained by a rate equation (derived by L. S. Kassel) based on a number of successive dehydrogenation steps following the initial synthesis of ethane.

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

RAMAN SPECTRA STUDIES.[1] I. DIPHENYLMETHANE, ALIPHATIC BROMIDES AND MERCAPTANS

BY ELIZABETH A. CRIGLER

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Introduction

During the past five years experimental investigations and theoretical development of the Raman effect have contributed much to our knowledge of the structure and chemical behavior of molecules by identifying Raman lines with the chemical bond.[2] The energy changes represented by Raman lines were early associated with fundamental molecular frequencies,[3] and the relation of Raman frequencies to the vibrational energy of the molecule has recently been presented and discussed by Andrews.[4]

The present work includes a study of the Raman spectra of diphenylmethane, normal butyl and normal hexyl bromides, and normal amyl, normal hexyl, and normal heptyl mercaptans. It was suggested by the important function of Raman data in specific heat determinations and in the calculation of thermal energy associated with the vibrations of the different parts of the molecule.[5]

Apparatus

Light Source and Light Filter.—A helium spiral discharge tube similar to the one described by Wood,[6] and made by the Claude Neon Company of Baltimore, furnished the light for exciting the Raman lines recorded for diphenylmethane. The copper gauze electrodes of this discharge tube were connected to an oil transformer which converted the 220 volts across the alternating circuit to approximately 20,000 volts. The helium line, λ 3888.6, was transmitted by a nickel oxide glass filter.

A Cooper-Hewitt quartz mercury arc, maintained between 35 and 45 volts, was used to excite the Raman lines of all other substances. An aluminum reflector concentrated the mercury light on the Raman tube. In some instances the 4046 mercury group was eliminated by a 0.5% acid quinine sulfate filter.

An iron arc, taking 4 or 5 amperes, furnished comparison spectra for measuring the Raman lines.

Raman Tube.—The Raman tube, similar to those used by Wood, was 2.5 cm. in

[1] From the dissertation submitted by Elizabeth A. Crigler to the Faculty of Philosophy, The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Andrews, *Phys. Rev.*, **36**, 544 (1930); Bhagavantam, *Indian J. Physics*, **5**, 237 (1930); Kohlrausch, "Der Smekal-Raman Effekt," Julius Springer, Berlin.

[3] Raman, *Indian J. Physics*, **2**, 387 (1928); Raman and Krishnan, *Nature*, **122**, 278 (1928); Coblentz, *Phil. Mag.*, **7**, 203 (1929).

[4] Andrews, *Ind. Eng. Chem.*, **23**, 1232 (1931).

[5] Andrews and Southard, *Phys. Rev.*, **35**, 670 (1930); Smith and Andrews, THIS JOURNAL, **53**, 3644 (1931); Smith and Andrews, *ibid.*, **53**, 3661 (1931); McGraw, *ibid.*, **53**, 3683 (1931).

[6] Wood, *Phil. Mag.*, **7**, 859 (1929).

diameter and had a capacity of 60–65 cc. Instead of grinding a plane face on the end of the tube after it was made, a thin piece of glass, plane on both sides, was fused to the end. To prevent stray light from fogging the spectra, the tapered end and all parts of the tube not directly illuminated by the arc were either painted black or wrapped with black tar tape.

Spectroscope.—A Hilger quartz spectroscope was used with the helium discharge tube. A Bausch and Lomb glass prism spectroscope was used to analyze the light from the mercury arc.

Comparator.—The Raman lines were measured with a traveling micrometer by comparison with known iron lines. These readings plotted against the international standard wave lengths for the iron lines enabled one to interpolate with fair accuracy the wave lengths of the Raman lines.

Materials.—Normal butyl and normal hexyl bromides were compounds which have been previously described by R. F. Deese.[7] The mercaptans were pure compounds kindly loaned by Professor E. Emmet Reid and Doctor L. M. Ellis, Jr.[8]

Hammer Press Ultra Rapid plates, Agfa developer, and Eastman "hypo" were used in photographing the Raman spectra.

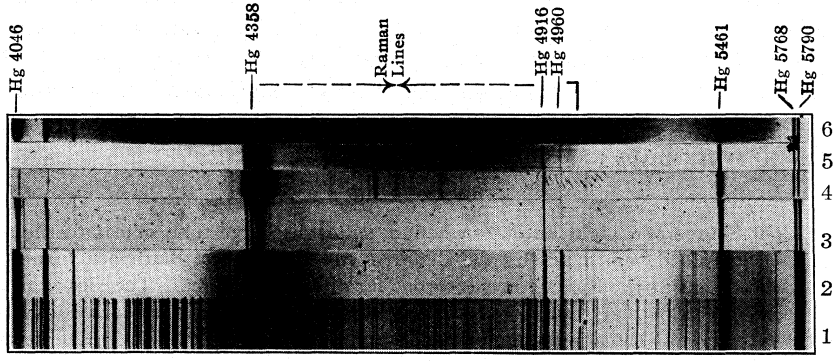

Plate I.—Comparison of spectra: 1, iron arc; 2, Hg arc (slit wide); 3, Hg arc (slit narrow); 4, benzene (quinine sulfate filter); 5, butyl bromide (quinine sulfate filter); 6, butyl bromide (no filter).

Technique and Procedure.—In general, Wood's method for obtaining Raman spectra was followed. In the set-up with the helium discharge tube, the Raman tube containing the diphenylmethane was slipped within the helium spiral, so that the substance under investigation was illuminated only by light passing through the nickel oxide glass filter. Forty-eight hour exposures were made. The photographic plates were backed with Duco enamel to prevent halation around the intense lines.

As the nickel oxide glass transmitted other helium lines, λ 3965 and λ 4045, falling in the same region as the Raman lines excited by the 3888.6 helium line, and since the Raman lines excited by the helium discharge tube were not as intense as those excited by the mercury arc, the latter was adopted as source of excitation for the remaining work.

In the set-up with the mercury arc the distance between the Raman tube and the spectroscope was 84 cm. The light coming from the face of the Raman tube was reflected by a small right angle prism down a long black iron tube to a double convex

[7] Deese, THIS JOURNAL, **53**, 3673 (1931).

[8] Ellis and Reid, *ibid.*, **54**, 1674 (1932).

lens which concentrated the light and focused a bright image of the prism face on the slit of the spectroscope. The prism was placed in a pasteboard box which fitted over the face of the Raman tube and the end of the iron tube in order to prevent reflection of stray mercury light.

Several preliminary experiments with the mercury arc showed the difficulties encountered in using the complete mercury spectrum. Most of the compounds investigated gave a continuous background in the presence of the 4046 mercury group. To eliminate this background the short-wave length mercury lines were absorbed by an acid quinine sulfate filter. The effect of this filter is shown in Plate I. The solution of quinine sulfate was slowly decomposed by the ultraviolet light from the quartz mercury arc, but by allowing it to circulate through a copper coil surrounded by a jacket containing ice and salt, the rate of decomposition was retarded sufficiently to allow time for an exposure of several hours.

Results

The third column in Table I gives the Raman lines for diphenylmethane. Photographs of these lines excited by the mercury arc were taken also; however, the lines were accompanied by such a dark continuous background that only results obtained with the helium discharge tube have been recorded. The diphenylmethane which was colorless

TABLE I

COMPARISON OF RAMAN LINES OF DIPHENYLMETHANE WITH THE RAMAN LINES OF COMPOUNDS OF SIMILAR STRUCTURE

Values given in wave numbers $[\Delta\tilde{\nu}] = \left[\frac{1}{\lambda_{ex}} - \frac{1}{\lambda_{Ra}}\right]$ cm.$^{-1}$

Ethylbenzene[a]	Diphenyl ether[b]	Diphenylmethane	Methane[c] (liq.)
153	231	178 (broad)	
482	309	468 (He)	
547		520	
620	615	599	
768	748	722	
962	794	791	
1003	1005	971	
1029	1021		
1157	1153		
		1170	
1203	1195		
1384			
1440		1425	
1604	1590		
		1659 (broad)	
2933		2898	2909
			2953
2962			2999
3002			3023
3052		3038 (broad)	3047
3063	3062		3071

[a] Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 329, $[\Delta\tilde{\nu}]$ = mean value.

[b] Kohlrausch, *ibid.*, p. 332.

[c] McLennan, Smith and Wilhelm, *Trans. Roy. Soc. Canada*, **23**, 279 (1930).

under ordinary conditions became yellow when exposed to the light of the mercury arc. This color disappeared when the substance was distilled *in vacuo*, but returned again upon exposure to the mercury light.

Results for normal butyl and normal hexyl bromides are recorded in Tables II and III. Plate I shows the rapid decomposition of the bromide under strong illumination both with and without the quinine sulfate filter. By cooling the Raman tube with water passed through a copper coil, a photograph of butyl bromide was obtained which showed a comparatively weak background and, therefore, could be used for measuring the Raman lines excited by both the 4046 and the 4358 mercury groups. A comparison of these lines with the ones given by Kohlrausch[9] is found in Table II. Hexyl bromide, illuminated with the use of a filter, gave the lines recorded in Table III. In Tables IV and V are listed the wave lengths and wave numbers for the Raman lines of normal amyl, normal hexyl and normal heptyl mercaptans together with the frequencies of the Raman lines of isoamyl and normal butyl mercaptans studied by Venkateswaran.[10]

TABLE II

RAMAN LINES OF NORMAL BUTYL BROMIDE

Exc. Hg line 4358.6 λ_{Ra} Å.	4358.6 $\Delta\tilde{\nu}_{Ra}$	4046 $\Delta\tilde{\nu}_{Ra}$	$\Delta\tilde{\nu}_{Ra}$ (K)[a]
4407.5–4411.2	254– 274	271– 291	279 (2)
4431.5	377	394	
4442.0–4447.5	431– 458	448– 475	
4462.3–4468.5	533– 564	550– 581	557 (5)
4479.5–4483.5	619– 639	636– 656	637 (2)
4503	736	753	
			794 (1/2)
4512	780	797	
			853 (1/2)
4524.5	841	858	
			1057 (1/2)
4598.3	1196	1213	1139 (1)
4669 –4674	1526–1548	1543–1565	1257 (1b)
			1440 (2b)
4969.5–4997.5	2819–2933	2836–2950	
			2865 (5)
			2930 (3)
			2962 (4)

[a] (K) = Kohlrausch, "Der Smekal-Raman Effekt," p. 308.

Discussion

Studies of Petrikaln and Hochberg[11] show no Raman lines but continuous spectra for solutions of diphenylmethane in alcohol and triphenylmethane

[9] Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 329.

[10] Venkateswaran, *Indian J. Physics*, **5**, 219 (1930).

[11] Petrikaln and Hochberg, *Z. physik. Chem.*, **B3**, 217 (1929).

TABLE III

RAMAN LINES OF NORMAL HEXYL BROMIDE

Exciting line = Hg 4358.6

w = weak s = strong

λ_{Ra} Å.	$\Delta\nu$
4387	149 (w)
4409.8	267 (w)
4432	380 (w)
4458	512 (s)
4468.5–4471.8	564–581 (s)
4480.5	626 (w)
4484.8–4489.2	644–668 (s)
4492	682 (w)
4497.5	708 (w)
4503.7	739 (w)
4508.6	764 (w)
4521.5	826 (w)
4529 –4536.7	864–901 (s)
4552	977 (s)
4572.6–4583.5	1074–1126 (s)
4593.5	1173 (w)
4603	1219 (w)
4613	1266 (s)
4623.8	1316 (s)
4630	1345 (w)
4640	1396 (w)
4650.3–4658	1439–1475 (s)
4927	2647 (w)
4937.5	2690 (w)
4877.5–5010.5	2853–2985 (s)
5021	3027 (s)

TABLE IV

RAMAN LINES OF MERCAPTANS

[λ in Ångström Units]

n-Amyl	*n*-Hexyl	*n*-Heptyl
4387.6		4409
4424.8	4425.7	4430.5
4456	4457.5	4445.8
4474	4479	4461.5
4484 –4488.5	4485.6–4491.5	4469.6
4496	4497.3	4478.8
4508.3	4505.2	4487.5–4491.7
4520	4517.7	4498.8
4532.6	4521.2	4507
4537.8	4534.6	4517.4
4556.8	4539	4525
4566.8	4553.5	4537
4572.3	4576.3	4576.3
4580.2	4584.3	4585.6
4598.2	4592	4594.3
4606.5	4600.3	4600.3
4612	4613.2	4614.5
		4620.7
4621.7	4624	4624.8
4628.6	4635.4–4643.4	4628
4643		
4648.6–4654.5	4650.2–4658.4	4634
4665.6	4672.8	4646
4896	4903.2	4651.2–4662.3
4908.5	4910.8	4901
4926		
4936.5	4927.5	4910.6
4952	4957.5	4944.5
4970.5	4974.5	4955
4977 –4989	4979 –5002.5	4978 –5014.5
5011.5–5015.5	5010.7	
5024	5019.5	5025

in ether. However, in the present case, when diphenylmethane was illuminated by the helium line, λ3888.6, a continuous background did not accompany the Raman spectrum.

Calculated frequencies for the stretching and bending of non-polar chemical bonds have been identified with known Raman lines.[12] A comparison of the Raman lines for diphenylmethane with those for diphenylether, ethylbenzene and methane, obtained by other investigators, shows definitely that certain frequencies can be attributed to vibrations of particular molecular groups and linkages. The lowest frequency, 178 cm.$^{-1}$ which does not appear in methane, has a corresponding value in ethylbenzene and diphenyl ether. This frequency is attributed to the bending of the

[12] Andrews, *Phys. Rev.*, **36**, 544 (1930).

TABLE V

RAMAN LINES OF MERCAPTANS

$$[\Delta\nu] = \left[\frac{1}{\lambda_{ex.}} - \frac{1}{\lambda_{Ra}}\right] \text{cm.}^{-1}$$

b = broad. V = Venkateswaran, *Ind. J. of Phys.*, **5**, 219 (1930).

n-Amyl	Isoamyl[V]	*n*-Hexyl	*n*-Butyl[V]	*n*-Heptyl
152	279 (5b)	348	298 (1)	262
343	422 (3b)		333 (2)	372
502		509	437 (0)	450
592		617	656 (6)	529
642–664	659 (5)	650–679	707 (0b)	570
701	719 (2)	708		616
761	741 (2)	747	843 (0)	659–680
819	818 (1b)	818		715
881	855 (0)	825	889 (0b)	755
906	929 (0)	891	951 (1)	807
998	955 (1)	912		
1046	1038 (0b)	982	1049 (1b)	844
1072	1114 (0b)	1091	1106 (0)	902
1110		1130		1091
1196	1185 (0b)	1166		1136
1235	1287 (1)	1205	1296 (2b)	
		1266		1177
1261	1300 (1)			1205
		1317		
1306	1337 (2)		1361 (0b)	1282
1338		1370–1407		1300
1405	1470 (6)	1439–1477		1321
1431–1459		1543	1438 (3b)	1336
1510		2548		1364
2519				1420
2570	2574 (10)	2580	2574 (10)	
2643		2649		1443–1494
				2539
2686		2772		2579
2749				2718
2824		2841		2762
2851–2899	2870 (10b)	2859–2945	2869 (8b)	
2989–3005	2929 (7b)	2986	2905 (7b)	2855–3001
3039	2962 (10b)	3021	2934 (10b)	3042

C–C–C linkage. Vibrational frequencies in the 900–1200 cm.$^{-1}$ region are associated with the stretching of the C–C bond, and occur in every case except methane. The calculated value for the H–C–H bending motion is 1430 cm.$^{-1}$. Ethylbenzene and diphenylmethane show Raman lines with frequencies of 1440 cm.$^{-1}$ and 1425 cm.$^{-1}$, respectively, whereas diphenyl ether shows no frequency in this region. The frequency 2898 cm.$^{-1}$ and the broad band at 3038 cm.$^{-1}$ indicate the difference between the C–H vibration of the aliphatic and aromatic linkages, both of which are present in diphenylmethane.

Differences in the values of corresponding Raman lines of butyl bromide, calculated from the two exciting mercury lines, Table II, are likely due to discrepancy in determining the true micrometer readings for the centers of the exciting mercury lines. The breadth and increased intensity of these lines toward the long wave length side make true readings difficult. This explanation is supported by the fact that practically the same variation occurs for each respective wave number. The wave numbers calculated from the 4046 mercury line agree more closely with the average values listed by Kohlrausch.[13] Greater accuracy is attained in measuring these lines since they fall in the shorter wave length region of higher dispersion than the Raman lines from the 4358 mercury line. Frequencies 1057 cm.$^{-1}$ and 1139 cm.$^{-1}$ recorded by other investigators for butyl bromide[13] were not found; however, hexyl bromide gave a broad line at 1074–1126 cm.$^{-1}$ and a less intense line at 1173 cm.$^{-1}$.

Mercaptans higher in the series than butyl mercaptan give at least twenty Raman lines. There seems to be only a slight increase in the number of lines after the molecule has added the fifth carbon atom to its chain. In Table V each group of values in brackets represents but one characteristic Raman frequency, as all values except the last in each group can be attributed to the 4339 and 4348 mercury lines found in the exciting mercury group. Raman and Krishnan[14] give 15, 30 and 200 as the relative intensities of the mercury lines λ 4339, λ 4347 and λ 4358. Therefore, duplication of weak- and high-frequency Raman lines by the two weak mercury lines seems improbable. Raman frequencies in the 2600 cm.$^{-1}$ region may be false, since there is a strong mercury line, λ 4916, in this region. The lines in the neighborhood of 2900–3000 cm.$^{-1}$ are very diffuse, and in the case of heptyl mercaptan completely overlap each other.

Several interesting relations from the data are noted. The close agreement in corresponding Raman lines for the mercaptans fails in the lower frequency region where the Raman frequencies characteristic of the wave motion of the molecule as a whole depend upon the length and modification of the carbon chain.[12] The C–S linkage has a strong characteristic frequency at approximately 600 cm.$^{-1}$ and two weaker vibrations in the 700 cm.$^{-1}$ region. The C–S linkage in thiophene, mercaptans and alkyl sulfides shows practically the same characteristic oscillations, namely, 607 cm.$^{-1}$ and 754 cm.$^{-1}$ for thiophene,[15] 659 cm.$^{-1}$ and 739 cm.$^{-1}$ for mercaptans,[16] and 651 cm.$^{-1}$ and 746 cm.$^{-1}$ for alkyl sulfides.[17] The single lines in both the 700 cm.$^{-1}$ and 300 cm.$^{-1}$ regions are replaced in the

[13] Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 308.
[14] Raman and Krishnan, *Indian J. Physics*, **2**, 399 (1928).
[15] Venkateswaran, *Indian J. Physics*, **5**, 145 (1930).
[16] Venkateswaran, *ibid.*, p. 219.
[17] Venkateswaran, *ibid.*, **6**, 51 (1931).

higher members of the mercaptans by two lines in each region. The S–H linkage at approximately 2575 cm.$^{-1}$ is identical with the S–H frequency of 2575 cm.$^{-1}$ for hydrogen sulfide.[18] This indicates that the frequency of vibration between these two atoms is negligibly affected by other atoms in the molecule. The lower frequency of the S–H linkage at 2575 cm.$^{-1}$ compared with the frequencies of the C–H and O–H linkages at 2930 cm.$^{-1}$ and 3388 cm.$^{-1}$, respectively, suggests a weaker binding force and more polar nature for S–H than for either C–H or O–H, and agrees with the fact that hydrogen sulfide and the mercaptans show acid properties not exhibited by water and the corresponding alcohols.

The author is grateful to Professor D. H. Andrews for his advice and encouragement during the course of the investigation. She wishes also to thank Professor R. W. Wood for the valuable suggestions which facilitated the experimental work.

Summary

The Raman spectra of diphenylmethane, normal butyl and normal hexyl bromides, and normal amyl, normal hexyl and normal heptyl mercaptans have been photographed and the corresponding lines measured. From a comparison of these lines with those of similar compounds several important relations have been noted.

Lines in the Raman spectrum of diphenylmethane exhibit frequencies characteristic of both aliphatic and aromatic linkages.

The number of Raman frequencies in the case of higher member mercaptans increases with the length of the carbon chain.

The respective values for the C–S and S–H vibrations are almost identical in thiophenes, mercaptans and the alkyl sulfides.

The S–H frequency at 2575 cm.$^{-1}$, lower than the corresponding C–H and O–H frequencies, indicates a fairly weak binding force and explains the slightly polar properties of hydrogen sulfide and the mercaptans.

BALTIMORE, MARYLAND

[18] Bhagavantam, *Nature*, **126**, 502 (1930).

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

RAMAN SPECTRA STUDIES.[1] II. THE RELATIVE INTENSITIES OF CHARACTERISTIC LINES IN RAMAN SPECTRA OF BENZENE–TOLUENE MIXTURES

BY ELIZABETH A. CRIGLER

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Introduction

Shortly after the discovery of the Raman effect, Daure[2] pointed out that the Raman spectrum of a mixture of benzene and toluene was the superposition of the spectra of the individual components. Dadieu and Kohlrausch[3] studied the Raman spectra of fifteen binary liquids and found no change in the characteristic frequencies of the components, except in a few cases where a slight shift occurred in a Raman line associated with a group having a high dipole moment.

Since the intensities of Raman lines produced under a given set of conditions depend upon the molecular density, it seemed probable that Raman spectra should prove useful not only for indicating the quality, but also for estimating the quantity, of substances present in mixtures. As previously noted[4] the Raman spectra of benzene–toluene mixtures of varying concentrations were photographed, the intensities of the lines recorded, and the relative heights of the intensity curves compared with the corresponding concentrations of the components taken. Benzene and toluene were chosen for this investigation, primarily because these substances furnish excellent Raman lines for intensity study; also, because they belong to a class of compounds commonly occurring in fractions of light oil mixtures.

In photographing Raman spectra for intensity measurements several factors which condition the density of spectral lines were considered. Experiments of Read and Johnson[5] show that the blackening produced on a photographic plate is a function of the intensity of light producing the blackening, the time of exposure, the wave length of light, the kind and age of the plate, and the conditions under which the plate is developed. Obviously, optimum results for the comparison study of Raman lines necessitated control of these variables. A method was adopted, therefore, by which as many conditions as possible could be maintained constant.

Apparatus.—The mercury arc was a Hanovia Advanced Research

[1] From the dissertation submitted by Elizabeth A. Crigler to the Faculty of Philosophy, The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Daure, *Compt. rend.*, **186**, 1833 (1928).

[3] Dadieu and Kohlrausch, *Physik. Z.*, **31**, 514 (1930).

[4] Crigler, *Phys. Rev.*, **38**, 1387 (1931).

[5] Read and Johnson, *Phil. Mag.*, **11**, 1152 (1931).

Model. This type, encased with a cooling coil and aluminum reflector and connected with a variable resistance, produced a steady light source for intensity work. The Raman tube was the same as used in Part I. Both the arc and Raman tube were cooled by a small electric fan. A Bausch and Lomb glass prism spectroscope analyzed the scattered light.

A Moll densitometer was used for recording the intensity of the Raman lines. The lines of each spectrum were focused on the face of the thermocouple tube and, as they passed between the light source and the slit of the tube, the intensity of the light falling on the thermocouple varied with the density of the intervening lines. The thermocouple was connected to a galvanometer, and every time a Raman line intercepted the light falling on the thermocouple the mirror of the galvanometer was deflected. This deflection was recorded by a narrow beam of light reflected from the mirror to photographic paper which was mounted on a revolving drum. The drum, in gear with the holder carrying the Raman plate, was run by an electric motor.

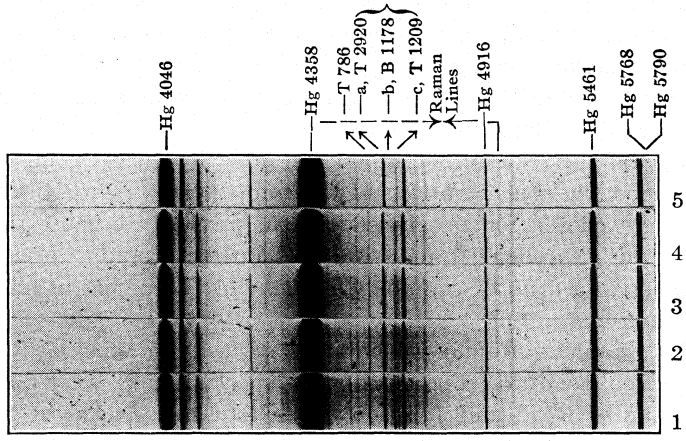

Plate I.—% Benzene–toluene: 1, B 0, T 100; 2, B 25, T 75; 3, B 50, T 50; 4, B 75, T 25; 5, B 100, T 0.

Materials.—Freshly distilled samples of Baker's C. P. benzene, specific gravity 0.88, and Baker's C. P. toluene, specific gravity 0.87, were used in making all mixtures.

The same kinds of photographic materials were used for this work as were used in Part I. Eastman's P. M. C. bromide paper, No. 2, smooth, was used in the densitometer for photographing the intensity curves.

Adjustment and collimation of the spectroscope were first secured. After the metal pieces forming the slit were carefully polished, and placed parallel to ensure spectral lines of uniform width, the spectroscope was leveled and the collimator and camera adjusted so that when the mercury

arc was placed in front of the spectroscope a horizontal spectrum of mercury lines was projected on the ground glass plate of the camera. The Raman tube, firmly supported by an iron clamp, was brought in line with the collimator by focusing an image of the tube in the center of the spectroscopic field. The light from the mercury arc was reflected back and forth through the liquid by a tin-foil reflector. The face of the Raman tube was almost tangent to the end of the spectroscope. This arrangement prevented stray light from entering the slit. The proximity of the tube to the spectroscope increased the intensity of the incident light.

After alignment of the apparatus, all parts except the Raman tube were left intact for each series of photographs made. In changing the material in the tube it was found more convenient to leave the tube clamped to the ring stand and to move the stand and Raman tube as a unit. In this way, each time the tube was emptied and refilled, it could readily be placed in the original position by adjusting the position of the stand. Shadows of the Raman tube formed on the box of the mercury arc and reflections from the uneven edges of the Raman tube face served as excellent reference marks for adjusting and replacing the tube.

The voltage across the mercury arc was regulated by a rheostat in series with the arc, and did not vary more than one or two volts during any exposure.

After the apparatus was in line with the spectroscope and the voltage across the arc carefully regulated, the width of the slit and time of exposure were varied alternately until a combination of the two yielded spectra showing marked and measurable variations with small changes in concentration. With two-hour exposures the best results were procured when the mercury arc was maintained at 50 volts, the temperature of the Raman tube was kept at 35°, and the width of the slit was 0.07 mm.

All plates were developed under the same conditions. The solutions used in developing and in fixing the image and the water used for washing the plates were kept at 0° by immersing the developing trays in an ice-bath. Each plate was developed for ten minutes in 100 cc. of Rhodinal solution, 1 to 20 dilution, then rinsed in ice

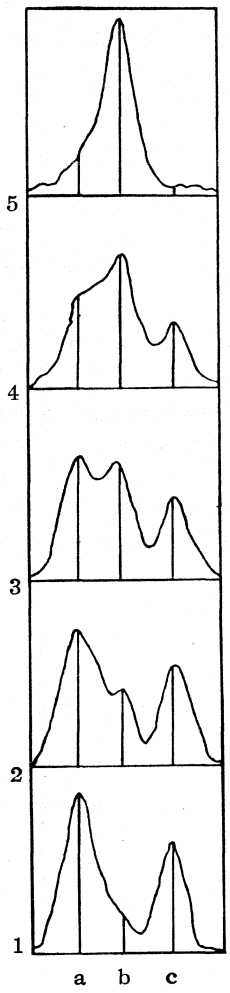

Fig. 1.—Section of photometric curve. % Benzene–toluene: 1, B 0, T 100; 2, B 25, T 75; 3, B 50, T 50; 4, B 75, T 25; 5, B 100, T 0. $\Delta\nu$ Raman line: a, T 2920 [Hg 4046]; b, B 1178 [Hg 4358]; c, T 1209 [Hg 4358].

water and fixed in a solution of Eastman's hypo for ten minutes. Care was taken to wash the plate free from the salt left by the hypo solution.

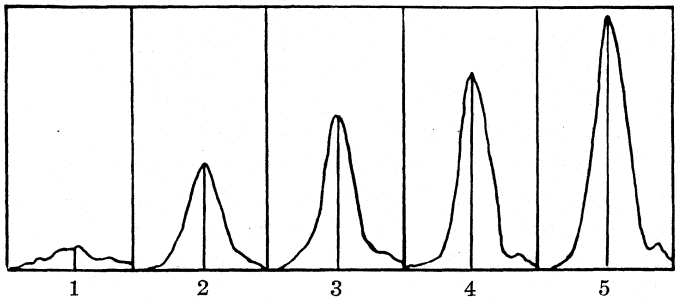

Fig. 2.—Intensity curve of toluene line $\Delta\nu$ 786. % Benzene–toluene: 1, B 100, T 0; 2, B 75, T 25; 3, B 50, T 50; 4, B 25, T 75; 5, B 0, T 100.

The trays in which the plate was developed were agitated to keep the solution constantly washing the gelatin surface in order to leave an even film on the glass. Plates treated in this manner and carefully dried showed a uniform, fine-grained background, with well-developed lines suitable for photometric measurements.

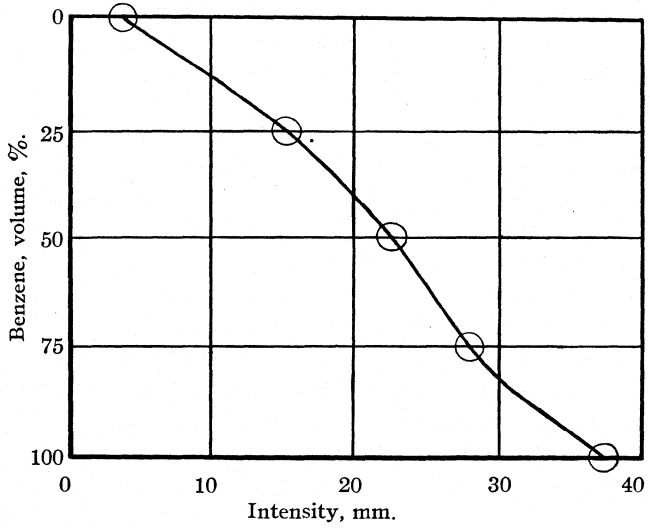

Fig. 3.—Relative intensity of characteristic benzene line [$\Delta\nu$ = 1158] with change in concentration.

In measuring the relative heights of the Raman lines the same horizontal section of each spectrum was chosen for each series of photographs in order that any gradation or imperfection in one spectrum, due to experimental conditions, would be recorded for every spectrum.

Halation around the stronger mercury lines and a slight continuous background prevented the use of a single standard line for measuring all of the Raman lines. Instead, a line for each group of Raman lines was chosen, and this same line used as reference throughout a series of measurements.

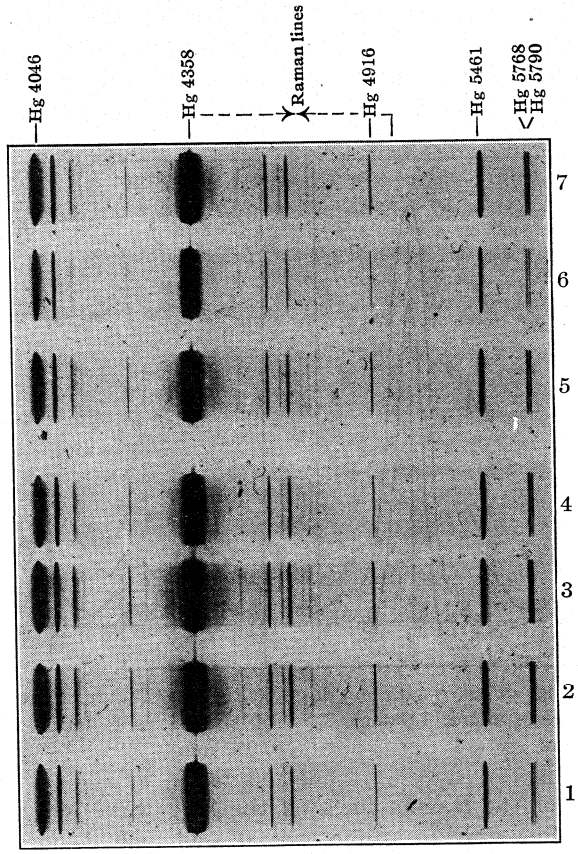

Plate II.—Variation of slit and exposure: 1, [−2]—1 hr.; 2, [−2]—2 hrs.; 3, [−4]—2 hrs.; 4, [−4]—1 hr.; 5, [+2]—2 hrs.; 6, [+2]—1 hr.; 7, [−7]—1 hr.

Good intensity measurements seemed to depend largely upon the nature of the photographs and the technique of using the densitometer. After spectra of sharp contrast and uniform background were obtained it was necessary, due to the sensitivity of the densitometer, to duplicate the photometric curves before making final intensity measurements. Raman photographs were duplicated which gave photometric curves in which the height of the most intense lines varied less than 1 mm. Likewise,

duplicate intensity curves of the same photograph showed less than a 0.5 mm. change for any Raman line.

Results

Photographs of the first Raman spectra of mixtures of 25% variation in concentration are reproduced in Plate I where the appearance, disappearance, and the change in density of certain Raman lines can be observed. Further evidence of these intensity changes is shown by the photometric curves in Figs. 1 and 2 and by the intensity curves plotted in Fig. 3.

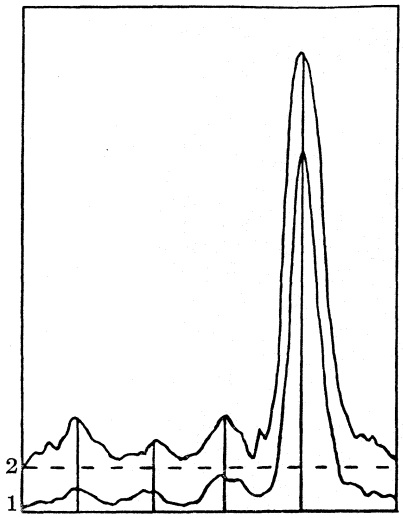

Fig. 4.—Change of curve with length of exposure: 1, exposure, 1 hour; 2, exposure, 2 hours.

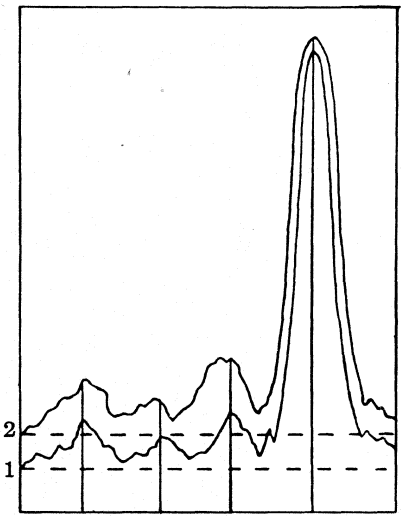

Fig. 5.—Change of curve with width of slit: 1, slit, 0.071 mm.; 2, slit, 0.089 mm.

At first, all of the Raman lines on the long wave length side of the 4358 mercury line were measured, but it was soon discovered that the group of Raman lines in the region between 600 and 1000 cm.$^{-1}$ exhibited the greatest variations in intensity with change in concentration. The work, therefore, was devoted to measuring and comparing lines falling within this particular region.

The fact that the first results did not show measurable differences for small changes in concentration suggested improvement in technique. The importance of finding a favorable combination of slit and exposure, in photographing Raman spectra for intensity study, is strikingly brought out in the gradations shown in the spectra of Plate II and in the photometric curves of Figs. 4 and 5. From these illustrations it is evident that a narrow slit with long exposure is preferable to a wide slit with short

exposure. Spectrum (5) in Plate II proved the most satisfactory type for the present work.

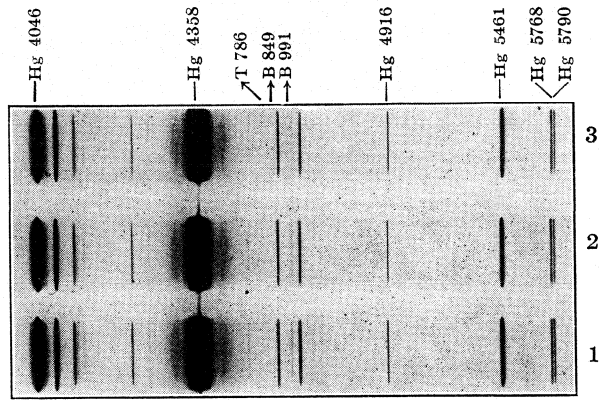

Plate III.—% Benzene–toluene: 1, B 95, T 5; 2, B 90, T 10; 3, B 85, T 15.

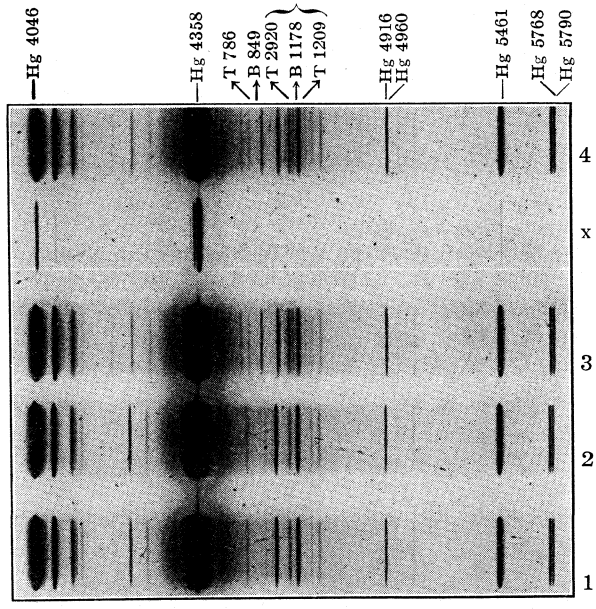

Plate IV.—% Benzene–toluene: 1, B 95, T 5; 2, B 95 T 5; 3, B 0, T 100; 4, B 5, T 95; x, Hg lines.

Plates III and IV, Figs. 6 and 7, and Tables II, III and IV give results obtained under the optimum conditions and show that 5% changes in concentration are easily measurable.

TABLE I

RELATIVE INTENSITY OF RAMAN LINES FOR 25% CHANGE IN CONCENTRATION OF BENZENE–TOLUENE

Exciting mercury line		4358		4046		4358		4358	
Raman line		T 786		T 2920		B 1178		T 1209	
% (vol.) B–T	Mole, % B–T		Δ I		Δ I		Δ I		Δ I
100–0	100–0	2.7		8.5		37.2		1.5	
			17.2		10.2		9.0		11.7
75–25	78–22	19.9		18.7		28.2		13.2	
			7.1		6.9		5.6		2.1
50–50	54–46	27.0		25.6		22.6		15.3	
			8.2		2.2		7.5		3.7
25–75	28–72	35.2		27.8		15.1		19.0	
			10.5		4.4		11.4		3.6
0–100	0–100	45.7		32.2		3.7		22.6	

TABLE II

RELATIVE INTENSITY OF RAMAN LINES [HT. IN MM]

Exciting mercury line	4358		4358		4347		4358	
Raman line	T 786		B 849		B 991		B 991	
% (vol.) B–T		ΔI		ΔI		ΔI		ΔI
95– 5	6.3		10.1		13.0		92.7	
		1.5		1.1		2.0		1.6
90–10	7.8		9.0		11.0		91.1	
		1.2		1.2		1.0		0.5
85–15	9.0		7.8		10.0		90.6	

TABLE III

DIFFERENCES IN HEIGHT BETWEEN B 991 [4358 Hg] AND NEIGHBORING LINES [HT. IN MM.]

Exciting mercury line	4358		4358		4347	
Raman line	T 786		B 849		B 991	
% (vol.) B–T		ΔI		ΔI		ΔI
95–5	85.2		81.7		78.5	
		2.9		0.3		0.7
90–10	82.3		82.0		79.2	
		2.0		0.3		0.7
85–15	80.3		82.3		80.5	

TABLE IV

RELATIVE INTENSITY OF RAMAN LINES [HT. IN MM.]

Exciting mercury line	4358		4358		4046		4358		4358	
Raman line	T 786		B 849		T 2920		B 1178		T 1209	
% (vol.) B–T		ΔI		ΔI		ΔI		ΔI		ΔI
0–100	31.2		54.0		39.0		11.7		23.2	
		3.7		3.5		3.7		4.8		0.7
5–95	27.5		50.5		35.3		16.5		27.5	

Discussion

As can be seen in the spectra photographed, the complete mercury spectrum was used in producing Raman lines for intensity measurements. In the section chosen for study the Raman lines were excited by the mercury lines λ4046, λ4339, λ4347 and λ4358. There was an advantage in using the high frequency Raman lines excited by the 4046 mercury line, as they were more intense than the corresponding lines excited by the 4358 mercury line. In the case of high frequency Raman lines the intensity increases with the frequency of the exciting line much more rapidly than the fourth power law.[6]

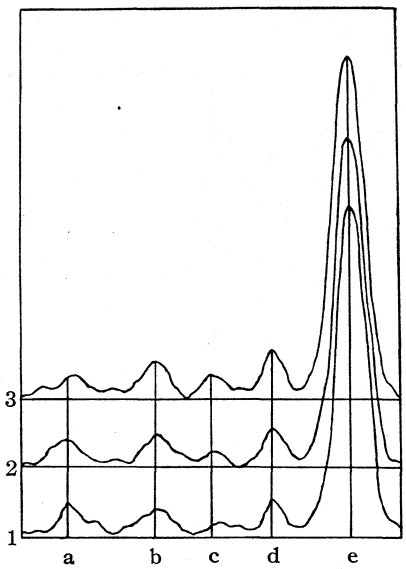

Fig. 6.—Section of photometric curve. % Benzene–toluene: 1, B 85, T 15; 2, B 90, T 10; 3, B 95, T 5. $\Delta\nu$ Raman line: a, T 786 [Hg 4358]; b, B 849 [Hg 4358]; c, B 991 [Hg 4339]; d, B 991 [Hg 4347]; e, B 991 [Hg 4358].

A study of Raman spectra and of intensity values shows that the Raman line at 786 cm.$^{-1}$ is by far the best indicator for toluene. This characteristic toluene line was perceptible in the spectrum of a mixture containing 5% toluene obtained after only one hour of exposure. However, short exposures necessitating a fairly wide slit are not suitable for intensity comparisons.

The concentration of benzene in a mixture can be estimated from the intensity of either the 849 cm.$^{-1}$ frequency or the 991 cm.$^{-1}$ frequency, both strong Raman lines of benzene. It is interesting to note that the weak 4347 mercury line excites a Raman line at 991 cm.$^{-1}$ which apparently gives with the densitometer greater intensity variation with small changes in concentration than the same line excited by the strong 4358 mercury line.

In the case of benzene–toluene mixtures the toluene line at 1002 cm.$^{-1}$ might be expected to interfere somewhat with the actual height and contour of the benzene line at 991 cm.$^{-1}$. Although the shape of the curve for this line is slightly changed and the peak of the curve shifted with increase in toluene, it invariably decreases in height with decrease in the concentration of benzene.

Table III shows a method for measuring the intensities in terms of the differences in height between a given Raman line, chosen as standard,

[6] Sirkar, *Indian J. Physics*, **5**, 593 (1930).

and each neighboring Raman line. Perhaps this method is less subject to error than the more direct method of measuring relative heights, because in using the differences between the peaks of lines the arbitrary choice of a reference line is eliminated. Since measurements of this kind show a difference of 50 mm. from the top of a strong toluene line in 100% toluene to the top of a strong benzene line in 100% benzene, surely much less than 5% change in concentration should be detectable from intensity measurements.

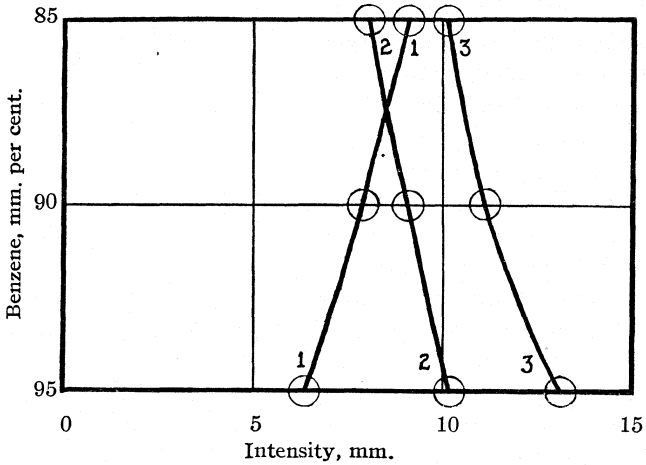

Fig. 7.—Relative intensity of Raman lines in benzene–toluene mixtures: 1, T 786; 2, B 849; 3, B 991.

The relative intensities of Raman lines, which depend upon molecular density,[7] intensity and frequency of the exciting line,[6] and experimental conditions under which the lines are produced,[8] offer excellent opportunity and possibility for investigating the nature and determining the composition of mixtures and solutions. Recently the sensitivity of Raman lines in testing for the presence of the double bond has been reported to be as high as 1.2–2.4%.[9]

The author wishes to express her appreciation to Professor D. H. Andrews for his many helpful suggestions.

Summary

By means of a simple experimental procedure, measurements of the relative intensities of characteristic Raman lines of benzene–toluene mixtures were obtained which show with 5% change in the concentration

[7] Cabannes and Daure, *Compt. rend.*, **186**, 1533 (1928).

[8] Merton and Nicholson, *Phil. Trans.*, **A217**, 237 (1918); Read and Johnson, *Phil. Mag.*, **11**, 1152 (1931).

[9] Lespieau, Bourquel and Wakeman, *Compt. rend.*, **193**, 238 (1931).

of either benzene or toluene a change of several millimeters in the height of the photometric curve.

BALTIMORE, MARYLAND

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

A STUDY OF SOLUTIONS OF ETHYL ALCOHOL IN CYCLOHEXANE, IN WATER, AND IN CYCLOHEXANE AND WATER

BY ROBERT D. VOLD AND E. ROGER WASHBURN

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The results of a previous investigation[1] have indicated some of the problems involved in a study of ternary solubilities and the distribution of ethyl alcohol between water and a hydrocarbon. In the previous work it was found that ethyl alcohol is monomolecular in water solutions and associated in benzene solutions according to freezing point data. On the other hand, according to distribution experiments it was found to have the same molecular form in both solutions. As a step toward the solution of similar problems this investigation was undertaken, substituting cyclohexane for benzene.

Materials

Ethyl Alcohol.—A standard commercial grade of absolute alcohol was refluxed over freshly burned lime and distilled from an all-glass apparatus until density determinations showed it to be 99.91% alcohol.[2]

Cyclohexane.—The best grade of cyclohexane obtainable from the Eastman Kodak Co. was further purified by alternate fractional crystallizations and distillations. Finally, it was dried over sodium and distilled from an all-glass apparatus. The final product had a density of 0.77379 g. per ml. and a freezing point of 6.20°. Several fractions of lower freezing point were obtained which were later found to give the same results as the better grade in solubility determinations.

Water.—Laboratory distilled water was redistilled from potassium permanganate in a tinned boiler provided with a block tin condenser. The specific conductance of the distillate at 25° was 2.51×10^{-6} mhos.

Ternary Solubilities and the Distribution of Ethyl Alcohol between Water and Cyclohexane.—The distribution of alcohol between water and cyclohexane was determined by a procedure similar to that of other investigators of such systems.[3,4,5,1] Definite amounts of cyclohexane and alcohol were weighed into 100-cc. glass-stoppered Erlenmeyer flasks on an analytical balance. The flasks were suspended in a hand-operated bath maintained at 24.8° and water added from a weight pipet until phase

[1] Washburn, Hnizda and Vold, THIS JOURNAL, **53**, 3237 (1931).

[2] "International Critical Tables," The McGraw Hill Book Co., New York, 1929, Vol. III, p. 116.

[3] Taylor, *J. Phys. Chem.*, **1**, 461 (1897).

[4] Barbaudy, *Rec. trav. chim.*, **45**, 207 (1925).

[5] Hand, *J. Phys. Chem.*, **34**, 1961 (1930).

separation just occurred, whether it was evidenced by drop formation, opalescence, mistiness or actual emulsification. In order to ensure permanent phase separation after each addition of water, the flasks were alternately shaken for thirty seconds and allowed to stand for thirty seconds for at least five minutes. Titration to the appearance of a second phase was selected as the end-point rather than titration of a two-phase system to a homogenous solution since it has been found[6] to give a sharper end-point. During the titrations the flasks were kept stoppered except during addition of water from the pipet. A study of the change in weight due to evaporation showed that at most it amounted to only two or three parts per thousand.

Hand[5] claims to have eliminated all uncertainty regarding the end-point in similar titrations by recording the amounts of titrating liquid definitely insufficient and then definitely in excess by working first at 22° and then at 25°. In the present work it was found that such systems are very sensitive to temperature variations, a very small change in temperature being sufficient in some concentration ranges to produce a dense milkiness in the solution. Consequently, it appears that there is no method for determining the end-point between the two extremes used by Hand. Therefore, it is believed that direct observation of the point of phase separation provides a more accurate determination of the end-point despite its difficulty.

The results of these titrations are collected in Table I and shown graphically in Fig. 1. The starred values were extremely difficult to obtain.

TABLE I

SOLUBILITIES OF ETHYL ALCOHOL–CYCLOHEXANE AND WATER AT 25°

No.	C_6H_{12}, g.	Alc., g.	Water, g.	Wt. % C_6H_{12}	Wt. % alc.	Wt. % water	Refractive index
1*	0.0346	0.8248	9.9554	0.32	7.63	92.05	1.33749
2*	.0739	2.5107	9.9377	.59	20.05	79.36	1.34622
3	.0402	19.6007	28.1032	.08	41.06	58.86	1.35707
4	.0971	7.7960	10.1346	.54	43.24	56.22	1.35799
5	.2511	15.6421	15.1538	.81	50.38	48.81	1.36012
6	.3951	15.6588	13.0224	1.36	53.85	44.79	1.36120
7	.7837	15.6074	8.9327	3.09	61.63	35.28	1.36339
8	.8103	7.7775	3.0218	6.98	66.99	26.03	1.36568
9	2.0129	15.5899	5.1660	8.84	68.47	22.69	1.36684
10	1.5615	7.7915	1.8890	13.88	69.31	16.81	1.36947
11	2.3427	7.8054	1.3486	20.38	67.89	11.73	1.37276
12	3.0952	7.7919	1.0258	25.98	65.41	8.61	1.37549
13	3.8837	7.8089	0.9863	30.63	61.59	7.78	1.37843
14	7.6998	7.8026	.6954	47.54	48.17	4.29	1.38816
15	7.6724	3.9236	.2455	64.79	33.14	2.07	1.39900
16	19.4184	3.9360	.2106	82.41	16.70	0.89	1.41051
					Water saturated with cyclohexane		1.33255
					Cyclohexane saturated with water		1.42348

[6] Bogin, *Ind. Eng. Chem.*, **16**, 380 (1924).

Those solutions undoubtedly contained a small amount of undissolved cyclohexane but since it was in a few relatively large insoluble drops it had little or no effect on the refractive index of the solution. Therefore it caused no appreciable error in the later graph of amount of alcohol against refractive index of solution. Attention is called to the fact that composition is expressed in terms of weight per cent., rather than in mole fraction or mole per cent. This is advisable since in these solutions the molecular form of the alcohol is not only unknown but is probably changing.

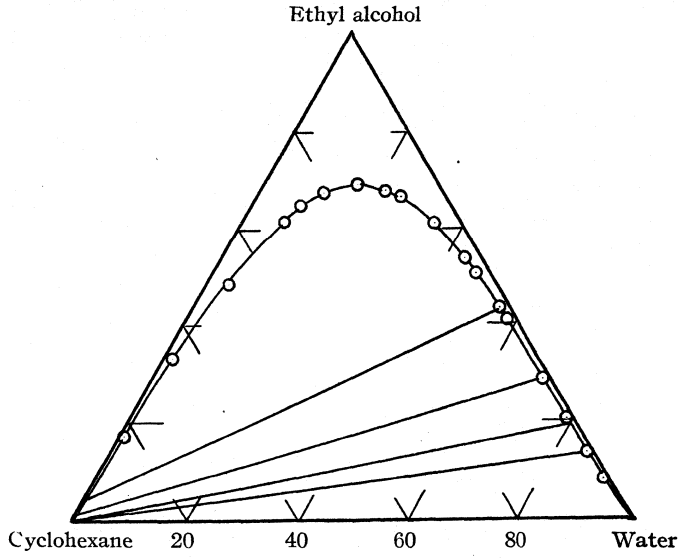

Fig. 1.—Concentration in wt. %.

The refractive indices at 25° of the saturated ternary solutions for the D line of sodium were then determined by an immersion refractometer equipped with a closed metal cup to prevent evaporation of the solutions. Temperature was kept at 25.00° during the determinations by dipping the whole lower end of the instrument directly into an electrically controlled thermostat. This temperature was selected 0.2° above the titration temperature in order to clear up the solutions so as to permit accurate determination of the refractive index. No appreciable error is introduced by this procedure since the excess water necessary to cause visible phase separation at 24.8° may be assumed to just dissolve at 25.00°, thus leaving a clear, saturated, single solution phase ternary solution. This information is also tabulated in Table I and is shown in Fig. 2.

The curve in Fig. 1 shows the composition of the various possible saturated ternary solutions of ethyl alcohol, cyclohexane, and water. This solubility curve is made up of two curves which approach and finally

meet, one giving the solubility of alcohol in cyclohexane saturated with water and the other the solubility of alcohol in water saturated with cyclohexane.

It can be shown from phase rule considerations that there are three degrees of freedom in this system which must be specified before the equilibrium is determined and the position of the curve fixed. In this work these were chosen as temperature, pressure, and an initial concentration ratio of cyclohexane to alcohol. Actually atmospheric pressure was used and it was assumed to remain constant throughout the experiment.

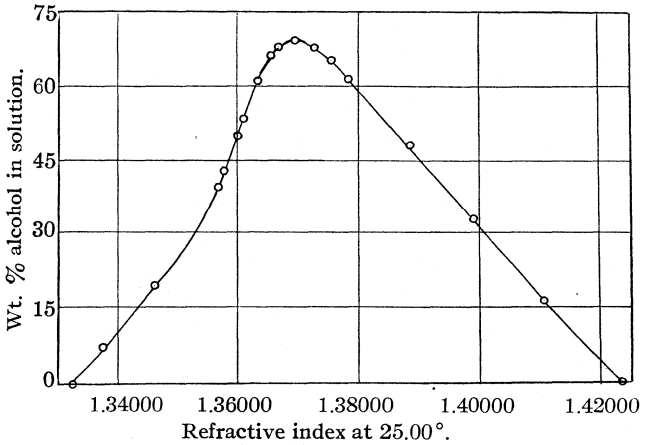

Fig. 2.—Ethyl alcohol–cyclohexane–water.

A change in the concentrations in the solution as a result of a change in external pressure is brought about by its effect on the vapor pressures of the liquids. This effect is given by the equation $dp/dP = v/V$, where p is the vapor pressure of the liquid, P the external pressure and v and V are, respectively, the molecular volumes of the substance as liquid and vapor. Consequently, since this is very small, even relatively large changes of external pressure would not noticeably affect the equilibrium concentrations of the three liquids in single phase saturated solution.

This conclusion seems to be a contradiction of an observation made by a previous worker,[5] who found that the composition of his saturated solutions in certain concentration ranges was very sensitive to changes of external pressure. In the present investigation a procedure similar to his was used except that any pressure variations were eliminated. Nevertheless, a result similar to that obtained by him was observed. In view of the fact that these systems are very sensitive to temperature changes in certain concentration ranges, it seems probable that the observed changes in the system are due to incidental temperature variations rather than to any effect of external pressure changes.

Figure 2 shows the variation of refractive index of saturated ternary solutions of ethyl alcohol, cyclohexane and water with the weight per cent. of alcohol present. At the one end of the curve is the refractive index of water saturated with cyclohexane and at the other end is the refractive index of cyclohexane saturated with water. In this, as in a similar system,[1] the curve has a dip in the water-rich solutions and does not rise to its maximum with uniformly changing slope.

To determine the distribution ratio of alcohol between cyclohexane and water, samples were made up of approximately 10 cc. of water and 10 cc. of cyclohexane mixed in glass-stoppered bottles. To these mixtures different amounts of alcohol were added and the bottles then suspended in the thermostat at 25.00° for twelve hours to ensure attainment of equilibrium. The refractive index of each of the two separated phases was then determined as before and from the graph of Fig. 2 the concentration of alcohol in each phase was found. The distribution ratio was calculated as the simple quotient of the weight per cent. of alcohol in the water layer divided by the weight per cent. of alcohol in the cyclohexane layer. The results appear in Table II.

TABLE II

IN ALL CASES THE ALCOHOL WAS DISTRIBUTED BETWEEN APPROXIMATELY TEN CC. OF WATER AND TEN CC. OF CYCLOHEXANE

No.	Ref. ind. of water layer	Wt. % alc.	Ref. ind. cyclohexane layer	Wt. % alc.	Total amt. alc.	Dist. ratio
A	1.33306	0.72	1.42351	0.0	0.1	..
B	1.33494	3.30	1.42351	0.0	0.5	..
C	1.33524	3.68	1.42340	0.0	0.6	..
D	1.33723	6.65	1.42334	?	1.0	?
E	1.34148	12.74	1.42321	0.20	2.0	63.7
F	1.34562	18.80	1.42311	0.37	3.0	50.8
G	1.35106	28.10	1.42280	0.64	5.0	43.9
H	1.35804	43.60	1.42230	1.20	10.0	36.3

Freezing Point Studies.—For this work a standard Beckmann apparatus was constructed and the usual precautions[7] observed in its use. A weighed amount of cyclohexane was placed in the inner tube and its freezing point determined. Weighed amounts of alcohol were then added from a weight pipet and the freezing points of the solutions determined. The molal freezing point constant for cyclohexane was calculated to be 14 from the data of Mascarelli and Pestalozza[8] and Baud[9] by the equation $K = mdW/w$, where m is the molecular weight of the solute, W the grams

[7] Findlay, "Practical Physical Chemistry," Longmans, Green and Co., New York, 5th ed., 1931, p. 120.

[8] Mascarelli and Pestalozza, "International Critical Tables," The McGraw-Hill Book Co., New York, 1929, Vol. IV, p. 133.

[9] Baud, *ibid.*, p. 107.

of cyclohexane, d the freezing point depression and w the grams of solute. Using this value for the constant the theoretical depression of the freezing point for each concentration of alcohol was calculated on the basis that the alcohol was monomolecular. The apparent molecular weight of the alcohol at each concentration was also calculated.

TABLE III

FREEZING POINTS OF ETHYL ALCOHOL–CYCLOHEXANE SOLUTIONS

Wt. % alc. in cyclohexane	Observed depression	Calculated depression	App. mol. wt. of alc.
1.15	1.56	3.54	104
1.18	1.57	3.63	106
3.11	2.92	9.78	154
4.25	3.53	13.49	176
4.61	3.68	14.71	184
6.09	4.32	19.72	210
8.56	5.06	28.48	259
16.60	6.74	60.58	414

These results appear in Table III. The variation of the observed from the calculated depression of the freezing point is shown in Fig. 3. Curve B is the theoretical freezing point lowering curve for solutions of ethyl alcohol in cyclohexane, while curve A shows the actual lowering.

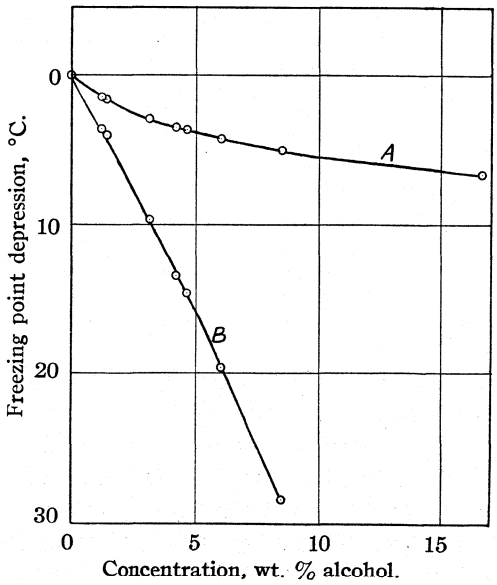

Fig. 3.—Ethyl alcohol–cyclohexane.

Discussion

If absolutely constant values of the distribution ratio had been obtained it would have shown (1) that the alcohol had the same molecular form in the two solvents, (2) that the mutual solubility of the two solvents was equally affected by the presence of the alcohol and (3) that the deviations from the laws of perfect solutions were the same in both the water and cyclohexane solutions of alcohol. Actually, up to a certain concentration, practically all the alcohol dissolved in the water layer and above this the value of the ratio steadily decreased as the concentration of alcohol was further increased.

The steady decrease in the value is due to the fact that weight per cent.

was chosen as the method of expressing concentration. This is equivalent to using an expression of the form

$$K = \frac{A_1}{A_1 + B_1 + C_1} \Big/ \frac{A_2}{A_2 + B_2 + C_2}$$

where A, B and C are the three liquids, the subscripts 1 and 2 denoting in which phase they are present. Since, as is shown by the solubility curve of Fig. 1, the solubilities of water in cyclohexane and of cyclohexane in water are unequally affected by the addition of alcohol, it is obvious that strictly constant values of the ratio will not be obtained even though the other conditions are fulfilled. The distribution law was developed in terms of the ratio of grams of A to grams of B divided by the ratio of grams of A to grams of C. Nevertheless, it seems more reasonable to use the expression with weight per cent., since the alcohol is actually distributed between saturated solutions of cyclohexane in water and water in cyclohexane and not between pure water and pure cyclohexane. Furthermore, some variation is probably due to the use of the improbable assumption that the alcohol has the same activity in water, a polar solvent of the same type as alcohol itself, that it has in cyclohexane, a non-polar hydrocarbon.

The fact that the change in the value of the ratio is relatively so small is therefore strong evidence that the alcohol has the same molecular form in the two phases.

On first consideration freezing point data seem to contradict this conclusion. Several investigators have shown that the freezing point depression caused by addition of alcohol to water is normal over a large concentration range.[10,11] Our results indicate that in cyclohexane the alcohol is highly associated, the apparent molecular weight varying from about one hundred to four hundred. Despite the uncertainty involved in attributing all variations from the freezing point law to association of the solute,[12] nevertheless, it is reasonable to assume that the alcohol is associated since even in dilute solutions the observed depression of the freezing point varied several hundred per cent. from the calculated value. Therefore, the conclusion is that alcohol has a different molecular form in water than it has in cyclohexane.

This conclusion is not a contradiction of that deduced from the distribution ratio if the presence of a small amount of a third liquid is sufficient to change the alcohol to simple molecules in the cyclohexane phase or to associated molecules in the water phase. This hypothesis is supported by the peculiar behavior of the system on addition of alcohol when the

[10] Pickering, *J. Chem. Soc.*, **63**, 998 (1893).

[11] Pictet, *Compt. rend.*, **119**, 678 (1894).

[12] Hildebrand, "Solubility," Am. Chem. Soc. Monograph, Chemical Catalog Co., New York, 1924, p. 160.

alcohol content is low. This is just the region where the value of the distribution ratio should be most nearly constant since the solutions are extremely dilute. Actually, however, it is in this region that the values of the distribution ratio would be changing most rapidly if a sufficiently delicate analytical method could be devised for determining the concentration of the alcohol in the cyclohexane so as to permit calculation of the ratio.

The peculiar dip in the curve of refractive index against weight per cent. of alcohol is possibly another indication of the validity of the assumption. Since refractive index depends not only on density but also on molecular complexity of the solution, this variation may indicate some change taking place in the molecular form of the dissolved alcohol. In any event, whether the explanation is correct or not, the fact remains that depression of the freezing point and calculation of distribution ratios cannot always be used as interchangeable methods for the determination of molecular form.

It is of interest to compare this system with the similar system ethyl alcohol–benzene–water[13] from the standpoint of differences in physicochemical properties of the various liquids involved. In general the phenomena are very similar for the two systems. Ethyl alcohol appears to be associated in benzene as it is in cyclohexane, judging from the results of freezing point data. In both systems the value of the distribution ratio for alcohol distributed between water and the hydrocarbon decreases as the concentration of alcohol is increased. In the cyclohexane system, however, much larger concentrations of alcohol are required to bring about formation of a one-phase solution than are required in the benzene system.

Comparison of physical properties shows that benzene has a relative internal pressure of 6.48[14] and cyclohexane of 5.56,[15] both calculated from surface tension divided by molecular volume to the one-third power. Alcohol and water, on the other hand, are both liquids of high internal pressure. According to the modern conception substances having like values of internal pressure are most soluble in each other and tend to form the more perfect solutions. Thus, ethyl alcohol and water are completely miscible while water and the hydrocarbons are but sparingly soluble. Ethyl alcohol and cyclohexane are completely soluble above $-15°$[16] but below this temperature form a two-phase system, indicating a large variation from ideality. Thus it is to be expected that more of the alcohol dissolves in the water phase than in the hydrocarbon phase in distribution experiments.

[13] Washburn, Hnizda and Vold, THIS JOURNAL, **53**, 3237 (1931).

[14] Hildebrand, Ref. 12, p. 111.

[15] Jones and Betts, *J. Chem. Soc.*, 1177 (1928).

[16] Jones and Amstell, *ibid.*, 1316 (1930).

Furthermore, addition of a third liquid of intermediate internal pressure increases the solubility of two liquids of greatly different internal pressures since each dissolves more in the third liquid than it could in the other. Thus, the increased solubility of water in cyclohexane and of cyclohexane in water is predicted by this theory since the internal pressure of alcohol is intermediate between those of cyclohexane and water. In addition, the fact that a greater concentration of alcohol is required to bring about complete solubility in the case of the cyclohexane system than in the case of the benzene system may be qualitatively predicted from the fact that cyclohexane has a lower relative internal pressure than benzene.

Consideration of the relative magnitudes of dielectric constant and entropy of vaporization, both measures of the relative polarity of a liquid, leads to identically the same qualitative conclusions as in the case of internal pressure. By both measurements water is by far the most polar liquid, alcohol next, benzene low and cyclohexane very low. Liquids of the same degree of polarity tend to be most soluble in each other and therefore the same conclusions may be drawn concerning the relative solubility relations as have been discussed under internal pressure.

This work is being continued on similar systems and certain related properties such as vapor pressures, viscosities and heat and volume changes on mixing are being studied.

Summary

1. The equilibrium concentrations of ethyl alcohol, cyclohexane, and water in single phase saturated ternary solutions at 25° have been determined.

2. The tie lines for the system have been determined and the values of the distribution ratio for ethyl alcohol distributed between water and cyclohexane calculated.

3. The freezing point curve for solutions of ethyl alcohol in cyclohexane up to sixteen weight per cent. alcohol has been determined.

4. It has been shown that lowering of the freezing point and distribution experiments cannot always be used interchangeably in the determination of molecular form in solution.

5. It has been shown that the observed solubility relations can be qualitatively predicted from the physico-chemical properties of the three components.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

PHOTOCHEMICAL TECHNIQUE. III. QUARTZ CAPILLARY ARC LAMPS OF BISMUTH, CADMIUM, LEAD, MERCURY, THALLIUM AND ZINC

BY ROBERT M. HOFFMAN AND FARRINGTON DANIELS

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In a previous communication a simple mercury lamp[1] of high intensity was described. The object of the present investigation has been to develop similar lamps with other metals in order to make available intense light for a wider selection of wave lengths. Mercury lamps are more convenient because mercury is a liquid at room temperature, it is not oxidized, and it does not adhere to the quartz. The other metals tend to break the quartz lamps on solidifying.[2] It is desirable then to make a lamp so simple and so cheap for photochemical work that it can be discarded when the current is turned off at the end of an experiment.

Construction and Operation of Lamps

The lamp is shown in Fig. 1. It is made by fusing a 12-mm. section of quartz capillary, 1 mm. inside diameter and 2 mm. outside diameter, between two thin-walled quartz tubes, 2 mm. in outside diameter and 5 cm. long. Thin bulbs are blown out at these joints to localize the arc. The end-pieces may be used over and over again. The upper electrode is formed by stopping the lower end of the capillary with a pointed iron rod and gently melting down small pieces of metal to fill the whole capillary and the upper tube. Any bubbles are floated out of the molten metal. The lower electrode is cast or scraped down from a larger rod so as to fit snugly into the lower quartz tube.

It is pointed, and set so as to leave a short gap between the two electrodes. The metal at both ends of the lamp is then melted and short iron wires connected to flexible leads are inserted. The connections are insulated and rendered gas tight with de Khotinsky cement. The air space in the lower bulb serves as a spark gap, for starting the lamp, and as a reservoir into which the molten metal runs down from the capillary when the arc is struck. The pressure under which the lamp operates, and the resistance of the lamp, are largely determined by the volume of this air space.

The water jacket is indicated by dotted lines. A quartz tube about 1.2 cm. in diameter and 10 cm. long surrounds the lamp and two T tubes of Pyrex glass are attached with rubber tubes. The insulated leads protrude from the T tubes through rubber tubes closed with screw clamps. A stiff spring centers the lamp and prevents vibration. For use with a monochromator a metal tube (not shown) with a large slit is placed inside the quartz as a shield. The upper electrode is made the negative terminal.

A rapid stream of water is forced in at the bottom and the lamp L is then started by passing a spark of electricity across the air gap between the two electrodes while the

[1] Daniels and Heidt, THIS JOURNAL, **54**, 2381 (1932).

[2] Bates and Taylor added tin to a cadmium lamp to prevent breaking. THIS JOURNAL, **50**, 772 (1928). Smits and Frederikse used lead in quartz at high voltages. *Z. Elektrochem.*, **34**, 350 (1928). Earlier lamps are reviewed by Forbes, *J. Phys. Chem.*, **32**, 486 (1928).

circuit is closed. An induction coil N giving at least a 1-cm. spark is connected with a condenser C and spark gap S, and two adjustable spark gaps G as shown at the right in Fig. 2. The adjustable gap is made by attaching wires to a double pole switch which is adjusted for maximum efficiency with a long insulated handle. A high-resistance shunt (not shown), grounded at the center, and two 100-turn inductance coils (not shown) must be placed in the lamp circuit to protect the line against the high frequency spark discharge. The lamps must be operated on direct current and in most cases a potential of at least 150 volts seems to be necessary for starting.

In some cases the arc can be started by heating the capillary with a blast lamp; but the breakage is then very high. Dr. L. W. Morris of the Physics Department, in using these lamps, eliminated the spark circuit by connecting the two electrodes with a small fuse wire of the same metal. An initial current of high amperage through the lamp melts the metal and strikes the arc.

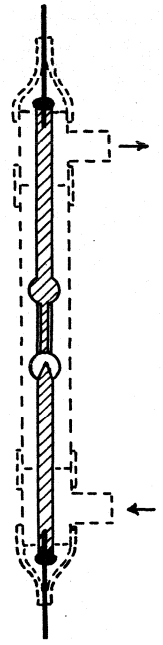

Fig. 1.—Capillary quartz lamp for solid metals. Water jacket in broken lines

Adjustment of External Resistance.—The steadiness of the lamps depends to a large extent on the control of the wattage by proper adjustment of the external resistance. The wattage and the rate of external cooling determine the temperature of the lamp which in turn determines the vapor pressure of the metal. The resistance of the lamp increases as the vapor pressure increases. When the lamp is operating on a fixed line voltage with an external resistance in series the consumption of energy depends entirely on the resistance of the lamp.

The problem may be analyzed by considering the lamp and an external fixed resistance R connected in series across a fixed line voltage V. If the calculated wattage W through the lamp is plotted against the changing resistance r of the lamp, a maximum is obtained when the resistance of the lamp is equal to the external resistance.

In this graph the curve rises steeply when $r < R$, but, beyond the maximum, where $r > R$, the curve descends slowly. Differentiating the expression $W = V^2r/(r + R)^2$, and setting dW/dr equal to zero, it is

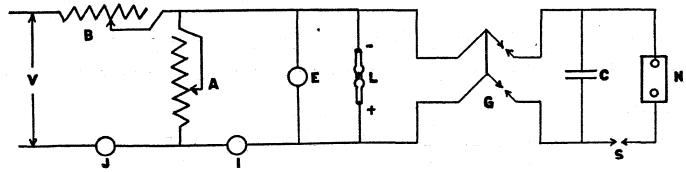

Fig. 2.—Lamp circuits: starting circuit at right; operating circuit with external resistances at left.

evident that a maximum, where W is independent of r, must be obtained when r is equal to R. When dW/dr is positive, an increase in lamp resistance increases the wattage through the lamp and, unless the cooling

system can handle this increase, the temperature, vapor pressure and resistance again increase. A regenerative process is thus set up which eventually causes the lamp to blow up, particularly in the case of the lamps of high-melting metals. When dW/dr is negative, any increase in the lamp's resistance decreases the wattage and cools the lamp and restores it to its original condition. These considerations show that the external resistance should not be greater than the resistance of the lamp for then dW/dr is positive; it may, however, be somewhat less.

The metal arc lamps described here range in lamp voltage from 60 to 400 volts depending on the air volume and on other specific factors. A 550-volt generator was used in all cases but this voltage is theoretically too high for any lamp with a voltage drop of less than 275 volts. The difficulty can be met with the help of a shunt but then the rule that R should be equal to r no longer holds. The problem was solved in the following manner, where A is the adjustable shunt resistance and B is the adjustable series resistance as shown in Fig. 2. Let S be the resistance of A and r in parallel, I, the amperage through the lamp, J the total amperage, and E the voltage drop across the lamp.

Then
$$E = \frac{S}{S+B}V \tag{1}$$

but since
$$S = \frac{Ar}{A+r} \qquad E = \frac{ArV}{Ar+AB+Br} \tag{2}$$

Also
$$W = \frac{E^2}{r} = \frac{(AV)^2 r}{(Ar+AB+Br)^2} \tag{3}$$

Then
$$\frac{dW}{dr} = \frac{(AV)^2}{(Ar+AB+Br)^2} - \frac{2W(A+B)}{(Ar+AB+Br)} \tag{4}$$

Letting
$$\frac{dW}{dr} = 0,\ W_{max.} = \frac{(AV)^2}{2(Ar+AB+Br)(A+B)} \tag{5}$$

Equating W and $W_{max.}$
$$\frac{Ar+AB+Br}{2(A+B)} = r \text{ and } AB = Ar + Br \tag{6}$$

This equation shows the conditions under which the lamp has reached its stable point, *i. e.*, the wattage of the lamp is independent of the resistance of the lamp when the series and shunt resistances are such that their product is equal to their sum, multiplied by the resistance of the lamp. But it cannot be used directly; it must be converted into terms which can be obtained from the voltmeter and two ammeters in the circuit.

Substituting
$$A = \frac{E}{J-I},\ B = \frac{V-E}{J} \text{ and } r = \frac{E}{I} \tag{7}$$

equation (6) becomes
$$\frac{E(V-E)}{J(J-I)} = \frac{E^2}{(J-I)I} + \frac{(V-E)E}{JI} \tag{8}$$

and solving for J
$$J = \frac{2I(V-E)}{V} \tag{9}$$

V is fixed at 550 volts and E and I are read directly from a voltmeter and ammeter connected to the lamp. If, after starting, the lamp instruments read 5 amperes and 100 volts, for example, the proper value of J can be determined at once by solving equation (9).

$$J = \frac{2 \times 5\,(550 - 100)}{550} = 8.2 \text{ amp.}$$

The shunt resistance A and series resistance B are then decreased simultaneously in such a way that the amperage and voltage of the lamp are not changed but the total amperage J through the whole circuit reads 8.2 amperes. This calculation and adjustment is made immediately, before the lamp has a chance to burn out. Although these conditions make $dW/dr = 0$, it has been found in practice that the lamp burns more steadily when the total amperage is slightly greater than the calculated value. When J is greater than the calculated value, dW is negative and there is a compensating effect in the circuit. J, then, may be regarded as the lower limit of the stable range.[3]

The shunt circuit entirely eliminated the earler tendency of certain lamps to burn out, due to simultaneous rise of lamp resistance and wattage. In general the stabilizing effect is great enough to cause a noticeable decrease in the fluctuations of the lamp. An automatic record of the thermopile–galvanometer deflections on a single wave length showed a variation of 5.2% over a period of ten minutes, but when the circuit was properly balanced the maximum variation dropped to 3.7%. A considerable part of this variation was due to fluctuations in the dynamo and drifts in the zero point of the thermopile–galvanometer. When a mazda lamp was substituted for the arc the variation was still as great as 2.8%.

Measurement of Energy Distribution

The lamps were studied with a Hilger quartz monochromator (4 cm. prism), provided with a Coblentz linear thermopile and a Leeds and Northrup galvanometer having a sensitivity of 15 mm. per microvolt. The thermopile–galvanometer deflections were recorded photographically in a simple manner. A carrier holding photographic bromide paper, $6\frac{1}{2} \times 8\frac{1}{2}$", slides on a vertical track in a light-tight box at a distance of 2 meters from the galvanometer. The vertical galvanometer beam enters through an adjustable horizontal slit, thus making a small point of light on the paper. The carrier is suspended by a strong linen thread which passes over two small pulleys and down to an axle upon which it is wound in a single layer. This axle is attached directly to the wave length drum which rotates the prism. The monochromator is so constructed that twelve revolutions of the drum cover the range from 2000 to 7000 Å. and the axle is of such diameter (6 mm.) that these twelve revolutions cause the plate to drop a vertical distance equal to its own height as the thread is unwound. The galvanometer deflec-

[3] The resistance of all the capillary lamps described here increases with temperature, but in some low-pressure lamps an increase in temperature and vapor pressure may lead to a decrease in resistance. In such a case the conditions would be reversed and the lamp would be more stable when dW/dr is positive. J would then be the *upper* limit.

tions are recorded as horizontal displacements and thus continuous curves are automatically obtained with intensities graphed against wave lengths. The rotation of the axle and drum is slowed down to approximately one revolution per minute with the help of a variable-speed motor and reducing pulleys.

The single filament galvanometer lamp is operated at slightly more than the normal current, in order to give sufficient intensity for recording. The greatest difficulty lies in the fact that in the flat hollows of the curve the beam is traveling over the paper at the rate of perhaps 1 cm. per minute but as it approaches the peaks it may be traveling at the rate of 1 cm. per second. On account of this variation in exposure time a flat developer of metol or pictol is used.

A wave length scale was prepared on a film placed in the carrier. The galvanometer and monochromator were disconnected, the drum stopped at integral wave lengths and a line was exposed by flashing on an electric light. The peaks were identified with the help of this scale by reference to Eder and Valenta's "Atlas typischer Spektren" (Österreichischen Staatsdruckerei, Wien, 1924). The identification was facilitated also by comparison with spectrograms of the lamp taken with a large Fuess quartz spectrograph which gave nearly the same dispersion as the graphs.

The capillary dimensions, which bring most of the radiation to the slit of the monochromator, combined with the large input of energy, give such high intensities that it is possible to use a monochromator with a narrow slit and still obtain adequate deflections with a thermopile and galvanometer. This method is superior to the more common method in which spectrograms are analyzed by measuring the density of the lines on the photographic plate. In the spectrographic method the blackening of the plate does not depend alone on the intensity of light; but the thermopile–galvanometer deflections obtained by the method described here are directly proportional to the intensity at all wave lengths.

In the graphs the emission lines are labeled and their energies in ergs per second falling on 1 sq. mm. of the thermopile, with the monochromator, are given in the accompanying tables. The energy entering the monochromator slit is much greater with the capillary lamps than with commercial mercury lamps of larger dimensions.

Calibration against a radiation lamp, C44, of the U. S. Bureau of Standards showed that the sensitivity of the thermopile and galvanometer was such that a deflection of 1 cm. was produced by 15.68 ergs of radiation per sec. per sq. mm. In the case of the most intense lines the deflections passed beyond the photographic recording-box and were determined by visual observation. In Figs. 5–8 a shunt was used which reduced the sensitivity to 29.7 ergs per sec. per sq. mm. for a deflection of 1 cm.

The slit at the thermopile was 0.22 mm. in width, 8.9 mm. in length and 1.96 sq. mm. in area. The effective slit width is shown in the circular insert in Fig. 3. It is the same for all the figures. In determining this width it was found that the image of the front slit moved across the face of the thermopile a distance of 10.5 mm. in changing from 5970 to 2570 Å., while the distance between the same wave lengths on the photographic paper, amplified by the drum movement and thread, was 98 mm. The effective slit width on the graphs was then 98/10.5 times the actual slit width. The front slit was 0.382 mm. for Figs. 3–5 and 0.254 mm. for Figs. 6–8.

For photochemical purposes the thermopile slit may be broadened, thus giving a proportional increase in intensity. In the distribution curves a narrow slit is required to show the valleys between peaks, but in photochemical work one isolated line may be focused on the center of a broader slit without overlapping. The effective slit width may be nearly as great as the distance to the adjoining peaks. With the apparatus described here it would be safe in most cases to treble the slit width to 0.66 mm. and then the total energy available may be obtained by multiplying the values in Figs. 3–8 by a

Wave length, Å.	Ergs sec. × mm.²
A 5552	67
B 4723	160
C 4308	17
D 4122	67
E 3888	5
F 3596	78
G 3511	74
H 3397	67
I 3068	298
J 3025	154
K 2993	138
K 2989	
L 2938	111
M 2898	64
M 2864 (Hg)	
N 2731	17
O 2697	13
P 2628	33
Q 2525	31
Q 2516	
R 2490	22
S 2431	19
T 2401	13
U 2309	3
V 2231	3

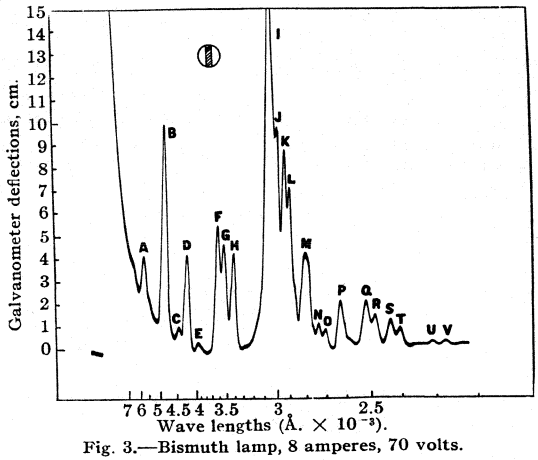

Fig. 3.—Bismuth lamp, 8 amperes, 70 volts.

Wave length, Å.	Ergs sec. × mm.²
A 7399	122
B 6439	1030
C 5086	950
D 4800	824
E 4678	824
F 4415	44
G 3729	49
H 3610	1010
I 3466	680
J 3404	512
K 3261	174
K 3253	
L 3133	82
M 2981	201
N 2881	108
O 2764	33
P 2678	19
Q 2329	5
R 2288	5

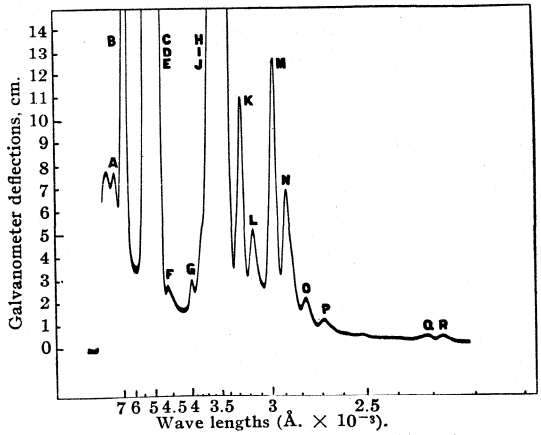

Fig. 4.—Cadmium lamp, 5.2 amperes, 110 volts.

Wave length, Å.	Ergs sec. × mm.²
A 7229	398
B 6002	202
C 5006	175
D 4386	48
E 4168	33
F 4062	487
F 4057	
G 3740	520
G 3684	
G 3640	
H 3221	64
I 3151	80
J 2873	122
K 2833	214
K 2802	
L 2698	36
M 2663	107
N 2614	68
O 2577	56
P 2476	24
Q 2444	28
R 2394	33
S 2333	3

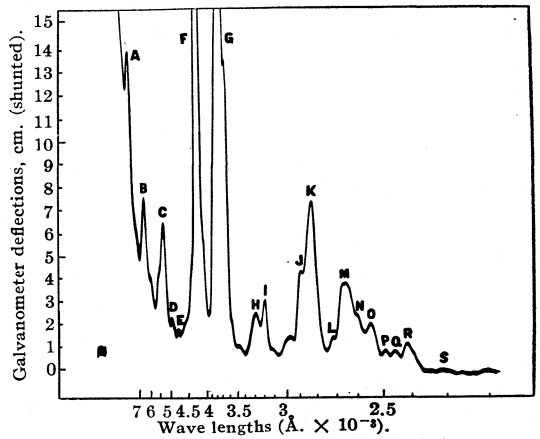

Fig. 5.—Lead lamp, 5.4 amperes, 100 volts.

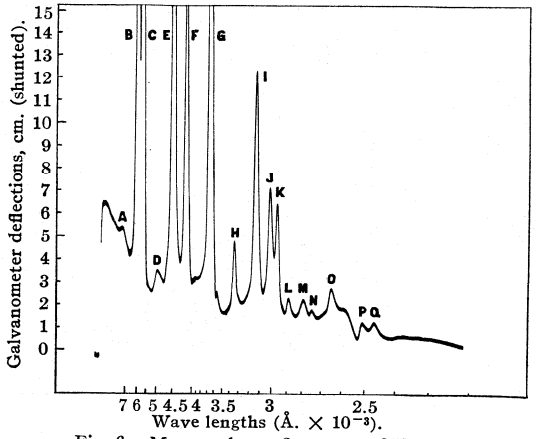

Fig. 6.—Mercury lamp, 2 amperes, 350 volts.

Wave length, Å.	Ergs sec. × mm.²
A 6907	166
B 5790	1125
B 5769	
C 5461	1285
D 4916	107
E 4359	962
F 4047	546
G 3650	843
H 3341	145
I 3131	371
J 3023	214
K 2967	193
L 2894	71
M 2804	68
N 2753	53
O 2652	80
P 2536	36
Q 2482	36

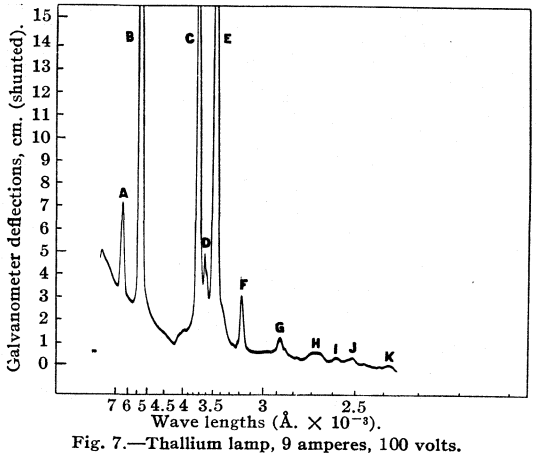

Fig. 7.—Thallium lamp, 9 amperes, 100 volts.

Wave length, Å.	Ergs sec. × mm.²
A 6550	199
B 5351	1390
C 3776	600
D 3650 (Hg)	137
E 3519	655
F 3230	83
G 2922	33
H 2768	15
H 2709	
I 2609	9
J 2580	12
K 2380	6

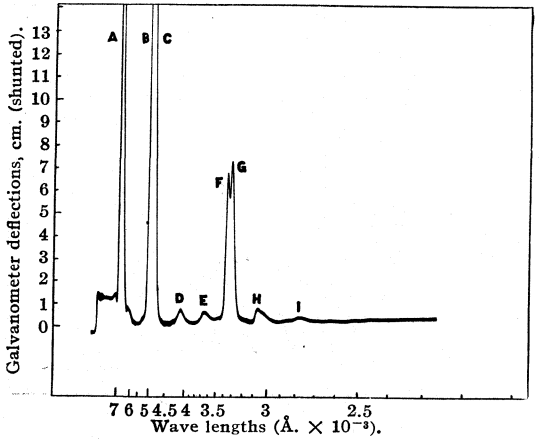

Fig. 8.—Zinc lamp, 6 amperes, 100 volts.

Wave length, Å.	Ergs sec. × mm.²
A 6362	511
B 4811	644
C 4722	623
C 4680	
D 4062 (Pb)	27
E 3684 (Pb)	21
F 3346	202
G 3303	217
G 3282	
H 3072	21
H 3036	
H 3018	
I 2801	6
I 2771	
I 2757	

factor of 5.9 sq. mm. A large monochromator, already described,[4] gives about ten times the radiation intensity per sq. mm. recorded here and the slit height is 20 mm. With such an instrument, using a slit 0.66 mm. wide, the values given in Figs. 3–8 may be multiplied by a factor of 133. The intensities may be still further increased by increasing the wattage through the lamp.

In comparing the different lamps it must be remembered that the voltage and amperage vary greatly with different lamps depending on the air space and on other specific factors. It is difficult to make two lamps with just the same characteristics but the relative intensities of the different lines are roughly constant. In some cases a film of silicate is formed on the inside of the lamp which diminishes the intensity of the ultraviolet lines more than the lines in the visible. Many of the lamps operated successfully for ten hours or more. Further investigation is necessary to determine whether some metals at the high operating temperature of the lamps (above the melting point of quartz) are able to reduce the silica itself. In some cases the purification of the metal and the exclusion of oxygen tended to prevent the deterioration. The lamps may be filled with nitrogen or other inert gas by making a tiny hole in one electrode and subjecting to alternate evacuation and filling with the inert gas.

Characteristics of the Different Lamps

Bismuth.—The bismuth lamp described in Fig. 3 proved to be simple to make and operate. It ran smoothly without extensive deterioration of the quartz. It is excellent for the production of ultraviolet light, having many strong, easily separable lines, and giving measurable intensities down to 2271 Å. The most intense line is at 3068–3025 but prominent, well isolated lines occur also at 4723, 4122, 3511, 2898 and 2628. A spectrogram showed that the 3068 line is reversed, *i. e.*, light of exactly 3068 Å. is absorbed by the un-ionized bismuth vapor in the lamp.

Cadmium.—The cadmium lamp described in Fig. 4 is particularly useful as a source of red light, the line at 6439 Å. being very intense and well isolated. There are three intense lines at 5086, 4678 and 4415, and another group at 3610, 3466 and 3404. The lines at 3261, 3133 and at 2981 are intense and well isolated. The cadmium lamp however tends to form an inner film (probably of cadmium silicate) which absorbs the ultraviolet radiation after running for a short time. The visible light is not seriously reduced. The electrodes must be pure and they must not be overheated in making the lamp because they oxidize quickly. Moisture seems to accelerate the formation of the glass film. Inasmuch as some lamps last considerably longer than others it was thought that oxygen might be the limiting factor in the deterioration but nitrogen-filled lamps did not seem to be much better.

Lead.—The lead lamp described in Fig. 5 gives a spectrum which is rich in ultraviolet. The most intense region is at 3740–3640 Å. Well isolated lines are found at 2833–2802 and at 2663. The violet line at 4062–4057 is intense and well isolated. Reversals are noted in the spectrogram at 2833, 2802, 2663, 2614, 2577, 2476, 2444 and 2394.

[4] Heidt and Daniels, THIS JOURNAL, **54**, 2384 (1932).

The lead must be pure as the film inside the lamp which forms rapidly with impure lead is opaque.

Mercury.—The mercury lamp is too well known to warrant a discussion. It is shown in Fig. 6 so that it may be used as a reference in estimating the behavior of the lamps of the other metals, when the behavior of a mercury lamp with a certain photochemical set-up is known. Its construction and operation are simpler[1] and the lamp may be used over again after being stopped.

Thallium.—The thallium lamp has a simple spectrum as shown in Fig. 7. Greater intensity was obtained with the 5351 line of thallium than with any other lamp. The lines at 5351, 3776 and 3519 are very intense and well isolated. A weaker line at 3230 is also suitable for photochemical use. The metal is rather expensive and it oxidizes readily. A spectrogram showed the black central lines of reversal at 3776, 3519, 2922 and 2768.

Zinc.—The zinc lamp shown in Fig. 8 gives three excellent lines for photochemical work. The red line at 6362 Å. is even more isolated than the red line of cadmium, and the lines at 4811–4680 and at 3346–3303 are intense and unusually well isolated. The lamp is not seriously affected by the formation of inside coatings. One lamp was still operating satisfactorily when it had to be turned off after operating for fifteen hours.

Miscellaneous.—Lamps of silver, copper and aluminum were tried, but without success. Tin gives a number of ultraviolet lines but an air-filled tin lamp was unsuccessful, burning out in about five minutes. Antimony in an air-filled lamp attacked the quartz and lasted only a few minutes; but another, nitrogen-filled lamp lasted for more than ten hours. Antimony has practically no lines in the visible but many in the ultraviolet, especially below 3000 Å. The lines are too close for convenient isolation with a monochromator but the lamp might be useful for general ultraviolet radiation.

A lamp was constructed with the eutectic alloy of bismuth and lead. A spectrogram showed all the lines of both metals. Alloy lamps may be convenient for getting lower melting points and for general radiation, but they are not satisfactory for isolating intense lines because the lines are too close together and because the energy of the lamp is distributed among many lines, leaving individual ones weaker.

The authors are glad to acknowledge the support of the Research Committee of the University of Wisconsin in purchasing a dynamo which was isolated to give constant current while the measurements were made.

Summary

1. A quartz capillary lamp has been developed for metals other than mercury. The lamps can be used only once but they are comparatively inexpensive.

2. A circuit is described for starting the lamps by sparking.

3. The distribution of energy in capillary arcs of bismuth, cadmium, lead, mercury, thallium and zinc has been determined.

4. A photographic method is described for recording the thermopile–galvanometer deflections.

5. Intense sources of light, comparable with those of the constricted mercury arc, can be obtained for several additional wave lengths.

6. When an external resistance is used the potential drop across the lamp should be at least half the line voltage. When this condition cannot be met a shunt is used, and a method for adjusting to maximum constancy is described.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. X. THE DETERMINATION OF ANTIMONY AND ARSENIC[1,2]

BY N. HOWELL FURMAN

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Introduction.—Conflicting evidence has been reported by Rathsburg[3] and by Willard and Young,[4] respectively, regarding the oxidation of trivalent antimony by ceric sulfate. In some preliminary work[5] our own conclusions differed somewhat from those of Willard and Young,[4] who stated that the oxidation was too slow to be practical at room temperature without the addition of a catalyst. The further work presented in this paper supports the conclusion of Rathsburg[3] that the reaction is sufficiently rapid at room temperature in solutions containing *high concentrations of hydrochloric acid* (one-sixth to one-third by volume of acid of sp. gr. 1.19). Rathsburg stated that antimony could be titrated in the presence of arsenic under these conditions. The author has found that the results for antimony tend to become erratic when the concentration of arsenious acid is roughly equivalent to that of the antimony. If the initial volume per cent. of hydrochloric acid is below 40, simultaneous oxidation of arsenic is apt to occur. When the amount of antimony exceeds that of the arsenic the results here presented show that it is possible to determine both antimony and arsenic in a single potentiometric titration with ceric sulfate. After the end-point of the oxidation of the antimony, iodine monochloride

[1] Presented at the Eighty-third meeting of the American Chemical Society, New Orleans, La., 1932.

[2] For previous papers of this series, see THIS JOURNAL, **50,** (a) 755, (b) 1675 (1928); **51,** (c) 1128, (d) 1449 (1929); **52,** (e) 1443, (f) 2347 (1930); **53,** (g) 1283, (h) 2561 (1931).

[3] Rathsburg, *Ber.*, **61,** 1664 (1928).

[4] Willard and Young, THIS JOURNAL, **50,** 1376 (1928).

[5] Furman and Wallace, unpublished, 1928.

is added as a catalyst and the arsenic is then determined as was suggested by Willard and Young.[4]

Experimental

Apparatus and Materials.—The potentiometric titrations were in part made with the apparatus used in previous studies of this series, and in part with the continuous reading device described by Furman and Wilson.[6] The preparation and standardization of ceric sulfate solutions has also been described.[2c] Antimony solutions were prepared by dissolving weighed quantities of the metal in concentrated sulfuric acid, and adding hydrochloric acid to prevent hydrolysis (250 cc. of hydrochloric acid of sp. gr. 1.19 per liter). Pure sublimed arsenious oxide was dissolved in alkali, and the solution neutralized with hydrochloric acid. Both materials were from a supply used in previous investigations. Portions of the solutions were titrated with potassium bromate which had been standardized against Bureau of Standards arsenious oxide. The content of the antimony solutions (per 25 cc.) found in this manner was on the average 1 part in 1250 lower than the quantity calculated from the weight of metal taken. The arsenic found agreed with the amount calculated from material weighed.

Iodine monochloride (0.005 *M*) dissolved in 1:1 hydrochloric acid was prepared as described by Willard and Young.[7]

Methyl orange was found to be a satisfactory indicator for the end of the oxidation of the antimony. Two drops (0.1 cc.) of a 0.1% aqueous solution were used. Methyl red was stated by Rathsburg[3] to be satisfactory, but our experience showed that it was less satisfactory than methyl orange because of its greater ease of oxidation by ceric sulfate.

Determination of Antimony.—Some results which indicate the accuracy and limitations of the method are given in Table I.

These results, and a number of others not presented here, indicate that the method is best applied to cases in which the quantity of arsenic is much exceeded by that of the antimony. The experiments indicated that the simultaneous oxidation of arsenic could be prevented by diminishing its absolute concentration by diluting the solution with hydrochloric acid (40% hydrochloric acid of sp. gr. 1.19 by volume). In one case, for example, a satisfactory determination of antimony was made in the presence of 1.8 times as much arsenic. If the concentration of hydrochloric acid is decreased (Expt. 9, Table I) the arsenic begins to be oxidized before the completion of the oxidation of the antimony, and very erratic results are obtained.

Successive Determination of Antimony and Arsenic.—Measured volumes of arsenic and antimony solutions were mixed and enough hydro-

[6] Furman and Wilson, THIS JOURNAL, **50**, 277 (1928).

[7] Willard and Young, *ibid.*, **50**, 1322 (1928).

TABLE I

USE OF CERIC SULFATE IN DETERMINING ANTIMONY

A. No arsenic present

No	Antimony present, g.	Ceric sulfate, cc.	Antimony found, g.	Error, mg.	Indicator	HCl (sp. gr. 1.19); per cent. by vol. Init.	Final
1	0.0503	8.80	0.0506	+0.3	M. orange	33	28.5
2	.0503	8.72	.0503	± .0	M. orange	71	57
3	.1256	21.77	.1257	+ .1	F. and W.	50	35
4	.1256	21.76	.1256	± .0	F. and W.	50	35
5	.1261	18.93	.1264	+ .3	F. and W.	50	36
6	.1261	18.90	.1262	+ .1	F. and W.	44	31
7	.1261	18.90	.1262	+ .1	F. and W.	37	25
8	.1261	18.89	.1261	± .0	F. and W.	28.6	18

B. Arsenic present

								As present, g.
9	0.1256	No end-point				33		0.0937
10	.1256	21.78	0.1257	+0.1	F. and W.	41	30	.0375
11	.1256	21.78	.1257	+ .1	M. orange	41	30	.0375
12	.1256	21.83	.1260	+ .4	M. orange	53	40	.0375
13	.1256	21.80	.1258	+ .2	M. orange	46	34	.0375

F. and W. refers to the galvanometric method of Furman and Wilson. The ceric solutions were: 0.0948 *N*, Expts. 1–4 and 9–13; 0.1097 *N*, Expts. 5–8. In Expt. 8 the reaction was very sluggish near the end-point due to the relatively low concentration of hydrochloric acid.

chloric acid, sp. gr. 1.19, was added to make up at least 40% of the total initial volume, which ranged from 40–70 cc. The completion of the oxidation of antimony was determined potentiometrically. Then 10 cc. of 0.005 *M* iodine monochloride was added, and the titration was continued to a second potentiometric end-point, which corresponded to the completion of the oxidation of the arsenic. If necessary the solution was adjusted to

TABLE II

USE OF CERIC SULFATE IN DETERMINING BOTH ARSENIC AND ANTIMONY

No.	Antimony present, g.	Ceric sulfate, cc.	Antimony found, g.	Error, mg.	Arsenic present, g.	Ceric sulfate, cc.	Arsenic found, g.	Error mg.
1	0.1256	21.82	0.1259	+0.3	0.0375	10.54	0.0374	−0.1
2	.0503	8.74	.0504	+ .1	.0937	26.53	.0943	+ .4
3	.0503	7.47	.0504	+ .1	.0375	9.17	.0379	+ .4
4	.0503	7.49	.0505	+ .2	.0375	9.13	.0378	+ .3
5	.1256	18.68	.1260	+ .4	.0375	9.15	.0378	+ .3
6	.1261	18.94	.1265	+ .4	.0374	9.09	.0374	± .0
7	.1261	18.95	.1265	+ .4	.0374	9.13	.0375	+ .1

NOTES: Ceric solutions: Expts. 1–2, 0.0948; Expts. 3–5, 0.1107 *N*; Expts. 6–7, 0.1097 *N*. Initial concentration of hydrochloric acid (sp. gr. 1.19), 40–50% by volume. Final concentration, 32–43%. The Furman and Wilson[6] galvanometric method was used in Expts. 1–2, 6–7; the classical potentiometric method with a Pt–normal calomel electrode system was used in Expts. 3–5.

the acid normality suggested by Swift and Gregory.[8] Figure 1 presents a graph of the data in a typical instance. Some representative results are given in Table II.

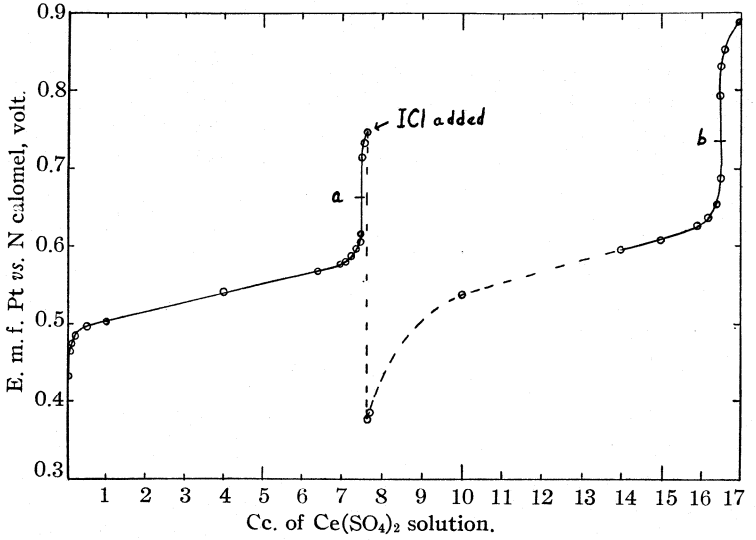

Fig. 1.—Graph of titration data for a mixture of 0.0503 g. of antimony and 0.0375 g. of arsenic in a solution containing 43% hydrochloric acid (sp. gr. 1.19) by volume. Point *a* is the end-point of the oxidation of the antimony (0.104 volt change per 0.03 cc. reagent), and *b* that for the end of the oxidation of the arsenic (0.093 volt per 0.04 cc. of reagent). The ceric sulfate was 0.1107 *N*. Data of Expt. 4, Table II.

Summary

Antimony may be determined by titration with standard ceric sulfate at room temperature without addition of a catalyst if 30–50% by volume of hydrochloric acid (sp. gr. 1.19) is initially present.

The method may be applied to the determination of antimony in the presence of a minor amount of arsenic. Simultaneous oxidation of arsenic may occur if the acid concentration is much below 40% by volume, or if the absolute concentration of the arsenic is relatively high.

After the end-point of the oxidation of antimony has been found, iodine monochloride catalyst may be added and the titration with ceric sulfate continued to a second end-point, which corresponds to the completion of the oxidation of the arsenic.

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[8] Swift and Gregory, THIS JOURNAL, **52**, 901 (1930).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A SERIES OF SIMPLE BASIC INDICATORS. II. SOME APPLICATIONS TO SOLUTIONS IN FORMIC ACID[1]

BY LOUIS P. HAMMETT AND ALDEN J. DEYRUP[2]

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A major incentive for the setting up of the series of indicators described in the previous article[3] was the expectation that such a series would be widely applicable to solutions in various solvents. We have therefore applied these indicators, previously standardized in mixtures of strong acids with water, to solutions in the anhydrous solvent formic acid. In this solvent two tests of the indicator system are possible. The results of one, the comparison of the relative basicities of indicators in the anhydrous solvent with the former standardization, have been included in the previous article; the detailed experimental data are given here. The other is the comparison of the results obtained with indicators with the electrometric[4] and conductivity[5] data already existing for the solvent. We have further tested the usefulness of the indicator system by extending our knowledge of ionization relations in this solvent and of the general properties of some very weak uncolored bases.

An acid–base system independent of the water system may be referred to formic acid in the same way as was first done by Franklin[6] with ammonia. We may therefore consider solutions as acid, neutral, or alkaline with respect to it as a solvent, we may speak of a concentration of solvated hydrogen ion, and we may determine that concentration if we possess a strong acid in whose solutions the hydrogen-ion concentration may be taken equal to the stoichiometric acid concentration. Likewise we may determine with reference to some strong base the concentration of formate ion, which in this solvent plays the part of hydroxyl ion in water. We may determine ionization constants of weak acids and bases, which will be different from the constants for the same substances in water or in other solvents. All such quantities partake very deeply of the nature of the particular solvent; we shall call them formic acid functions. They must be sharply distinguished from the H_0 and the pK' of the previous article, which are independent of the solvent system, and which we shall call general acid–base functions.

[1] This article is based mainly upon part of a dissertation submitted by Alden J. Deyrup to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, March, 1932.

[2] Gottsberger Fellow, 1931–1932.

[3] Hammett and Deyrup, THIS JOURNAL, 54, 2721 (1932).

[4] Hammett and Dietz, *ibid.*, **52**, 4795 (1930).

[5] Schlesinger and co-workers, *ibid.*, **33**, 1924 (1911); **36**, 1589 (1914); **38**, 271 (1916); **41**, 72, 1921, 1934 (1919).

[6] See for instance *ibid.*, **46**, 2137 (1924).

We shall use the following symbols

$$pH(\mathrm{HCOOH}) \equiv -\log C_{\mathrm{H^+(HCOOH)}} \quad (1)$$

where $C_{\mathrm{H^+(HCOOH)}}$ is the concentration of the solvated hydrogen ion in formic acid.

$$pK_{\mathrm{S}}(\mathrm{HCOOH}) \equiv -\log C_{\mathrm{H^+(HCOOH)}} C_{\mathrm{COOH'}} \quad (2)$$

$$pK'_{\mathrm{B}}(\mathrm{HCOOH}) \equiv -\log \frac{C_{\mathrm{H^+(HCOOH)}} C_{\mathrm{B}}}{C_{\mathrm{BH^+}}} = pH(\mathrm{HCOOH}) - \log \frac{C_{\mathrm{B}}}{C_{\mathrm{BH^+}}} \quad (3)$$

$$pK_{\mathrm{B}}(\mathrm{HCOOH}) \equiv -\log \frac{C_{\mathrm{BH^+}} C_{\mathrm{COOH'}}}{C_{\mathrm{B}}} = pK_{\mathrm{S}}(\mathrm{HCOOH}) - pK'_{\mathrm{B}}(\mathrm{HCOOH}) \quad (4)$$

$pK'_{\mathrm{B}}(\mathrm{HCOOH})$ is the analog for formic acid solution of the logarithmic hydrolysis constant of the salt of an anhydro base in water, which may also[7] be considered the ionization constant of the cation of the base. pK_{B}-(HCOOH) is the analog of the ionization constant of the base in water. By combination of equation 3 with equation 4 of the previous article we obtain

$$pK'_{\mathrm{B}}(\mathrm{HCOOH}) - pK'_{\mathrm{B}} = pH(\mathrm{HCOOH}) - H_0 \quad (5)$$

which relates the formic acid functions to the general acid–base functions pK' and H_0.[8]

Materials and Procedure

The indicators and the sulfuric acid were the materials described in the first article of this series.[3] Formic acid, benzene sulfonic acid and sodium formate were obtained or purified as described by Hammett and Dietz.[4] For comparison, formic acid was also purified by the method of Schlesinger,[5] distillation from pure phosphorus pentoxide under reduced pressure at room temperature. The product obtained by the Coolidge method (that used by Hammett and Dietz) froze within 0.01° of that purified by the Schlesinger method. This corresponds to a difference in water content of less than 0.005 mole per liter. The bulbs containing the benzene sulfonic acid were filled with dried air before sealing off to eliminate the uncertainty of a buoyancy correction. The product analyzed 100.3% $C_6H_5SO_3H$ by titration.

Aniline was freshly redistilled, the middle portion (b. p. 183°) only being retained. Acetanilide was recrystallized twice from alcohol, and dried at 90–100°, m. p. 114°. Propionitrile was distilled twice from phosphorus pentoxide (b. p. 98°). Sodium sulfate and sodium bisulfate were dried to constant weight at 120°.

Procedure.—Solutions of weighed quantities of the various solutes in the purified formic acid were made up in volumetric flasks. In the case of benzene sulfonic acid the bulbs were broken and the solutions prepared as described by Hammett and Dietz.[4] Ten-cc. portions of the various solutions were transferred with a pipet to 12-cc. weighing bottles, which were then kept in a desiccator until used. In a blank experiment all of the manipulations involved in the preparation of the benzene sulfonic acid solutions were carried out on pure formic acid and a subsequent freezing point determination showed that absorption of water from the air under these conditions was negligible. Although the strongly acid solutions evolve bubbles of gas after several hours, the decomposition thus indicated was found to be insufficient to make any measurable difference in the indicator acidity at the beginning and at the end of a series of measurements.

[7] Brönsted, *Rec. trav. chim.*, **42**, 719 (1923).

[8] The definitions and equations for weak acids analogous to these for weak bases are obvious.

The indicators were added in the form of a measured number of drops of a solution in anhydrous formic acid exactly as described in the previous article. The colorimetric comparisons were carried out as there described, using the closed cell pictured in Fig. 1 of that article, and with solutions of the indicator in water or in 95% sulfuric acid as reference standards. The concentration of the indicator varied from 2×10^{-5} to 3×10^{-3}, and was in every case kept so low as to produce no significant change in the acidity of the solution under investigation.

Discussion of Results

The Indicator Constants.—From the values of I_w and I_h[3] given in Table II for solutions of sodium formate and of benzene sulfonic acid we have determined on a large scale chart the limiting values corresponding to complete conversion to the colored form. These quantities, S_w and S_h[3], were found to have in formic acid the values given in Table I. A series of experiments failed to detect any change in the color intensity of the completely converted indicator due to the addition of 0.5 molar sodium benzene sulfonate with indicators 4, 5, 8, 13, 15. It consequently seems safe to assume that S is constant throughout the range of 0 to 0.1 molar concentration and that the error due to the medium effect upon the specific color intensity of the colored form is negligible in the experiments here described.

Having the values of S and I the values of log $[BH^+]/[B]$ were calculated by equations 10 and 11 of the previous article and from these the relative basicities of the indicators by equation 3 of that article. *o*-Nitraniline was used as a reference base with which the others were compared, its pK' being taken as +0.13, the average of the values obtained in the previous work. The results are given in Table I. The significance of the concordance within experimental error of these values with those obtained in the aqueous mixtures was discussed in the previous article.[9]

TABLE I

PROPERTIES OF INDICATORS

No.	Name	S_w or S_h	pK_B(HCOOH)	pK'
2	*o*-Nitraniline	1.00 ± 0.07	1.22	(+0.13)
3	*p*-Chloro-*o*-nitraniline	1.00 ± .03	1.99	−0.64
4	*p*-Nitrodiphenylamine	1.00 ± .03	3.56	−2.21
5	2,4-Dichloro-6-nitroaniline	1.00 ± .05	4.36	−3.01
8	2,4-Dinitroaniline	0.63 ± .02	..	..
7	2,6-Dinitro-4-methylaniline	.88 ± .02	..	..
13	6-Bromo-2,4-dinitroaniline	.68 ± .02	..	..
15	2,4,6-Trinitroaniline	.61 ± .03	..	..
6	*p*-Nitroazobenzene (extrapolated)	.50 ± .03	4.34	−2.99

[9] In agreement with predictions based on Table I of the previous article, *p*-nitraniline was found to be very largely ionized even in 0.1 *m* $NaHCO_2$ solution, and the following indicators were found to be only partially ionized in 0.1 *m* $C_6H_5SO_3H$ solution: 2,6-dinitro-4-methylaniline, 2,4-dinitroaniline, N,N-dimethyl-2,4,6-trinitroaniline; benzalacetophenone, β-benzoylnaphthalene, *p*-benzoyldiphenyl, 6-bromo-2,4-dinitroaniline, anthraquinone, 2,4,6-trinitroaniline.

Strong Acids and Bases.—Values of H_0 are by definition immediately deducible from indicator measurements, and the results for solutions of sulfuric acid, benzene sulfonic acid, sodium formate and aniline are given in Table II, and are plotted against the logarithm of the concentration

TABLE II

STRONG ACIDS AND BASES

Sodium Formate Solutions

Concn.	I_w	Log $\frac{[BH^+]}{[B]}$	H_0	I_w	Log $\frac{[BH^+]}{[B]}$	H_0
	o-Nitraniline			*p*-Chloro-*o*-nitraniline		
0.1011	0.54	−0.07	+0.20	0.85		
.0482	.333	+ .30	− .17	.67		
.0263	.243	.51	− .38	.65	−0.28	−0.36
.0245	.234	.52	− .39	.66	− .28	− .36
	.246	.49	− .36			
.0115	.156	.73	− .60	.57	− .12	− .52
	.159	.72	− .59			
.0063	.100	.96	− .83	.44	+ .11	− .75
	.099	.97	− .84			

Benzene Sulfonic Acid Solutions

	o-Nitraniline			*p*-Chloro-*o*-nitraniline		
0.00555	0.0021	+2.84	−2.71	0.0124	+2.00	−2.64
.0110	.0016	2.98	−2.85	.0073	2.20	−2.84
.0257				.0049	2.40	−3.04
.0378				.0026	2.61	−3.25
				.0031	2.53	−3.17
	p-Nitrodiphenylamine			2,4-Dichloro-6-nitroaniline		
0.00555	0.27	+0.43	−2.64	0.68	−0.33	−2.68
.0110	.222	.55	−2.76	.62	− .21	−2.80
.0257	.111	.90	−3.11	.49	+ .02	−3.03
.0378	.085	1.03	−3.24	.36	.25	−3.26
.144	.0294	1.52	−3.73	.167	.70	−3.71

	p-Nitroazobenzene I_h		
0.00555	0.166	−0.31	−2.68
.0110	.206	− .15	−2.84
.0257	.284	+ .12	−3.11
.0378	.273	.08	−3.07

Sulfuric Acid Solutions

	p-Nitrodiphenylamine			2,4-Dichloro-6-nitroaniline		
0.1064	0.020	+1.69	−3.90			
	.019	1.71	−3.92			
.0903	.022	1.65	−3.74			
	.023	1.63	−3.72			
.0531	.038	1.40	−3.61	0.27	+0.43	−3.44
.0451	.052	1.26	−3.35			
	.054	1.25	−3.34			
.0266	.096	0.97	−3.18	.42	.14	−3.15

TABLE II (*Concluded*)

Aniline Solutions

Concn.	I_h	Log $\frac{[BH^+]}{[B]}$	H_0
	o-Nitraniline		
0.1023	0.53	−0.05	+0.18
	.55	− .09	+ .22
.0511	.39	+ .19	− .06
	.40	+ .18	− .05
.0256	.278	+ .42	− .29

in Fig. 1. In order to calculate any of the formic acid functions it is necessary to refer to solutions of strong acids and bases in that solvent. Hammett and Dietz[4] found that the behavior in electrometric titrations of benzene sulfonic acid and sodium formate was indistinguishable from that of strong electrolytes. The indicator data confirm this conclusion for sodium formate by showing a close agreement in the acidity of equimolar solutions of sodium formate and aniline and a small deviation of both from the 45° straight line which would be followed by completely ionized bases in the absence of salt effects. Indeed it may be calculated from these data that the ratio of the activity coefficients of a univalent ion in 0.01 and 0.1 molar solution is 1.20, not very different from the value obtained in aqueous solution.

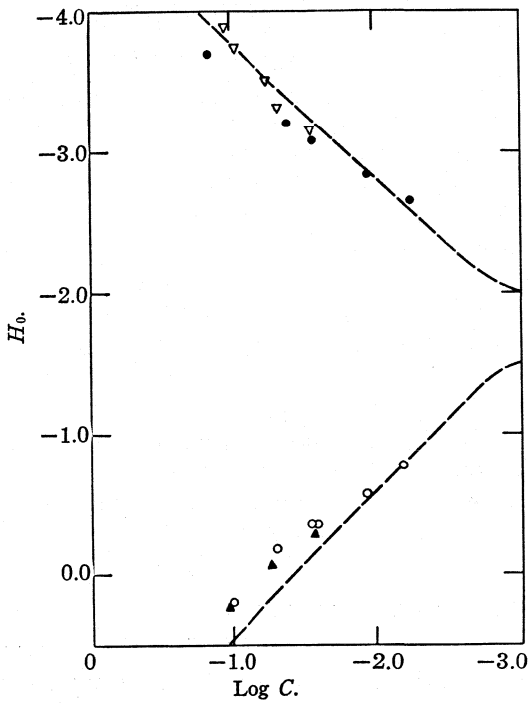

Fig. 1.—▽, H_2SO_4; ●, $C_6H_5SO_3H$; ○, $NaCHO_2$; ▲, $C_6H_5NH_2$.

With respect to benzene sulfonic acid the results do indicate a small but probably significant incompleteness of ionization. The reaction of a strong monobasic acid with a basic indicator

$$H^+(HCOOH) + B \rightleftharpoons BH^+ + HCOOH$$

should be displaced by a change in ion concentration only as a result of specific variations in activity coefficients.[10] Except for the result of such

[10] Brönsted, *J. Chem. Soc.*, **119**, 574 (1921).

specific effects the H_0-log C plots for sulfuric acid and benzene sulfonic acid should coincide with each other and with the 45° straight line if both are strong monobasic acids. The close agreement obtained with sodium formate and aniline makes it improbable that such specific effects are large enough to account for the deviations observed. The difference in the results for the two acids cannot be attributed to the secondary ionization of the sulfuric acid. Using indicator 4 we have found the H_0 value for a 0.14 molar solution of sodium bisulfate in formic acid to be −2.20, only 0.4 unit more acid than the pure solvent; using indicator 2 we have found the H_0 for a 0.101 molar solution of sodium sulfate to be −0.25, which is 0.45 unit less "alkaline" than an equimolar sodium formate solution. From the latter figure the extent of the solvolysis

$$SO_4'' + HCOOH \rightleftharpoons HSO_4' + COOH'$$

is 35% and the ionization constant $[H^+(HCO_2H)][SO_4'']/[HSO_4']$ is 2×10^{-5}. The secondary ionization of sulfuric acid must therefore be negligible in the acid solutions under consideration.

Further evidence that benzene sulfonic acid is not quite a strong acid is offered by an experiment in which the acidity, H_0, of a solution containing 0.0121 molar sulfuric acid and 0.0945 molar sodium benzene sulfonate was determined with indicator 4 and found to be −2.59, which is 0.25 unit less acid than is benzene sulfonic acid in 0.0121 molar concentration.

We conclude therefore that sulfuric acid is a strong monobasic acid in formic acid, and that benzene sulfonic acid is nearly but not quite a strong electrolyte. The ionization of the latter is estimated at 60% in 0.1 molar solution and very nearly 100% in 0.01 molar solution.

The Ion Product Constant of the Solvent.—We may set the concentration of solvated hydrogen ion in a solution of a strong acid equal to the stoichiometric concentration of the acid and compare the pH(HCOOH) thus obtained with the H_0 value. From Fig. 1 we obtain as a best value

$$pH(\text{HCOOH}) - H_0 = 4.85 \qquad (6)$$

Substituting in equation 2

$$pK_S(\text{HCOOH}) = -\log C_{COOH'} + H_0 + 4.85 \qquad (7)$$

Since sodium formate and aniline are strong bases we may set $C_{COOH'}$ equal to the stoichiometric concentration of base. Substituting the best values of H_0 from Fig. 1 we have for the logarithmic ion product constant pK_S(HCOOH) at 0.1 molar ionic strength, 6.03; at 0.01 molar ionic strength, 6.17. Substituting in equation 7 we have

$$\log C_{COOH'} = H_0 - 1.32 \qquad (8)$$

which we shall use in calculating the ionization constants of weak bases.

From pK_S(HCOOH) = 6.17, the pH(HCOOH) of pure formic acid is 3.09 and from equation 6 the acidity H_0 of the pure solvent is −1.76. A direct determination of this quantity by measurements on the pure solvent

is possible with a solvent as highly ionized as formic acid, and furnishes a valuable check on the ion product constant. The experiments were carried out with indicator concentrations (given under the heading c_i in Table III) too small to displace significantly the acidity of the pure solvent. The formic acid used, purified by the Schlesinger method, is estimated from its freezing point to contain less than 0.005 mole per liter of water. From the results given in Table III the mean observed value of H_0 is -1.8 in excellent agreement with the above calculated value.

TABLE III

ACIDITY OF PURE FORMIC ACID

c_i	I_w	Log $\frac{[BH^+]}{[B]}$	H_0	c_i	I_w	Log $\frac{[BH^+]}{[B]}$	H_0
	o-Nitraniline				*p*-Nitroazobenzene		
0.00005	0.081	+1.05	−1.69	0.00005	0.037	−1.10	−1.89
.00004	.084	+1.04	−1.68	.00002	.042	−1.04	−1.95

Comparison with Conductivity and Electrometric Data.—Hammett and Dietz calculated from Schlesinger's conductivity data a value for pK_S(HCOOH) of 6.3. The agreement of indicator and conductivity results is therefore excellent.

It is to be expected that the indicator acidity H_0 will only agree with the electrometrically measured values in the special case of unchanging medium. Barring large specific effects upon activity coefficients or difficulties due to liquid junction potentials there should, however, be agreement between electrometric and indicator values of the formic acid functions. An approximate agreement does indeed exist between the indicator value of pK_S(HCOOH) and the electrometric value of Hammett and Dietz, the difference being about 0.3 unit at 0.1 molar ionic strength, and smaller at lower concentrations. This difference is due chiefly to the assumption made in calculating the electrometric value that benzene sulfonic acid is completely ionized; in fact values of pK_S(HCOOH) calculated from the indicator data on the same assumption agree excellently with the electrometric results. It should be emphasized that the differences between electrometric and indicator results and the previous failure to recognize the incompleteness of ionization of benzene sulfonic acid derive from the inherent uncertainty of any electrometric determination of ion concentrations,[11] and that the general picture of the electrolytic properties of the solvent formic acid obtained by Hammett and Dietz is in every way supported by the indicator results.

Some Weak Bases.—By the equation[12]

$$pK' = H_0 - \log \frac{C_B}{C_{BH^+}}$$

[11] Taylor, *J. Phys. Chem.*, **31**, 1478 (1927); Guggenheim, *ibid.*, **33**, 842 (1929); **34**, 1540, 1758 (1930).

[12] Equation 4 of the previous article.

the pK' of a base may be determined by measurement of the acidity, H_0, of a solution of known concentration of the base and its corresponding ion. We now possess sufficient information about the solvent formic acid to enable us to calculate the requisite concentrations from the H_0 measurement itself. Thus for a moderately strong base we may measure the H_0 of a solution of the base in formic acid, read from the curve in Fig. 1 the concentration of formate ion corresponding to that acidity, set this equal to the concentration of the ion BH^+, and obtain the concentration of the base B as the difference between the concentration of BH^+ and the stoichiometric concentration of base. For a weaker base we may determine the acidity of a solution containing known concentrations of the base and of a strong acid, read from Fig. 1 the concentration of solvated hydrogen ion, and set the concentration of BH^+ equal to the difference between this and the stoichiometric concentration of acid. In Table IV such data and results are given for three very weak bases. In this C is the stoichiometric

TABLE IV

STRENGTHS OF SOME WEAK BASES

C	C_a	H_0	C_{BH^+}	C_B	pK_B(HCOOH)	pK'
Base acetanilide, indicators 2 and 3						
0.0768	0	−0.72	0.0089	0.0679	2.93	−1.60
.1526	0	−0.51	.0158	.1378	2.74	−1.45
Base propionitrile, indicators 4, 5 and 6						
0.1231	0.0134	−2.69	0.0071	0.116	5.25	−3.90
Base water, indicators 4, 5, and 6						
0.167	0.0390	−2.77	0.0301	0.137	4.78	−3.43

concentration of base, C_a is the stoichiometric concentration of acid (for which benzene sulfonic acid was used), C_B is the true concentration of the base, C_{BH^+} the true concentration of the ion of the base, pK_B(HCOOH), calculated by equations 4 and 8, is the logarithmic ionization constant of the base in the formic acid system, H_0 and pK' have their usual meaning in this work.

The results lead to a smaller basicity for the nitrogen compounds than is indicated by previous work in other solvents. From Hall's survey[13] we may derive a value for the pK' of these substances by comparison of his $pK'^{(HAc)}$ with the value for *p*-nitraniline, the value of +1.40 for the pK' of the latter being the basis of our whole system. The result is −1.9 for propionitrile and −0.83 for acetanilide. The values derived from direct measurements on aqueous solutions differ even more from our values, being −0.8 for propionitrile and +0.4 for acetanilide. These discrepancies are no greater than is to be expected from the attempt to measure the strength of bases as weak as are these in water and even in acetic acid.

[13] Hall, THIS JOURNAL, **52**, 5124 (1930).

Our value (−3.43) for the pK' of water is much smaller than the value (−1.8) calculated by Brönsted and Wynne-Jones[14] and used by them and others in the interpretation of kinetic data in aqueous solution. Their value is based upon the identification of the true concentration of water with the total concentration of water in a dilute aqueous solution, and upon the identification of the concentration of oxonium ion with the total concentration of solvated hydrogen ion in the same solution. The first assumption neglects the association of the water; the second, the possible further hydration of oxonium ion. The sign of the difference indicates that such further hydration decreases the true concentration of OH_3^+ to a greater extent than does association the water concentration.

Our value of the ionization constant of water in formic acid agrees in order of magnitude with the rough estimate which Hammett and Dietz based upon electrometric measurements (pK_B(HCOOH) = 5.5), but much greater confidence may be placed in the new figure. This results not only from the greater speed with which colorimetric measurements may be made and the greater certainty with which the solutions may be protected from atmospheric or other contamination, but from the actually greater precision of colorimetric measurements. It is very easy to be blinded by the precision of a potentiometric measurement to the fact that no measurement of ion concentration or activity based upon a cell with liquid junctions has any significance to a precision greater than that equivalent to a few millivolts.[11]

Summary

The ease, reliability and precision of properly carried out indicator measurements have been verified on a non-aqueous solvent.

The relative values of basicity of a series of simple basic indicators determined in solutions in formic acid agree very closely with those obtained in mixtures of strong acids and water.

The investigation of the properties of formic acid as an ionizing solvent by the indicator method leads to results in essential agreement with those obtained by electrometric and conductivity methods.

In this solvent sulfuric acid is a strong monobasic acid, benzene sulfonic acid is nearly but not quite a strong acid, sodium formate and aniline are strong bases.

The ionization constants in this solvent of bisulfate ion, propionitrile, acetanilide and water have been determined and also the general acid–base functions (pK') of the bases.

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[14] Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 327]

A PHOTOCHEMICAL REACTION INVOLVING ZINC OXIDE AND OXYGEN

BY JOHN MCMORRIS AND ROSCOE G. DICKINSON

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Zinc oxide has been found to act as a sensitizer in a number of photochemical reactions. In the course of the observation of some of these, Winther[1] found that when certain samples of zinc oxide were strongly illuminated, in the presence of air, by light filtered through ordinary glass, a substance appeared in the gas phase which was capable of oxidizing iodide to iodine. In view of its mode of preparation, its effect on iodide, and because it appeared to attack rubber membranes, the oxidizing substance was assumed to be ozone. However, Kistiakowsky[2] has remarked that the experiments showed only the presence of a volatile peroxide, and has suggested hydrogen peroxide as an alternative to ozone.

More elaborate experiments have been made by Jung and Kunau[3] with the purpose of ascertaining why only certain samples of zinc oxide produced the oxidizing substance. They prepared zinc oxide from pure zinc and oxygen, zinc carbonate, zinc sulfate and zinc nitrate and also prepared samples purposely contaminated with the oxides of several other metals. Again using the liberation of iodine from iodide as a detector, they found that only those samples which had been prepared by roasting the nitrate were active, and that even this activity disappeared on prolonged heating. It was accordingly suggested that a zinc oxynitrate was the photosensitizing agent rather than the oxide. Since considerable pains were taken to remove water, the oxidizing product was considered not to be hydrogen peroxide, and since the oxidizing product did not appear when nitrogen was employed in place of oxygen, the product was considered not to be nitrogen dioxide.

In these experiments a number of hours of passing oxygen over illuminated zinc oxide were required for the coloration of a small quantity of potassium iodide–starch solution, and since the quantity of oxidizing agent formed was evidently very small, the possibility of hydrogen peroxide formation from remaining traces of water does not appear to us to be convincingly excluded. Moreover, nitrogen dioxide likewise remains as a possibility; its absence when nitrogen is used instead of oxygen might well arise from the necessity of oxygen as a reactant rather than as a mere

[1] O. Winther, *Z. wiss. Phot.*, **21**, 168 (1921).

[2] G. B. Kistiakowsky, "Photochemical Processes," The Chemical Catalog Co., New York, 1928, p. 156.

[3] G. Jung and E. Kunau, *Z. physik. Chem.*, **15B**, 45 (1931).

vehicle to convey to the test solution nitrogen dioxide photochemically liberated from the solid.

Interest attaches to the question as to whether ozone can really be formed from oxygen through the agency of radiation in the near ultraviolet since the energy of light quanta in this spectral region is distinctly smaller than that involved in either the direct photochemical or the mercury-sensitized formation of ozone. We have accordingly undertaken experiments with the particular object of identifying the oxidizing substance by chemical tests.

Test Solutions.—The problem was, then, to distinguish between ozone, hydrogen peroxide and nitrogen dioxide contained in minute amount in a stream of oxygen. We have examined a number of the tests for this purpose which are to be found described in the literature, and have found some of them too insensitive and others fallacious. The tests which we have finally used are given in Table I.

TABLE I

TESTS FOR DISTINGUISHING OZONE, HYDROGEN PEROXIDE AND NITROGEN DIOXIDE

	Reagent solution	Coloration produced	Substance giving coloration
1	KI–starch	Blue	O_3, H_2O_2, NO_2
2	Neutral KI with cresol red	Red	O_3, H_2O_2
3	Fluorescein	Decoloration	O_3
4	$FeCl_3$ with $K_3Fe(CN)_6$	Blue or green	H_2O_2, NO_2
5	Sulfanilic acid with α-naphthylamine	Red	NO_2

Neutral potassium iodide with starch is sensitive but, of course, does not distinguish between ozone, hydrogen peroxide and nitrogen dioxide. However, the action of ozone or of hydrogen peroxide on potassium iodide renders the solution alkaline, while the action of nitrogen dioxide in low concentration leaves it neutral ($4NO_2 + 2KI = 2KNO_3 + I_2 + 2NO$). Consequently the presence of ozone or hydrogen peroxide may be detected by adding a suitable indicator to a potassium iodide solution through which the gas has been bubbled. We have used cresol red for this purpose.

The bleaching of an alkaline solution very dilute in fluorescein has been proposed[4] as a specific test for ozone. We have found this reagent, when prepared so dilute as to have a barely distinct color, to be decolorized by about the same quantity of ozone which would give a detectable color to an equal volume of potassium iodide–starch solution. The fluorescein reagent was found not to be attacked by oxygen nor by dilute solutions of hydrogen peroxide or nitrogen dioxide.

It has been stated[5] that an aqueous solution of ferric chloride and potassium ferricyanide is reduced by hydrogen peroxide to give Prussian blue but

[4] L. Benoist, *Compt. rend.*, **168**, 612 (1919); N. Allen, *Ind. Eng. Chem., Anal. Ed.*, **2**, 54 (1930).

[5] E. Keiser and L. McMaster, *Am. Chem. J.*, **39**, 96 (1908).

is unaffected by ozone or nitrogen dioxide. We have, however, found the blue coloration to be produced by nitrogen dioxide as well as hydrogen peroxide but not by ozone. This was shown in the case of nitrogen dioxide by adding to the iron reagent either a dilute solution of nitric and nitrous acids obtained by passing into water a small amount of nitrogen dioxide prepared by heating lead nitrate, or by adding a very dilute solution of sodium nitrite.

A specific reagent for nitrite (and hence for nitrogen dioxide) is afforded by an acetic acid solution of sulfanilic acid and α-naphthylamine (Griess–Ilosva reaction).[6] The reagent is colorless and is not colored by hydrogen peroxide; a large concentration of ozone gives a yellowish coloration. With nitrite the reagent forms a red dye and furnishes an extremely delicate test for NO_2.

Identification of the Oxidizing Product.—In the conduct of a series of experiments, zinc nitrate was first dehydrated and baked in a casserole at about 350° until brown fumes of nitrogen dioxide were no longer evident. The oxide was then pulverized and placed in a Pyrex tube 30 cm. in length and of 1 cm. bore fitted with ground-in end joints. The tube was surrounded by an electric furnace and the oxide roasted for at least two hours more at 350° in a stream of oxygen. Without removing the oxide from the tube, the furnace was removed and replaced by a Pyrex water-jacket through which tap water flowed in an annular space of 5 mm. A horizontal type Pyrex mercury arc lamp with an arc length of 25 cm. was placed alongside about 2 cm. from the oxide. An oxygen stream was maintained whose rate of flow was about 100 cc./min.; after passing through the zinc oxide tube, the oxygen bubbled through pure water or a reagent solution contained in a small test-tube. A plug of glass wool served to prevent any particles of oxide from being swept into the reagent.

The results of experiments made with three different samples of oxide are given in Table II; in this table, the experiments are listed in the order made. Samples 1 and 3 were made from commercial C. P. zinc nitrate, sample 2 was made from zinc nitrate prepared from C. P. zinc and nitric acid. In the experiments with sample 1, the oxygen was first bubbled through 6 *N* sulfuric acid (p_{H_2O} about 14 mm.); in the other experiments it was bubbled through concentrated sulfuric acid. It is evident from these results that we have been able to verify the appearance of an oxidizing substance in the issuing gas when zinc oxide from the nitrate is illuminated through glass in a stream of oxygen. However, in view of the positive tests given by the sulfanilic acid–α-naphthylamine solution and the absence of such a test when illumination was omitted, and in view of the failure to bleach fluorescein solution, we believe we have shown that the oxidizing substance is not ozone but is in fact nitrogen dioxide. It is

[6] F. Usher and B. Rao, *J. Chem. Soc.*, **111**, 789 (1917).

possible that a small amount of hydrogen peroxide might have been formed in addition to nitrogen dioxide but experiments 15 and 16 render this improbable.

TABLE II

RESULTS OF ILLUMINATING ZINC OXIDE AND OXYGEN

Expt.	Sample of oxide	Duration of test, hrs.	Illumination	Reagent	Result	Substance identified
1	1	2	Ill.	(1)	Slight blue	Oxidizing agent
2	1	12	Dark	(1)	No color	.....
3	1	6	Ill.	(4)	Blue color	H_2O_2 or NO_2
4	1	6	Ill.	(5)	Pink color	NO_2
5	1	12	Dark	(5)	No color	.....
6	2	12	Ill.	(5)	Pink Color	NO_2
7	2	12	Dark	(5)	No color	.....
8	2	12	Ill.	(5)	Pink color	NO_2
9	2	12	Ill.	(3)	No change	No O_3
10	2	4	Ill.	(5)	Pink color	NO_2
11	3	3	Dark	(5)	No color	.....
12	3	3	Ill.	(5)	Pink color	NO_2
13[a]	3	6	Ill.	(5)	No color	.....
14[b]	3	3	Ill.	(5)	No color	.....
15	3	3	Ill.	(5)	Pink color	NO_2
16	3	8	Dark	(2)	Trace of pink	.....
17	3	8	Ill.	(2)	Trace of pink	No O_3 or H_2O_2

Key to reagents: (1) KI–starch solution; (2) neutral KI solution with subsequently Congo red; (3) fluorescein solution; (4) $FeCl_3$–$K_3Fe(CN)_6$ solution added to water through which the gas had bubbled; (5) sulfanilic acid–α-naphthylamine solution.

[a] $K_4Fe(CN)_6$ solution used in water jacket.

[b] Pure dried nitrogen was used in this experiment instead of oxygen.

It is interesting that, in agreement with the experiments of Jung and Kunau, no nitrogen dioxide was obtained when (Expt. 14) nitrogen was used in place of oxygen.

In Expt. 13 a 0.065 formal solution of potassium ferrocyanide was flowed through the condenser jacket instead of tap water. This solution in the thickness used (5 mm.) transmitted the visible freely but fairly completely removed the ultraviolet. The negative result obtained with this filter showed that the effective wave lengths lie in the ultraviolet region.

In conclusion, then, it may be said that those experiments which have been carried out in such a way as to distinguish between hydrogen peroxide, ozone and nitrogen dioxide have always indicated nitrogen dioxide. It is still possible that ozone may have been the product in experiments made by other investigators, but there appears to be no reason for assuming that such was the case.

Summary

Experiments have been made in which zinc oxide (prepared from zinc nitrate) was strongly illuminated, in the presence of oxygen, by mercury

arc radiation filtered through water and Pyrex glass; in these experiments nitrogen dioxide (not ozone as previously supposed) appeared in the gas. Radiation in the near ultraviolet but not in the visible was found to be effective.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 18]

THERMODYNAMIC PROPERTIES OF FUSED SALT SOLUTIONS. VI. RUBIDIUM BROMIDE IN SILVER BROMIDE

BY EDWARD J. SALSTROM

RECEIVED JUNE 29, 1932 PUBLISHED NOVEMBER 5, 1932

The investigation described in this paper represents a continuation of a series of studies dealing with the thermodynamic properties of fused salt solutions. The present system, rubidium bromide in silver bromide, concludes that particular phase of the investigation dealing with the change in activity of silver bromide upon dilution with an alkali metal bromide.[1]

Experimental Part

The rubidium bromide was prepared by the neutralization of its hydroxide with pure hydrobromic acid. The neutralization was carried out in a platinum cylinder. After obtaining the rubidium bromide by crystallization from its saturated solution the salt was finally dried by fusing it in a quartz dish. The remaining materials, apparatus and procedure were similar to those previously described in the lithium bromide–silver bromide investigation.[1a]

Briefly the method consisted of applying a reversible bromine gas electrode to the study of fused salt solution cells of the type, Ag(s), AgBr(l), RbBr(l), Br_2(g). Hydrolysis and oxidation products occasioned by the filling and sealing of the cell container were removed by bubbling dry hydrogen bromide gas through the melt for at least two hours. Bromine gas generated by electrolysis of fused lead bromide was then bubbled over a treated[2] graphite rod dipping into the melt. After equilibrium was reached, readings were taken at regular temperature intervals in both ascending and descending series. Both series were in complete agreement. The exact composition of each solution was finally determined by electrolytic analysis of the cell contents.

Table I gives the observed results plus a correction to take care of the thermoelectric effect[3] involved in each cell. Figure 1 presents the results

[1] (a) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4650 (1930); (b) Salstrom, *ibid.*, **53**, 1794 (1931); *ibid.*, **53**, 3385 (1931).

[2] Salstrom and Hildebrand, *ibid.*, **52**, 4641 (1930).

[3] Ref. 2, p. 4644.

graphically. The e. m. f. values for the cell containing pure silver bromide are those obtained in the previous silver bromide–lithium bromide investigation.[1a] The extreme deviation of the results from a straight line drawn through them in Fig. 1 is 0.4 millivolt, while the mean deviation is less than 0.2 millivolt.

TABLE I

Ag(s), AgBr(l), RbBr(l), Br_2(g)

Mole fraction of AgBr	Temp., °C.	E. m. f. obs., volt	Mole fraction of AgBr	Temp., °C.	E. m. f. obs., volt
1.000A	456.0	0.7989	0.596C	537.7	0.8304
1.000A	467.0	.7956	.596C	557.9	.8254
1.000A	490.9	.7887	.596C	579.0	.8203
1.000A	499.9	.7866	.596C	598.0	.8154
1.000A	521.4	.7803	.596C	598.1	.8153
1.000A	524.4	.7795	.596C	617.0	.8112
1.000A	531.7	.7769	.467D	488.8	.8723
1.000A	538.3	.7751	.467D	519.5	.8653
1.000A	556.2	.7702	.467D	537.4	.8609
1.000A	565.0	.7680	.467D	557.2	.8564
0.747B	462.8	.8215	.467D	557.9	.8562
.747B	495.3	.8128	.467D	584.0	.8504
.747B	504.9	.8101	.467D	595.0	.8478
.747B	519.4	.8065	.467D	617.6	.8429
.747B	519.8	.8062	.352E	518.5	.9001
.747B	544.2	.7997	.352E	528.7	.8981
.747B	560.9	.7956	.352E	539.1	.8958
.747B	580.7	.7905	.352E	549.3	.8937
.747B	601.0	.7852	.352E	561.1	.8913
.747B	617.9	.7811	.352E	573.6	.8891
.596C	468.8	.8478	.352E	592.5	.8853
.596C	494.7	.8411	.352E	592.7	.8852
.596C	505.9	.8383	.352E	609.3	.8812
.596C	506.1	.8486	.352E	621.7	.8788

In order to determine the volume changes involved in the mixing of rubidium bromide and silver bromide, density determinations were made upon a fused solution containing a half mole fraction of each salt. The method employed consisted of weighing a quartz bulb weighted with tungsten, first in air, then in water and finally at various temperatures in the fused salt solution. At each temperature corrections[4] were made for the expansion of quartz. To avoid the accumulation of any gas bubbles on the bulb it was sharply tapped before each reading. The observed density values are given in Table II.

[4] A calculation of the effect of the buoyancy of air upon the bulb was made and found to be negligible. Data are not available for calculating the effect of surface tension of the fused solution upon the suspending platinum wire but since its diameter did not exceed 0.09 mm. it is believed that such corrections would also prove negligible.

TABLE II

DENSITIES OF 0.5 MOLE FRACTION OF RUBIDIUM BROMIDE IN SILVER BROMIDE

Temp., °C.	514.0	527.2	537.5	551.5	563.2	576.6	591.0	609.0	623.6
Density	3.838	3.822	3.808	3.791	3.778	3.762	3.743	3.720	3.702

The above density values may be expressed by the equation $d^t = 4.470 - 0.00123t$. With the aid of the density values for silver bromide obtained

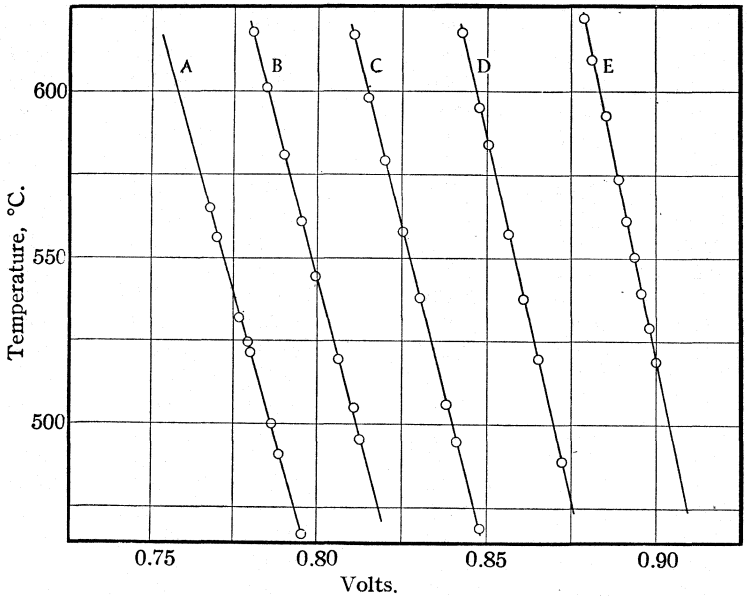

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Ag–AgBr–RbBr–Br_2. Mole fraction of silver bromide in A is 1.000, B is 0.747, C is 0.596, D is 0.467, and E is 0.352.

by Lorenz and Hochberg[5] and for rubidium bromide obtained by Brunner,[6] the molal volumes of silver bromide and rubidium bromide at 600° have been calculated to be 34.74 cc. and 59.07 cc.,[7] respectively. A solution containing a half mole fraction of each salt has an observed molal volume of 47.32 cc., which is 0.42 cc. more than additive.

Discussion of Results

To show the effect of both temperature and composition upon the thermodynamic properties of the fused salt solution the plot shown in Fig. 1 was made upon a large scale and the values of the e. m. f., **E**, determined for each

[5] Lorenz and Hochberg, *Z. anorg. allgem. Chem.*, **94**, 288 (1916).

[6] Brunner, *ibid.*, **38**, 350 (1904).

[7] Since rubidium bromide is solid below 683°, this molal volume would be for the hypothetical supercooled liquid.

composition by noting the intersections of the lines with the temperature ordinates at 500, 550 and 600°. From these values have been calculated by the aid of the usual thermodynamic equations, values of the entropy of formation, ΔS_1, the entropy change upon dilution or the partial molal entropy, $\bar{S}_1$, the free energy of formation, ΔF_1, the free energy of dilution or the partial molal free energy, $\bar{F}_1$, the heat of formation, ΔH_1, and the heat of dilution, $\bar{H}_1$, the activity of silver bromide, a_1, and the activity coefficient, a_1/N_1, where N_1 represents the mole fraction of silver bromide.

The values so calculated are given in Table III and in Fig. 2 are shown in Curve A, values of $-\bar{F}_1$ at 600° plotted against log $(1/N_1)$. If it is assumed that the activity is proportional to the mole fraction, it is found that both the assumption of complete ionization of both salts or of no ionization yield the same results, namely, $a_1 = N_1$. A calculation of $\bar{F}_1$ on this basis, represented by curve B, Fig. 2, is much lower than the observed. There is, therefore, a strong negative deviation from Raoult's law, *i. e.*, the activity is less than the simple mole fraction. Attention may be called to the fact that the calculated values of $\bar{F}_1$ would not differ from those calculated above if both salts were assumed to be equally ionized regardless of the degree. However, it is believed desirable not to consider partial ionization.

TABLE III

ENERGY RELATIONS OF SILVER BROMIDE WHEN DILUTED WITH RUBIDIUM BROMIDE

N_1	1.000	0.747	0.596	0.467	0.352
$dE/dT \times 10^6$ (volts/deg.)	−290	−260	−247	−229	−207
ΔS_1 (cal./deg.)	−6.69	−6.00	−5.70	−5.28	−4.78
$\bar{S}_1$ (cal./deg.)	0.00	0.69	0.99	1.41	1.91
500°, E (volt)	0.7865	0.8116	0.8398	0.8697	0.9040
500°, ΔF_1 (cal.)	−18150	−18730	−19380	−20070	−20860
500°, $\bar{F}_1$ (cal.)	0	−580	−1230	−1920	−2710
500°, ΔH_1 (cal.)	−23320	−23370	−23790	−24150	−24550
500°, $\bar{H}_1$ (cal.)	0	−50	−470	−830	−1230
500°, a_1	1.000	0.686	0.449	0.287	0.172
500°, a_1/N_1	1.000	0.918	0.754	0.614	0.487
550°, E (volt)	0.7720	0.7986	0.8275	0.8582	0.8937
550°, ΔF_1 (cal.)	−17810	−18430	−19090	−19800	−20620
550°, $\bar{F}_1$ (cal.)	0	−620	−1280	−1990	−2810
550°, a_1	1.000	0.687	0.457	0.297	0.180
550°, a_1/N_1	1.000	0.920	0.767	0.635	0.511
600°, E (volt)	0.7577	0.7856	0.8151	0.8468	0.8833
600°, ΔF_1 (cal.)	−17480	−18130	−18810	−19540	−20380
600°, $\bar{F}_1$ (cal.)	0	−650	−1330	−2060	−2900
600°, a_1	1.000	0.688	0.466	0.306	0.188
600°, a_1/N_1	1.000	0.921	0.782	0.655	0.535

The theoretical significance of the deviation of this system from Raoult's law together with a comprehensive treatment of the three previous studies

on silver bromide–alkali metal bromide solutions is being presented in the following paper.

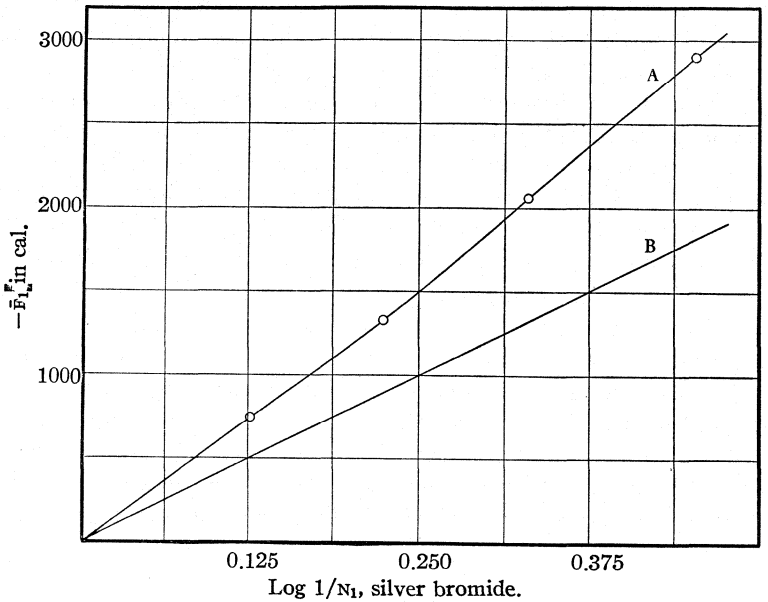

Fig. 2.—Change in free energy of silver bromide at 600° upon dilution with rubidium bromide: A, observed; B, calculated.

Summary

1. A reversible bromine gas electrode has been applied to the study of the thermodynamic properties of fused solutions of rubidium bromide in silver bromide.

2. E. m. f. values are given for the cell, Ag(s), AgBr(l), RbBr(l), Br_2(g), at 1.000, 0.747, 0.596, 0.467 and 0.352 mole fractions of silver bromide.

3. The density of a half mole fraction solution of rubidium bromide in silver bromide has been measured between the temperatures 514 and 624°.

4. Calculations of the free energy of formation, free energy of dilution, heat of formation, entropy changes, activity and activity coefficients are given at the temperatures 500, 550 and 600°.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AND FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THERMODYNAMIC PROPERTIES OF LIQUID SOLUTIONS OF SILVER BROMIDE WITH ALKALI BROMIDES

BY JOEL H. HILDEBRAND AND EDWARD J. SALSTROM

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The series of investigations begun by us,[1] and since continued by the junior author, on the free energy of dilution of molten silver bromide by the alkali bromides, now includes all of the latter except cesium bromide and has reached a stage where their theoretical interpretation may be attempted, for the regularities are such that the inclusion of cesium bromide could hardly yield any additional information of importance.

A graphic summary of the results[2] is given in Fig. 1, where $\bar{F}_1 - \bar{F}_1^i$ is plotted against N_2^2. $\bar{F}_1$ is the partial molal free energy of the silver bromide in the solution, connected with the activity by the relation $\bar{F}_1 = RT \ln a_1$. If the solution were ideal, a_1 would equal N_1 and $\bar{F}_1^i = RT \ln N_1$. From this it is seen that $\bar{F}_1 - \bar{F}_1^i = RT \ln a_1/N_1 = RT \ln \gamma_1$, where γ_1 is the activity coefficient. N_2 is the mole fraction of the alkali bromide.

It is evident, from Fig. 1, that the data plotted in this way show a remarkably linear relation. The pairs of points are for 550 and 600°; they fall so close together as to indicate that temperature is practically without effect. We may conclude from this that the partial molal entropy is the same as it would be in an ideal solution, *i. e.*, $\bar{S}_1 - \bar{S}_1^i = 0$, or $\bar{S}_1^i = R \ln N_1$, indicating that the randomness of the arrangement is the same in both cases. These systems agree with the senior author's definition of regular solutions.[3]

The deviation from ideal behavior of the solutions with lithium bromide and sodium bromide is in the direction of unmixing, while those with potassium bromide and rubidium bromide deviate in the direction of compound formation. This is in harmony with the fact reported by Sandonnini and Scarpa[4] of the non-congruent freezing-out of a solid, probably AgBr·RbBr,

[1] E. J. Salstrom and J. H. Hildebrand, THIS JOURNAL, **52**, 4650 (1930); E. J. Salstrom, *ibid.*, **53**, 1794, 3385 (1931); **54**, 4252 (1932).

[2] Since publication of the paper on the system AgBr–LiBr, an additional cell has been studied containing a solution with 17.63 mole per cent. of AgBr, yielding the following results

t, °C.	$E - E_0$ millivolts	$-\bar{F}_1$, cal.	$\bar{F}_1 - \bar{F}_1^i$, cal.	γ
500	61.7	1425	1240	2.20
550	69.9	1610	1230	2.11
600	78.0	1800	1210	2.01

These data have been included in Fig. 1.

[3] J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

[4] Sandonnini and Scarpa, *Atti accad. Lincei*, **22** [II], 517 (1913).

in the case of the last-named system. This suggests that the solutions deviating in this direction may be explained by assuming an equilibrium of the type $Br^- + AgBr = AgBr_2^-$. We shall not adopt this point of view, however, because, first, it seems not to harmonize with the above-mentioned fact regarding the entropy and, second, a different type of explanation would then have to be applied to the solutions with lithium bromide and sodium bromide, whereas it is evident from Fig. 1 that we are dealing with a family of curves showing a quite regular trend from one extreme to the other, and that a single type of explanation should, if possible, be found for all four systems.

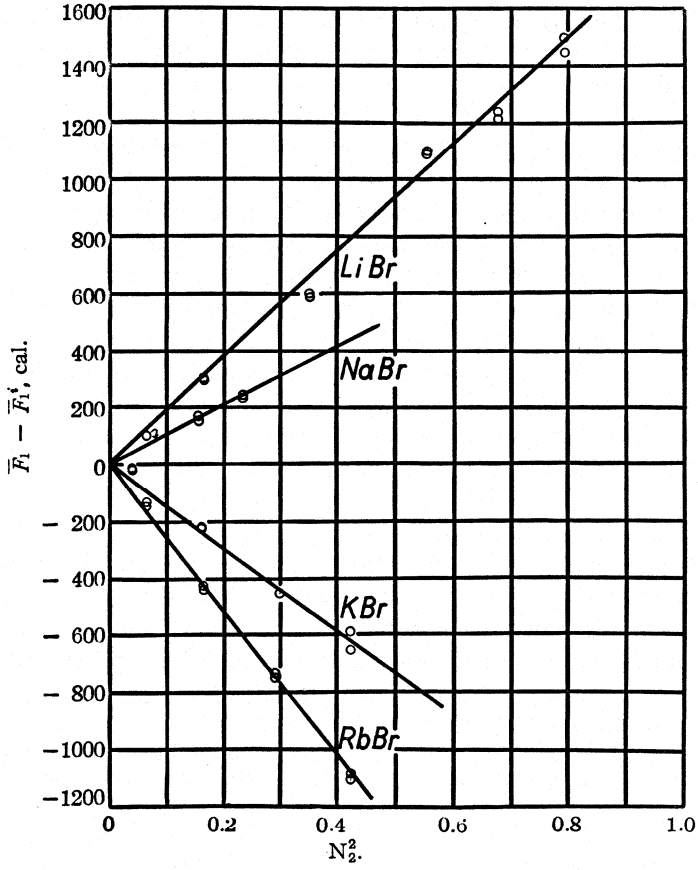

Fig. 1.

We will consider, first, the magnitude and nature of the interionic forces involved. All of the salts comprised in these systems crystallize in simple cubic lattices. The lattice constants are given in order in Table I.

TABLE I

	LiBr	AgBr	NaBr	KBr	RbBr
Lattice constant, Å.	2.745	2.885	2.97	3.29	3.43
Molal volume, cc. at 700°	35.4	35.6	43.4[a]	55.4[a]	61.5

[a] Extrapolated below the freezing point.

It is seen that silver bromide falls almost midway between lithium bromide and sodium bromide. The molal volumes of the molten salts, also given in Table I, show that lithium bromide and silver bromide are in this respect nearly identical. If, as is probable, something like the simple cubic arrangement persists in the liquid state, we might expect the electrostatic "lattice energies" of these two salts to be nearly identical (except for the uncertainty of the repulsive term for Ag^+) and their solutions to show a close approximation to Raoult's law, which is far from being the case. However, the energy involved in forming solid silver bromide from its gaseous ions is greater than the corresponding figure for lithium bromide, and, on account of the greater expansion of the latter on melting, the difference for the molten salts would be still greater in favor of silver bromide. Evidently, then, the "lattice energies" for the liquids are in the order silver bromide, lithium bromide, sodium bromide, potassium bromide, rubidium bromide, while the order indicated by Fig. 1 would have to be lithium bromide, sodium bromide, silver bromide, potassium bromide, rubidium bromide. Moreover, while likeness in "lattice energies" might be expected to lead to ideal solutions, unlikeness in the *magnitudes* of internal forces usually leads to positive deviations for both components, regardless of which is greater, and not to the negative deviations shown with potassium bromide and rubidium bromide.

Positive deviations from Raoult's law are frequently accompanied by an expansion on mixing and *vice versa;* this might be expected to cause a weakening or strengthening, respectively, of the internal forces accounting for the direction of the departure from ideality. However, such an explanation is not applicable to these systems. The changes of volume, in cc., on mixing 0.5 mole of silver bromide with 0.5 mole each of lithium bromide, sodium bromide, potassium bromide and rubidium bromide are, respectively, -0.13, $+0.17$, $+0.27$, $+0.42$. These volume changes are in the opposite order to that required by the above explanation.

We are led, consequently, to the conclusion that the behavior of these systems depends upon a difference in the kind of bond existing in silver bromide on the one hand and the alkali bromides on the other, the latter being completely, the former incompletely, ionic. We may note that the electric conductivity of liquid silver bromide has a temperature coefficient very different from those of the alkali bromides. The melting point of silver bromide is much lower than that of lithium bromide, in spite of the similar lattice constant. We recall the existence of $AgBr_2^-$ in aqueous solution

and the solid, probably $RbAgBr_2$, mentioned earlier. These and other differences indicate that a simple electrostatic treatment of silver bromide is inappropriate. We will accordingly regard the bond between silver and bromine as tending to tighten into a non-polar bond, this tendency being hindered most by the presence of the small lithium ion and assisted most by the large rubidium ion, but without, in any case, altering the lattice arrangement.

It is possible to justify the form of the equation, $\bar{F}_1 - \bar{F}_1^i = bN_2^2$, by the following statistical treatment, based upon that of Heitler[5] for non-ionic solutions.

Let us consider a solution of n_1 moles of silver bromide with n_2 moles of MBr, M being any alkali metal. We will assume that Ag^+ and M^+ can replace each other without altering the arrangement, which is probably simple cubic, although the following analysis will apply to any arrangement. The potential of a silver ion will be altered by the substitution of an alkali ion by an amount depending upon the distance of the latter from the former. We will designate the nearest as first order, the next as second order, etc. In a simple cubic lattice there are twelve first order positive ions, six second order, twelve third order, etc.; but we will make the treatment general for other types of lattice by denoting these by $2q$, $2q'$, $2q''$, etc. The probability that a given pair of ions in any order are both Ag^+ is N_1^2; the probability for two M^+ is N_2^2 and that one is Ag^+ and the other M^+ is $2N_1N_2$, where N_1 and N_2 are the respective mole fractions. The total number of first order pairs is $(n_1 + n_2)qA$, where A is the Avogadro number. The number of first order pairs in which both are Ag^+ is $(n_1 + n_2)qAN_1^2$; for both M^+, it is $(n_1 + n_2)qAN_2^2$ and for one Ag^+ and one M^+ it is $2(n_1 + n_2)qAN_1N_2$. By substituting q' and q'', respectively, we obtain expressions for the number of second and third order combinations.

We will designate by φ_{11}, φ_{11}', φ_{11}'', etc., the contribution of each pair of Ag^+ toward the potential of the lattice and, similarly, use φ_{22} for $M^+ - M^+$ and φ_{12} for $Ag^+ - M^+$. The necessary Br^- will be considered as included in these potentials rather than accounted for by extra terms.

The energy of the lattice of $n_1 + n_2$ moles of solution can then be expressed by

$$E_{12} = (n_1 + n_2)\, A(N_1^2 \Sigma q\varphi_{11} + N_2^2 \Sigma q\varphi_{22} + 2N_1N_2\, q\Sigma\varphi_{12})$$

where $\Sigma q\varphi = q\varphi + q'\varphi' + q''\varphi'' + \ldots\ldots\ldots$

This expression we will abbreviate by substituting ϵ_{11} for $A\Sigma q\varphi_{11}$ and similarly, ϵ_{22} and ϵ_{12}, yielding

$$E_{12} = (n_1 + n_2)(N_1^2\epsilon_{11} + N_2^2\epsilon_{22} + 2N_1N_2\epsilon_{12})$$

The corresponding energies of the pure constituents would be $E_{11} = n_1\epsilon_{11}$ and $E_{22} = n_2\epsilon_{22}$, hence the energy of mixing, ΔE_{12}, remembering that

[5] Heitler, *Ann. Physik*, [4] **80**, 630 (1926).

$N_1 = n_1/(n_1 + n_2)$, etc., would be $\Delta E_{12} = \frac{n_1 n_2}{n_1 + n_2}(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$. It can be readily shown that this corresponds to $\bar{E}_1 - E_1 = N_2^2(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$ and $\bar{E}_2 - E_2 = N_1^2(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$, where $\bar{E}$ is the partial molal energy and E the molal energy.

From the equation $F = E - TS + PV$, we can write $\bar{F}_1 - \bar{F}_1^i = \bar{E}_1 - \bar{E}_1^i = T(\bar{S}_1 - \bar{S}_1^i) + P(\bar{V}_1 - \bar{V}_1^i)$, but $\bar{E}_1^i = E_1$ and $P(\bar{V}_1 - \bar{V}_1^i)$ is here negligible; furthermore, the measurements show (*vide supra*) that $\bar{S}_1 - \bar{S}_1^i = 0$, hence we can write $\bar{F}_1 - \bar{F}_1^i = N_2^2(2\epsilon_{12} - \epsilon_{11} - \epsilon_{22})$, which is the type of function shown in Fig. 1 to fit the data very satisfactorily. The slope of the line depends upon whether $2\epsilon_{12}$ is greater or less than $\epsilon_{11} + \epsilon_{22}$. We see no way, at present, of calculating this, except from the measurements themselves, which yield, for $\bar{F}_1 - \bar{F}_1^i$, when $N_1 = 0$, for silver bromide in lithium bromide, +1880 cal., in sodium bromide +1050 cal., in potassium bromide, −1480 cal., in rubidium bromide, −2580 cal.

Summary

The experimental data for the excess of the actual partial molal free energy over the ideal, for molten solutions of silver bromide in lithium bromide, sodium bromide, potassium bromide and rubidium bromide, are shown to fit the relation $\bar{F}_1 - \bar{F}_1^i = bN_2^2$; the values of b, in cal., are, respectively, 1880, 1050, −1480, −2580. The constant, b, is practically independent of temperature, hence the actual partial molal entropy is the same as the ideal for solutions of the same composition.

A statistical treatment of the solutions is shown to yield an equation of the above form. This is based upon the concept that the presence of a large alkali ion, such as rubidium ion, in a lattice of silver bromide allows a tightening of the bond between silver and bromine, while a small alkali ion has the reverse effect.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

THE REACTIONS OF HYDROGEN ATOMS WITH HYDRAZINE AND WITH AMMONIA

BY J. K. DIXON

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Introduction

The reactions of hydrogen atoms with ammonia and hydrazine which are reported on here, represent two of the possible reactions involved in the formation of ammonia and hydrazine from nitrogen and hydrogen atoms.[1] In order to obtain a valid mechanism for the modes of formation, it is necessary to have experimental data concerning the interaction of either hydrogen or nitrogen atoms with ammonia or hydrazine. The effect of nitrogen atoms (from active nitrogen) on ammonia is very small.[2] The reaction of hydrogen atoms with ammonia was studied semi-quantitatively by Boehm and Bonhoeffer[3] and no reaction was observed; but, since the result is of importance experimentally and theoretically, the experiments have been repeated with greater accuracy. Elgin and Taylor[4] showed that, in the photosensitized decomposition of hydrazine by mercury in the presence of hydrogen, hydrogen atoms and hydrazine must react and subsequently produce ammonia. Since the completion of the present experiments, Wiig and Kistiakowsky[5] have published the results of careful experiments on the photochemical decomposition of ammonia, in which use is made of the reaction of hydrogen atoms on hydrazine to account for the low quantum yield of the ammonia decomposition. In the present case this was the primary reaction studied, the method of production of the hydrogen atoms and the conditions being quite different from either of the above investigations.

Experimental Procedure and Apparatus

Materials.—Hydrogen from a tank was saturated with water and passed into the apparatus without further purification. Liquid ammonia was stored in a tank over metallic sodium. Gas from this tank was absorbed completely in water. Hydrazine hydrate was prepared from C. P. hydrazine hydrochloride by adding strong potassium hydroxide solution to the solid hydrochloride at 0–10°. The potassium chloride formed was filtered off and the hydrazine hydrate (with water) was dehydrated with solid potassium hydroxide. Dehydration was carried out in a vacuum by distilling the hydrazine through a series of traps containing solid potassium hydroxide, always at less than 50°. Analysis of the liquid obtained showed that it contained over 85% hydrazine.

Analyses.—Ammonia was determined by titration with standard sulfuric acid (*ca.*

[1] Steiner, *Z. Elektrochem.*, **36**, 807 (1930).

[2] Dixon and Steiner, *Z. physik. Chem.*, **B17**, 327 (1932).

[3] Boehm and Bonhoeffer, *ibid.*, **119**, 385 (1926).

[4] Elgin and Taylor, THIS JOURNAL, **51**, 2059 (1929).

[5] Wiig and Kistiakowsky, *ibid.*, **54**, 1806 (1932).

0.25 or 1.00 *n*). Hydrazine, when present alone, was determined by either of two methods, titration with sulfuric acid (0.25 *n*) or by titration with standard potassium iodate solution (0.25 *m*) according to the directions of Kolthoff.[6] Ammonia and hydrazine, when present together in a solution, were determined as follows: the sum of hydrazine plus ammonia in one-half of the solution by titration with sulfuric acid and the hydrazine in the other half by the potassium iodate method. Ammonia was found by difference. The method was checked by analyzing mixtures containing known amounts of hydrazine and ammonia and proved to be accurate to better than one per cent.

Apparatus.—The type of apparatus employed was similar to that previously described.[2] Hydrogen, ammonia and hydrazine were admitted to the apparatus through capillaries. The hydrazine flow rate was controlled by regulating the temperature of the hydrazine source and the flow rates of the other two gases by using various sized capillaries. In some cases the ammonia was heated before it entered the reaction tube by wrapping the inlet tube with nichrome ribbon for 15 cm. just before the point where connection was made with the reaction tube. The approximate temperature of the ammonia was determined by inserting a thermocouple junction at the connecting point to the reaction tube and standardizing at various currents in the nichrome coil. The hydrogen was activated in a 1.9 meter discharge tube by the current from a 3 k. v. a. transformer at 12,000 volts. The atoms from the discharge were pumped rapidly through a long reaction tube and through two traps. Connections from a McLeod gage were sealed in the reaction tube 8 cm. from the discharge and at the end. Ammonia or hydrazine was introduced into the reaction tube 16 cm. from the discharge (see Fig. 1). The traps were fitted with ground joints and cooled with liquid air. The outlet from the pumps was connected to a buret, so that the gases delivered could be collected and measured.

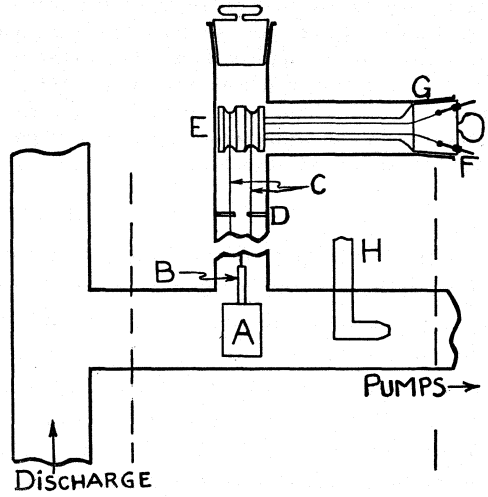

Fig. 1.—Calorimeter for measuring hydrogen atom concentrations.

The hydrogen atom concentrations were measured at a point 8 cm. from the discharge. The calorimetric method employed was similar to that which has been described by v. Wartenberg and Schultze[7] and by Smallwood.[8] It involved the measurement of the temperature rise of a known weight of platinum upon exposing the metal to the atom recombination for a definite length of time; 13.5 g. of sheet platinum were pressed into a flat unit to serve as a calorimeter, which is denoted by A in Fig. 1. A single copper–constantan thermocouple junction was inserted into the middle of the platinum and the leads were protected for two centimeters above the metal by a small platinum tube, B. The thermocouple leads, C, were guided by the glass rods, D, then passed over the grooved spool, E, and finally connected to the tungsten–glass seals at F. The calorimeter was raised or lowered by winding the thermocouple leads up or down on the

[6] Kolthoff, THIS JOURNAL, **46**, 2009 (1924).

[7] V. Wartenberg and Schultze, *Z. physik. Chem.*, **B6**, 261 (1930).

[8] Smallwood, THIS JOURNAL, **51**, 1985 (1929).

spool. The platinum hung freely in the reaction tube when in use. The connection to the McLeod gage is not shown in Fig. 1; the NH_3 or N_2H_4 inlet is shown at H. The reaction tube was maintained at a constant temperature between the dotted lines, 25 cm., by means of water contained in a copper box. The potential difference between the thermocouple junctions was determined with the aid of a Leeds and Northrup "low voltage" Type K potentiometer. The thermocouple was standardized before use at 100°.

Procedure.—After conditions reached a steady state the pressure at the calorimeter and the volume of hydrogen delivered per minute were determined and the discharge turned off. The calorimeter was lowered and the electrical connections at F were made. When the temperature of the calorimeter reached some point (about 5° above the temperature of the water-bath) the discharge was turned on for a suitable length of time, then shut off, and the cooling curve for the calorimeter was measured. The procedure for measuring the amount of decomposition in the reactions was similar to that described previously,[2] the accuracy of the results being much higher. Under strictly comparable conditions the amounts of ammonia (or hydrazine) passing through the apparatus in unit time were determined with and without activation of the hydrogen. Determinations of the pressures, flow rates, atomic hydrogen concentration and analyses of the products collected in the traps were made. The difference between these experiments was a measure of the extent and course of the reaction.

Results

The Hydrogen Atom Concentrations.—The maximum temperature rise of the platinum upon exposing it to the hydrogen atoms was not a true measure of the heat of atom recombination. The radiation loss during the time necessary for the attainment of temperature equilibrium was sufficient to give a low value for the temperature rise. After cutting off the supply of atoms, the time–temperature curve of the metal was measured. When the cooling curve was extrapolated to the time when the atoms were "shut off," the corresponding temperature was that which the calorimeter would have attained if there had been no time lag in the heat exchange. The difference between the extrapolated final temperature and the initial temperature gave the uncorrected temperature rise for the known heating period. The radiation loss during the heating period was calculated from the average slope of the cooling curve between two temperatures and the time the calorimeter was in this temperature range. Adding the radiation loss to the uncorrected temperature rise gave the true value. The results of some experiments are summarized in Table I. The values of the temperature rise and the radiation loss correspond to the heating periods shown in the third column. The number of calories liberated per minute was the product of the temperature rise, the weight and the specific heat of the platinum;[9] that is, $T \times 13.5 \times 0.0336$. The *percentage dissociation* of the hydrogen was calculated from the relation,

$$\% \text{ Dissociation of } H_2 = 100 \times \frac{T \times 13.5 \times 0.0336}{104{,}000 \times V}$$

[9] "International Critical Tables," Vol. V, p. 93.

where 104,000 represents the heat of formation of one mole of hydrogen from the atoms and V the number of moles of hydrogen passing through the apparatus per minute.

TABLE I

HYDROGEN ATOM CONCENTRATIONS AS DETERMINED CALORIMETRICALLY

Weight of platinum, 13.5 g. Pressure, 0.21–0.24 mm. Streaming velocity, 3.10–3.16 $\times 10^{-3}$ mole per minute

Milliamperes in discharge	Temperature rise, millivolts	Time, seconds	Radiation loss, millivolts	Temperature rise per minute, °C.	% H_2 Dissociation
30	1.70	42.0	0.53	76	11
50	1.93	23.0	.37	144	20
65	1.88	17.0	.27	182	25
65	2.05	18.0	.29	187	26
125	2.55	15.0	.25	268	37
125	2.23	14.0	.22	251	35
235	2.43	10.0	.16	389	54

The results of the experiments, as to the effects of pressure, temperature of the walls and current strength in the discharge, are similar to those obtained by previous investigators,[8,10] and it is reasonably certain that the measured atomic concentrations were accurate to better than ± 10%, which was sufficient for the purposes intended.

The Reaction of Hydrogen Atoms with Hydrazine.—When hydrogen atoms were mixed with hydrazine, there was a reaction with formation of ammonia and some gases not condensed by liquid air. Much heat and a weak green fluorescence were liberated at and near the point where the hydrazine and hydrogen atoms mixed. The fluorescence increased in intensity as the hydrazine or hydrogen atom concentrations increased and ceased *immediately* upon shutting off the hydrogen discharge or hydrazine supply. Further investigation of the fluorescence is described below.

The reaction was investigated by finding the effect of the hydrogen atom and hydrazine concentrations upon the amount of hydrazine decomposition and amount of ammonia formed. The results of some experiments are summarized in Table II. The effect of temperature on the extent of reaction was determined by varying the temperature of the water-bath which surrounded the reaction tube. Although this bath did not control the temperature of the entire reaction tube, it did, however, extend well past the region where the heat and fluorescence were given out. The pressures shown in Table III are those measured in the absence of hydrazine. Adding hydrazine increased the pressure by about 0.05 mm. as a result of reaction, which increase would have decreased the hydrogen atom pressure even if there had been no reaction. No correction has been made for this change. Experiments made in the absence of hydrogen atoms are recorded in Table II, in which cases $p_H = 0$.

[10] Wrede, *Z. Physik*, **54**, 53 (1929); Steiner and Wicke, *Z. physik. Chem.*, Bodenstein-Festband, 817 (1931).

TABLE II

THE REACTION OF HYDROGEN ATOMS WITH HYDRAZINE, SHOWING THE EFFECTS OF THE REACTION TEMPERATURE AND THE CONCENTRATIONS OF THE REACTANTS

Streaming velocity without hydrazine, 3.1–3.2 × 10^{-3} mole per minute

Expt.	$p_H + p_{H_2}$, mm.	p_H mm.	Reaction temp., °C.	Moles NH_4 × 10^3/min.	Moles N_2H_3 × 10^3/min.	% N_2H_4 dec.	Moles NH_3 / Moles N_2H_4 dec.
3	0.23	0.14	22	0.317	0.085	77.4	1.06
4	.17	.00	22	.000	.377	...	...
5	.24	.12	22	.214	.117	68.1	0.86
6	.23	.10	22	.189	.155	57.8	.89
7	.18	.00	22	.000	.355	...	...
13	.21	.15	22	.257	.215	62.6	.72
14	.20	.00	22	.000	.574	...	...
15	.22	.12	22	.262	.276	54.0	.81
16	.23	.10	22	.218	.346	42.3	.86
17	.18	.00	22	.000	.625	...	...
18	.24	.17	0	.299	.238	60.8	.82
20	.24	.12	0	.257	.312	48.6	.87
21	.24	.10	0	.220	.361	40.5	.89
22	.23	.00	0	.000	.616	...	...
23	.21	.14	22	.076	.000	100.0	.67
24	.21	.00	22	.000	.112	...	...
25	.21	.11	22	.081	.000	100.0	.72
26	.21	.09	22	.089	.000	100.0	.79
32	.21	.07	22	.097	.000	100.0	1.05
33	.21	.00	22	.000	.092	...	...

TABLE III

THE EFFECT OF THE AMOUNT OF WATER ON THE DECOMPOSITION OF HYDRAZINE BY HYDROGEN ATOMS

p_H	Moles NH_3 × 10^3/min.	Moles N_2H_4 × 10^3/min.	% N_2H_4 decomposed	Moles NH_3 / Moles N_2H_4 dec.	% H_2O in hydrogen
0.082	0.266	0.141	69.2	0.85	3
.080	.234	.120	71.0	.80	>5
.094	.248	.058	86.0	.70	>5
.081	.245	.056	86.5	.69	3

When Experiments 13–17 and 18–22 in Table II are compared, it is seen that a change in temperature had no appreciable effect on the amount of hydrazine decomposition or the amount of ammonia formed. For a constant initial hydrazine concentration the percentage decomposition of the hydrazine and amount of ammonia formed decreased as the atomic hydrogen concentration decreased (Experiments 3–7). It should be pointed out that the actual number of molcs of hydrogen atoms was always about three to ten times in excess of the moles of hydrazine. If the hydrogen atom concentration was held constant and the initial hydrazine concentration decreased, the absolute amounts of hydrazine decomposed and ammonia formed decreased too, but the percentage decomposition of the hydrazine increased. This is not true, of course, in the cases where all

of the hydrazine decomposed (see Experiments 23–33). From some fifty experiments carried out it was found that the ratio of NH_3 formed to N_2H_4 decomposed was between 0.67 and 1.0. Although these ratios are not as accurate as desired, a consideration of all the experiments indicated that the ratio increased as the excess of hydrogen atoms over hydrazine decreased. It was possible that some ammonia passed through the first trap without condensing, since the mass velocity of the gases was three meters per second. Several experiments, yielding negative results, were made to see whether any ammonia might be collected in the second trap by cooling with liquid air.

The "streaming velocity," which was the amount of gas delivered by the pumps per minute, was determined with and without hydrazine added to the hydrogen atoms. The difference between these values gave the net number of moles of permanent gas, presumably nitrogen, formed during reaction. The accuracy of these measurements was ± 2 cc. per minute (25° and 760 mm.) $\sim 0.09 \times 10^{-3}$ moles per minute, which permits only certain general conclusions to be drawn from the results. The ratio of the moles of gas formed to the moles of hydrazine decomposed per minute varied between 1.0 and 1.9, the average ratio from all experiments being 1.3. In Experiment 3, for example, the increase in streaming velocity was 12 cc. per minute; hence there is no doubt that in some cases the ratio exceeded 1.0.

One objection to the method employed in the present work is that water was introduced into the hydrogen and the possibility arises that the dissociation products of water from the discharge may have initiated the reactions observed. This objection is shown to be incorrect in the light of the experiments given in Table III in which the amount of water in the hydrogen was varied. The first two and the last two experiments should be compared.

A slight modification of the apparatus permitted the observation of the fluorescence through a quartz window waxed on the reaction tube, the spectrograph being sighted down the tube to obtain greater light intensity. A Schmidt and Haensch spectrograph, with an average dispersion of 70 Å. per millimeter between 5000 and 6500 Å. was used for photographing in the visible portion of the spectrum. The longest exposure of ten hours of the fluorescence with Eastman Hypersensitized plates showed many lines (or bands) stretching from 4800 to 6200 Å. and, since proper precautions had been taken, these were not to be identified as the hydrogen molecular spectrum reflected from the discharge. The lines were so faint and, in most cases, diffuse that only approximate values of the wave lengths were found. In the region between λλ5200–5700 Å. the wave lengths checked the strongest lines reported by Rimmer[11] for the so-called α-bands produced

[11] Rimmer, *Proc. Roy. Soc.* (London), **A103**, 696 (1923).

in an ammonia flame. The Schuster bands at λ 5635 and 5670 were not observed. The matter may be of interest in connection with the production of these bands or, if the bands can be definitely attributed to some molecule, as a means of identifying one of the intermediates in the reacting system.

The Reaction of Hydrogen Atoms with Ammonia.—A summary of the results of some of the experiments on the reaction of ammonia and hydrogen atoms is given in Table IV. The temperatures recorded are those of the ammonia at the entrance to the reaction tube, the temperature of the reaction tube being 20–25° in all cases. The percentage of water in the hydrogen was approximately 6% in Experiment III and 3% in Experiments I and II.

TABLE IV

EXPERIMENTS SHOWING THE EFFECT OF HYDROGEN ATOMS ON AMMONIA

Ammonia pressure, 0.06 mm. Streaming velocity of H_2, 2.9–3.1 × 10^{-3} mole/minute

Expt.	$P_H + P_{H_2}$, mm.	P_H, mm.	Temp., of NH_3, °C.	Moles NH_3 hr. × 10^3	Amt. of decomp., %	% corrected
I 1	0.17	0.11	25	42.0	2.1	1.6
II 1	.18	.12	25	42.3	3.3	2.8
II 4	.20	.12	25	42.7	2.5	2.0
II 5	.20	.08	25	43.4	0.7	0.2
III 7	.19	.00	170	39.5	...	...
III 8	.18	.12	260	37.4	5.5	5.0
III 9	.18	.12	105	38.0	4.0	3.5
III 10	.17	.11	50	38.0	4.0	3.5
III 11	.16	.00	50	39.6	...	...

The distance from the discharge to the ammonia inlet was only 16 centimeters; consequently the decomposition observed may have been due in part to a diffusion of the ammonia back into the discharge, followed by dissociation. Since nitrogen from an uncondensed discharge has no effect on ammonia,[2] the former was admitted to the discharge in place of hydrogen and the amount of decomposition was measured in the usual way. The percentage decomposition observed was 0.5, so this amount was subtracted from the percentages observed with hydrogen in order to obtain the corrected values shown in the last column of Table IV. The experiments III did not indicate any significant increase in reaction as the temperature of the ammonia was raised to 260°. The following factors may have been important on heating the ammonia above 100°. The number of "high temperature" ammonia molecules reaching the reaction tube may have been too small to give any reaction or the heated ammonia made the glass surface active so that the hydrogen atoms recombined on the walls. Finally, the differences in amounts of decomposition in Experiments II and III may have been due to the difference in amounts of water present, for oxygen atoms (from the water) may have reacted with the ammonia and accounted for all the decomposition observed. Only about ten per cent.

dissociation of the water, followed by reaction, will explain the results on this basis. The reaction of hydrogen and oxygen, initiated by the photochemical decomposition of ammonia, possesses an abnormal temperature coefficient and there is also evidence that ammonia or its dissociation products are involved in the reaction chains set up.[12] This suggested the possibility that ammonia was not reacting with hydrogen atoms, but with the dissociation products of water. As a basis for calculations, the percentage decomposition at 25° may be set equal to 3.0 at 25°, which is certainly an upper limit.

Discussion

The mechanism of the reaction of hydrogen atoms with hydrazine as given by Wiig and Kistiakowsky[5] is as follows

$$H + N_2H_4 = H_2 + N_2H_3 \quad (1)$$
$$N_2H_3 + N_2H_3 = 2NH_3 + N_2 \quad (2)$$

The results of the present investigation agree with the above scheme in that approximately one mole of ammonia and one of permanent gas are produced for every mole of hydrazine decomposed. The observed decomposition of one mole of hydrazine led to more than one mole of permanent gas and less than one mole of ammonia, indicating that some side reaction, perhaps heterogeneous, destroyed some N_2H_3. For example, $H + N_2H_3 = 2H_2 + N_2$ increases in rate as the hydrogen atom concentration increases, decreases the ammonia yield, and increases the yield of permanent gas above that expected, which is in accord with the results. Apart from a wall recombination of the hydrogen atoms, there is no explanation of the fact that the atom concentrations had to be ten times in excess of the hydrazine concentration in order to obtain total decomposition of the hydrazine. Several facts dealing with the photochemical decomposition of ammonia are of interest, since Equations (1) and (2) are involved in the mechanism. The over-all temperature coefficient of (1) and (2) was shown to be zero, hence the temperature coefficient of the quantum efficiency is not connected with these processes. The photochemical experiments of Gedye and Rideal,[13] carried out by a flowing method, showed that hydrazine was produced in concentrations of 0.02 to 0.7 mm., but, in formulating the reaction mechanism, they did not consider reactions similar to (1) and (2).[4] The reactions

$$H + N_2H_4 = NH_3 + NH_2 \quad (3)$$
$$2NH_2 = N_2 + 2H_2 \quad (4)$$

will not account for the results of the experiments described here. If, in the mechanism of Wiig and Kistiakowsky for the photochemical de-

[12] Professor H. S. Taylor at Princeton kindly communicated these results before their publication, for which I wish to express my thanks.

[13] Gedye and Rideal, *J. Chem. Soc.*, 1160 (1932). See also Koenig and Brings, *Z. physik. Chem.*, Bodenstein-Festband, 595 (1931)

composition of ammonia, (1) and (2) are replaced by (3) and (4), then, when there are no wall effects, one finds the quantum yield is independent of the light intensity and decreases as the pressure is raised. However, Reaction (4) must possess a temperature coefficient and the decomposition of one mole of hydrazine would lead to more than one mole of ammonia and less than one mole of permanent gas, which is not in accord with the results.

According to Steiner,[1] the formation of hydrazine from nitrogen atoms and hydrogen molecules takes place according to the reactions $N + H_2 = NH_2$ and $2NH_2 = N_2H_4$ in three-body collisions. A dissociation of the hydrogen, up to ten per cent., had little effect on the hydrazine yield, which would be understandable provided the hydrogen atoms had no effect on the hydrazine formed. However, Steiner's experiments show that the hydrazine pressures were of the order of 10^{-2} mm. and the hydrogen atom pressures 5×10^{-2} mm., hence the interaction between these two gases was considerable. Qualitatively, the results may be explained by postulating that nitrogen atoms decompose hydrazine into nitrogen and hydrogen (no ammonia was observed). Adding hydrogen atoms not only destroys hydrazine, but also nitrogen atoms, and the end result is an approximate constancy of the hydrazine yield. Since hydrogen and nitrogen atoms have little effect on ammonia, the yield of the latter increases as the concentrations of the former increase. The reaction[14] $X + NH + NH_3 = N_2H_4 + X^*$ does not enter into consideration when only nitrogen atoms and hydrogen molecules are present; in other cases the stability of ammonia toward hydrogen atoms is an indication that ammonia is too stable to react with NH.

Koenig and Wagner[15] find that hydrazine is formed in appreciable amounts when ammonia is passed through a silent discharge at high flow rates. They have not apparently taken into account the fact that hydrazine acts like ammonia when a mixture of these two is passed into sulfuric acid, neutralizing a part of the acid. Hence, the amounts of ammonia decomposition, calculated from their titrations, must be increased by an amount equal to the hydrazine formed. Using these corrected values, it is found that the number of moles of hydrazine formed per mole of ammonia decomposed does not exceed 0.30 even at the highest flow rate used. At nearly constant current strength, the amount of ammonia decomposed per minute was independent of the flow rate and the amount of hydrazine formed per minute varied only four-fold, even when the flow rate varied six hundred times. If one disregards the reactions due to the ions present in the discharge and substitutes current strength for light intensity, then these facts are in accord with the mechanism of Wiig and Kistiakowsky

[14] Bredig, Koenig and Wagner, *Z. physik. Chem.*, **A139**, 211 (1928).

[15] Koenig and Wagner, *ibid.*, **A144**, 213 (1929).

for the photochemical decomposition of ammonia. In the discharge the concentration of hydrazine is ca. 1×10^{-9} mole per cc. $\sim$ 0.02 mm.

The collision yield has been calculated for the reaction[16]

$$H + NH_3 = NH_2 + H_2 + 10 \text{ kg. cal.} \quad (5)$$

The average hydrogen atom concentration in the experiments was 0.06 mm., the ammonia pressure 0.06 mm., and the collision radius 3×10^{-8} cm. Since the reaction tube was 3.5 cm. in diameter and assuming a length for the reaction space of only 10 cm., the number of collisions was 0.44 mole per second. The largest amount of decomposition was about 3.5×10^{-7} mole per second, hence the collision yield was 8×10^{-7} and the corresponding activation energy 8.5 kg. cal. per mole. As pointed out above, the observed decomposition was an upper limit, so this activation energy is a lower limit. Correspondingly, the reverse of Reaction (5) possesses an activation energy > 18.5 kg. cal. per mole. Since the experiments yielded an upper limit for the amount of dissociation, which was small, rather than a true value, it is hardly justifiable to extend these calculations.

Summary

The reactions between hydrogen atoms and hydrazine or ammonia have been studied at low pressure by a flowing method. The concentrations of the atomic hydrogen were measured calorimetrically.

Approximately one mole of ammonia and one mole of permanent gas are produced in the decomposition of one mole of hydrazine by hydrogen atoms. The over-all temperature coefficient of the reactions involved is zero. The qualitative effects of the total pressure, concentration of atomic hydrogen and the concentration of hydrazine were determined. The fluorescence produced in the reaction is described.

Under the conditions of the experiments, the reaction between hydrogen atoms and ammonia was very small and the lower limit for the activation energy 8.5 kg. cal. per mole.

The mechanisms of these two atom reactions have been discussed, especially in connection with the photochemical and electrical dissociation of ammonia.

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[16] Dixon and Steiner,[2] give for the NH linkage in NH_3 a value of 96 kg. cal. This leads to a heat of reaction for (5) of 6 kg. cal., but, since the accepted value of the heat of dissociation of nitrogen is probably too high, the NH linkage is weaker and the reaction more exothermic. In connection with the heat of dissociation of N_2 see Mulliken, *Rev. Modern Physics*, **4**, 1 (1932), and Tate and Lozier, *Phys. Rev.*, **39**, 254 (1932).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE ANGLE BETWEEN THE OXYGEN BONDS BY THE COLLISION AREA METHOD

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The recent interesting predictions of Pauling[2] and Slater,[3] based on the quantum mechanics, regarding the angle between the valence bonds of the oxygen atom suggest the possibility and desirability of experimental test. Pauling states that the bond angle for the water molecule lies between the limits of 90 and $109\frac{1}{2}°$, closer to the former; while Slater believes it to be somewhat less than a right angle, assuming that the interaction of the two hydrogens would, by residual valence, decrease the normal angle. Both agree that except for the interaction of the two hydrogen atoms the bond angle would be about 90°, which is predicted to be the normal orientation of bonds formed by *p*-electrons.

The experimental evidence as to the angle of the oxygen bonds includes the following. (1) It has been shown by x-ray crystal structure studies that the angle between oxygen bonds in certain inorganic oxides, namely, Sb_4O_6 and As_4O_6, differs from the tetrahedral angle[4] by no more than 5°. (2) A simple potential energy study of the structure of the water molecule has been given by Debye,[5] who shows, assuming the water molecule to be made up of ions, that the only structure possible is that in which the ions are arranged in the form of an isosceles triangle; and by making use of the known values for the moments of inertia, he shows that the angle between the bonds must be approximately either 110 or 64°. Debye then proceeds to choose the smaller angle as more probable by a study of the dipole moment of the water molecule; but the choice is not very definite and we may consider either angle as possible. (3) The finite dipole moments of the ethers[6] indicate an angle of the oxygen bonds considerably less than 180°. (4) The ease of formation of the ozonides by bridging across double bonds and the entrance of oxygen into ring structures, as in the case of furan (which is nearly as stable as benzene), show that the oxygen bond angle is comparable with that between carbon bonds.

Our previous experience[7] with a method for matching molecule collision

[1] Du Pont Fellow at The Ohio State University, 1931–32.

[2] Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928); THIS JOURNAL, **53**, 1367 (1931).

[3] Slater, *Phys. Rev.*, **37**, 481 (1931).

[4] Ewald and Hermann, "Strukturbericht."

[5] Debye, "Polar Molecules," The Chemical Catalog Co., New York, 1929, p. 68.

[6] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, p. 87.

[7] (a) Melaven and Mack, THIS JOURNAL, **54**, 888 (1932); (b) Sperry and Mack, *ibid.*, **54**, 909 (1932).

areas, determined from gaseous viscosity, with average cross-sectional areas of models made to scale, suggested that it would be of interest to apply this method to an examination of the spatial configuration of the two phenyl groups in diphenyl ether, in an effort to arrive at a conclusion regarding the angle between the oxygen bonds which hold the phenyl groups.

Experimental

The sample of diphenyl ether, purchased from the Eastman Kodak Co., was fractionally distilled, washed with a concd. aqueous solution of sodium hydroxide, then several times with water, and finally dried over anhydrous calcium chloride. After repeated recrystallization from ethyl alcohol and from its own melt, it was twice fractionated in an efficient still-head and a portion having a boiling point of 257.3° (corrected at 746 mm.), and a melting point of 26.8–27.0°, was taken for use.

The viscosity of the vapor was measured over a temperature range of 176–363° by transpiration through a capillary in essentially the same manner already described. The only present differences in experimental technique involved the use of carefully constructed and controlled air-baths instead of water and oil thermostats, and the use of two sensitive quartz clicker-membranes instead of mercury manometers for measuring the influx and efflux pressures (p_1 and p_2). The latter change in apparatus was necessary because the volatilization temperature (150°) needed to produce the desired driving pressure would have developed a large enough pressure of mercury vapor, had mercury manometers been used, to interfere seriously with the rates of transpiration of the diphenyl ether vapor.

The usual precautions were taken to prevent turbulent flow; the viscosities η at the several temperatures were calculated[8] with Meyer's transpiration formula, as before,[7a] and were corrected for slip, η_c. Then the Sutherland constant, C, was computed graphically and the collision areas calculated by means of Chapman's equation.

TABLE I

VISCOSITY DATA AND COLLISION AREA FOR DIPHENYL ETHER

Temp., °C.	Influx press., p_2, cm.	Efflux press., p_2, cm.	Rate of flow, cc./hr.	η	η_c	C	Collision area, sq. Å.
176.0	2.272	0.13	0.5334[a]	0.8250×10^{-4}	0.8397×10^{-4}		36.32
199.1	2.335	.13	.5016	.8776	.8942		35.84
255.2	2.475	.17	.4550	.9680	.9956	400	36.10
330.8	2.550	.18	.3780	1.086	1.112		36.20
363.2	2.860	.19	.4302	1.138	1.165		36.20
							Av. 36.13

[a] The density of liquid diphenyl ether at 150°, the temperature at which volatilization occurred, was determined to be 0.9650.

Before a model of diphenyl ether was made, the viscosity of the vapor of diphenylmethane, as a check on the results, was measured over a similar temperature range, and its collision area calculated in the same way.

[8] The present capillary (Pyrex) had a length of 27.53 cm., and an average radius of 0.02510 cm. (measured with a mercury thread). Calibration with dry air gave the following results for the viscosity of air: at 63°, 199×10^{-6}; at 103°, 216×10^{-6}; at 168°, 247×10^{-6}; at 212.5°, 262×10^{-6}; at 232°, 272×10^{-6}.

TABLE II

VISCOSITY DATA AND COLLISION AREA FOR DIPHENYLMETHANE

Temp., °C.	Influx press., p_2, cm.	Efflux press., p_2, cm.	Rate of flow, cc./hr.	η	η_0	C	Collision area, sq. Å.
165.8	2.008	0.125	0.4909[a]	0.8110×10^{-4}	0.8264×10^{-4}		36.44
218.5	2.160	.115	.4217	0.9026	0.9223	387	36.41
307.7	2.260	.180	.3358	1.049	1.076		36.36
360.7	2.320	.200	.2996	1.132	1.163		36.36
						Av.	36.40

[a] The density of liquid diphenylmethane at 150°, the temperature at which volatilization occurred, was determined to be 0.9075. The melting point is 24.8°.

In the case of both substances, diphenyl ether and diphenylmethane, the plot of $T^{3/2}/\eta_c$ against T to get the Sutherland constant, C, gave points lying almost perfectly on a straight line. It will further be noted that the agreement between the two collision areas, 36.13 and 36.40 sq. Å., is gratifyingly close. This is as it should be, for the two molecules, both containing two phenyl groups and differing only to the extent that one contains an oxygen atom and the other a methylene group, should have substantially the same collision area. If we suppose that the two phenyl groups in *diphenylmethane* are attached to the carbon atom of the methylene group at a tetrahedral angle, as is probable, then it follows, quite apart from any model considerations, that the angle at which the two phenyl groups are attached to the oxygen atom in *diphenyl ether* is substantially tetrahedral.

Model Considerations.—A model of diphenyl ether was made up to scale, 1 inch = 1 Å., according to the principles of model construction already laid down.[9,7a] The benzene rings were flat hexagonal graphite rings, made of carbon atoms of diameter 1.42, with C–H internuclear distances of 1.02, and hydrogen atom gas kinetic domain radii of 0.72 (on the assumption that three hydrogen atoms per molecule partake in an average collision). A model of the ring dome domain (gas kinetic radius 2.0) was attached to each face of the benzene ring. The *aromatic* C–O internuclear distance was taken as 1.37, based on x-ray analysis,[10] and the oxygen domain radius as 1.20. This latter value was based on a consideration of the collision area of the water molecule, as well as on the collision area of carbon dioxide. Rankine[11] reports 1.17, and the radius of the oxygen ion is given by Wasastjerna as 1.32, which is doubtless a little too large for the domain radius of a chemically bound oxygen atom. As a matter of fact the size of the oxygen atom plays such an insignificant role in determining the total collision area of the molecule that any small error made in guessing its exact effective size can be neglected. The velocity of rotation about the spin

[9] Mack, THIS JOURNAL, **54**, 2141 (1932).

[10] Huggins, *Phys. Rev.*, **28**, 1094 (1926).

[11] Rankine, *Proc. Roy. Soc.* (London), **A98**, 369 (1921).

axes can readily be shown to be too slow to affect the collision area appreciably.

The shadow-graphic average cross-sectional area of the model at forty-two approximately equal-angle positions is given in Table III, where the various area values are listed for different angles between the oxygen bonds which hold the two phenyl groups.

TABLE III

SHADOW AREAS OF MODEL OF DIPHENYL

Angle of bonds	180°	150°	120°	90°	60°[a]	30°[a]
Shadow area	39.14	38.33	37.34	35.35	33.54	30.64

[a] The domes on the faces of the rings would not permit such small angles, unless the domes are fluid enough to bulge out on the opposite side of the ring. Such bulging is considered to be improbable.

While the shadow areas are not greatly different over this range of bond angles, they differ enough to allow a fairly clear-cut decision regarding the oxygen bond angles in diphenyl ether. The experimentally determined collision area of 36.13 sq. Å. (Table I) lies between the shadow areas corresponding to 120 and 90°. Even admitting a possible error of ±3% (and it could not be more than this even with a 10% error in the Sutherland constant) in the experimental collision area, the bond angle would have maximum and minimum values of about 130 and 85°. Interpolation of the actual experimental collision area of 36.13 sq. Å. yields 107°. Thus the angle between the oxygen bonds is found to be approximately tetrahedral in the diphenyl ether molecule.

Methyl Ether.—The viscosity data have been determined for methyl ether and the collision area (12.13 sq. Å.) calculated by Titani.[12] We have made a model of the molecule, using spinning methyl groups with a hydrogen domain radius of 0.49 as in the case of methane and ethane,[7a] and oxygen atom dimensions the same as in diphenyl ether, above. The value of the oxygen bond angle was varied from 180 to 90° (until the methyl groups slightly overlapped), and the following values were obtained for the model average cross-sectional areas (Table IV).

TABLE IV

SHADOW AREAS OF THE MODEL FOR METHYL ETHER

Bond angle	180°	150°	120°	90°
Shadow area	12.28	12.85	12.33	11.74

It will be observed that Titani's experimental value of 12.13 sq. Å. checks well with these listed values. Whether or not his value can be used to obtain a definite conclusion regarding the oxygen bond angle depends, of course, on the reliability of his data. It is most interesting to note,

[12] Titani, *Bull. Chem. Soc. Japan*, **4**, 277 (1929); **5**, 98 (1930).

however, that interpolation of his value between 12.33 at 120° and 11.74 at 90°, yields an oxygen bond angle of 110°, approximately tetrahedral.

Ethyl Ether.—Values for the viscosity of ethyl ether vapor are reported[13] over a considerable temperature range. Using these data we have calculated the Sutherland constant and the molecule collision area. The data and the results of the calculations are given in Table V.

TABLE V

VISCOSITY DATA AND COLLISION AREA FOR ETHYL ETHER

Temp., °C.	η	Sutherland constant	Collision area, sq. Å.
0.2	0.689×10^{-4}		18.14
7.4	.712		...
27.6	.771	380	...
100.2	.942		...
212.7	1.234		18.18

Since the molecule of ethyl ether is made up of two-link carbon chains which may coil up in various positions, it is impossible to draw a definite conclusion about the oxygen bond angle in this case. It is interesting, however, to assume a bond angle of about 110° and then to observe from model study the tightness of the average coiling in the gaseous state. The model of ethyl ether was therefore built, with a value of 0.63 for the hydrogen domain radius, on the assumption that two hydrogen atoms per molecule partake in an average collision. Three different structures were studied: (1) a molecule extended as nearly as possible in a straight line; (2) a molecule coiled as tightly as the end methyl groups (assumed to be spinning) would allow; (3) a molecule with static methyl groups, which allowed tighter coiling than in (2). The values obtained for the average shadow area of the different structures were

(1)	Ethyl ether (extended)	21.29
(2)	Ethyl ether (tightly coiled, spinning CH_3)	19.14
(3)	Ethyl ether (tightly coiled, non-spinning CH_3)	17.40
	Collision area from viscosity data	18.16

It will be observed that the molecule must be tightly coiled in the gaseous state, since the cross-sectional area of the extended model is much too large, even when neglecting the effects of spin around the longitudinal axis (small moment of inertia). This tightly coiled configuration agrees well with the tight coiling found for heptane (which one would predict also for pentane and hexane). In fact it is impossible to coil the molecule sufficiently to obtain a small enough collision area to fit the experimentally determined value; without assuming some inter-meshing of the end methyl groups, either spinning or non-spinning, perhaps in a cog-wheel manner.

[13] Landolt–Börnstein, "Tabellen," 1923, Vol. I, p. 171.

In concluding these remarks about the ether molecules it may be said that we were also interested in di-tertiary butyl ether. A search of the standard references indicated that the substance had never been prepared. A study of the model of this molecule makes it clear that it would be impossible to place two tertiary butyl groups on an oxygen atom at an oxygen bond angle as small as 110°. Hence it is probably difficult, if not impossible, to prepare this compound; or if formed at all it would probably be quite unstable. An attempt to prepare it by several standard methods of synthesis failed.

The nearly identical values of Sutherland's constant for diphenyl ether and diphenylmethane indicate that the attractive forces between the molecules in the gaseous state are nearly the same in the two cases, suggesting that the phenyl groups contribute all but an inappreciable fraction of the van der Waals forces of attraction in the vapor. It is rather surprising to note, however, that in the liquid state the two compounds have quite different molecular volumes. Thus at 150°, which should be a corresponding temperature since the boiling points are nearly the same, the densities differ by nearly 7%, the values being 0.9650 for the ether and 0.9075 for diphenylmethane. This relative decrease in the size of the molecular volume of the ether may plausibly be attributed to an increase in internal pressure arising from the presence of the oxygen atom, and due either to its strongly polar nature, or to a resulting orientation effect which permits a closer packing.

We wish to thank E. I. du Pont de Nemours and Company for the fellowship grant under which this investigation has been carried out.

Summary

An application of the shadow-graphic collision area method has been made in a study of the oxygen bond angle.

The collision areas of diphenyl ether and diphenylmethane, which should be approximately the same, are shown to be 36.13 and 36.40 sq. Å., respectively, and the oxygen bond angle in diphenyl ether is shown to be approximately tetrahedral. In methyl ether the bond angle is also probably closely tetrahedral.

The ethyl ether molecule is found to be tightly coiled; a prediction is made regarding the impossibility of preparing synthetically di-tertiary butyl ether; and some remarks are made about the molecular volume of liquid diphenyl ether.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

NITROGEN COMPOUNDS OF GERMANIUM. III. GERMANOUS IMIDE

BY WARREN C. JOHNSON, GLEN H. MOREY AND ARTHUR E. KOTT

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The ammonolysis of germanium tetrachloride has been studied[1,2] in liquid ammonia solution. The results clearly demonstrate germanic imide and ammonium chloride as the only two products of the reaction. A separation of these products was accomplished in ammonia through the low solubility of the imide and the relatively high solubility of the ammonium salt. However, in no instance was it found possible to obtain the imide of a purity greater than 97.2%. More recently, Karantassis and Capatos[3] passed dry ammonia gas into a solution of germanium tetraiodide in carbon tetrachloride. A white product was precipitated from the solution to which upon analysis the formula $GeI_4 \cdot 8NH_3$ is assigned. However, the analytical data given for this product are not sufficient to warrant the existence of this ammonate. Germanic iodide would not be expected to behave differently from germanic chloride in its reactions with ammonia.

According to the literature no studies have been made with solutions of germanous salts in liquid ammonia. One would predict a germanous salt to exhibit a greater stability toward ammonolysis than a germanic compound since the former is derived from a stronger base. The following report shows, however, that germanous iodide is completely ammonolyzed in liquid ammonia to germanous imide and ammonium iodide. The procedure employed in the investigation affords a convenient method for the study of this type of reaction, which necessitates the complete exclusion of air and moisture.

Experimental

The Preparation of Germanous Iodide.—Dennis and Hance[4] prepared germanous iodide by a reaction between germanium and iodine and also by the dissociation of germanium tetraiodide at temperatures above 440°. They found both of these methods impractical since small yields were obtained. Our attempts in this direction bear out their results.

Brewer and Dennis[5] found later that, when an excess of a mixture of the two hydrated oxides of germanium was allowed to react with concentrated hydriodic acid solution at low temperatures, below 40°, germanous iodide was obtained from the solution

[1] Schwarz and Schenk, *Ber.*, **63**, 296 (1930).

[2] Thomas and Pugh, *J. Chem. Soc.*, 60 (1931).

[3] Karantassis and Capatos, *Compt. rend.*, **193**, 1187 (1931).

[4] Dennis and Hance, THIS JOURNAL, **44**, 2854 (1922).

[5] Brewer and Dennis, *J. Phys. Chem.*, **31**, 1526 (1927).

on cooling. In our preparations germanous sulfide[6] was used in place of the hydrated oxides since it was available in considerable quantities.

Crystalline germanous sulfide was pulverized and then added to concentrated hydriodic acid, sp. gr. 1.7, at room temperature. The reaction was found to proceed slowly with the evolution of hydrogen sulfide. After several hours the reaction became sluggish due to saturation of the hydrogen iodide solution with germanous iodide. The temperature of the solution was increased to 50° in order to ensure complete solution of the product, then the supernatant liquid was decanted from the unreacted germanous sulfide and finally filtered. When this solution was cooled to −80° with a solid carbon dioxide–acetone mixture, an appreciable amount of germanous iodide separated as bright yellow crystals. The yields were found to be much smaller when the cooling was carried out with a hydrochloric acid–ice mixture. The crystals of the salt were collected on a Buchner funnel in an atmosphere of nitrogen to prevent any oxidation of the germanous compound. The filtrate, which contained some germanous iodide in the hydrogen iodide solution, was returned to the germanous sulfide crystals for further reaction. This procedure was repeated several times until the greater part of the hydrogen iodide had reacted with the sulfide. The combined lots of germanous iodide crystals were then washed with benzene to remove any germanic iodide and the product was finally dried over phosphorus pentoxide with the aid of a Hy-Vac pump.

Several different preparations of the iodide were analyzed for germanium by oxidation with nitric acid to germanic oxide.

Anal. Germanium, subs., 0.4502, 0.5921, 0.3631: GeO_2, 0.1441, 0.1902, 0.1162. Calcd. for GeI_2: Ge, 22.24. Found: 22.22, 22.29, 22.21.

The Volhard method for the determination of iodine was found impractical for germanous iodide.[7] This method invariably gives high results for iodine due to reduction of silver ion to metallic silver by germanous ion. No satisfactory method was found for the preferential oxidation of germanous ion in the presence of iodide ion. The iodine content of this salt was successfully determined by a procedure to be described later in this paper.

The Ammonolysis of Germanous Iodide.—Schwarz and Schenk[1] found germanium tetrachloride to be completely ammonolyzed in liquid ammonia to germanic imide

$$GeCl_4 + 6NH_3 = Ge(NH)_2 + 4NH_4Cl \qquad (1)$$

One would predict a germanous salt to possess a greater stability in ammonia than a germanic salt as regards ammonolysis. If the germanous ion is assumed to have a coördination number of four, it would be predicted that, in the formation of an ammonate, four molecules of ammonia would combine with one molecule of the germanous salt. However, experiments showed an increase in weight corresponding to only three molecules of ammonia when germanous iodide was subjected to liquid ammonia. This result allows for two possibilities, namely, the addition of three molecules of ammonia or the ammonolysis of the salt to germanous imide as expressed by the equations

[6] The germanium used in this investigation was obtained as germanous sulfide from germanite ore. For abstract of the process, see Kraus and Johnson, paper given before the Swampscott Meeting of the American Chemical Society, September, 1928.

[7] The authors are indebted to Mr. I. Aarons for the results of these studies, which were carried out in the quantitative laboratories.

$$GeI_2 + 3NH_3 = GeI_2 \cdot 3NH_3 \quad (2)$$
$$GeI_2 + 3NH_3 = GeNH + 2NH_4I \quad (3)$$

Subsequent experiments showed the reaction to proceed quantitatively according to equation (3).

The apparatus shown in Fig. 1 was used to study the ammonolysis of germanous iodide. Approximately 1 g. of the iodide was introduced into the reaction tube at E so as to assume the position indicated by H. When ammonia gas was allowed to enter at A through stopcock B to come in contact with the iodide at room temperature, reaction between the constituents took place immediately with the liberation of sufficient heat to decompose the unused germanous iodide to germanic iodide and finely divided germanium. This was quite evident according to the increase in temperature of the bulb and the appearance of the products of decomposition. Similar difficulties were experienced when liquid ammonia was allowed to come in contact with the iodide at $-33.5°$. In order to eliminate this decomposition, oxygen-free, dry nitrogen gas was first introduced into the reaction chamber at a pressure of one atmosphere and a temperature of $-33.5°$, the boiling point of liquid ammonia. Then ammonia gas was allowed to diffuse through the nitrogen at a pressure of about 85 cm. to reduce its concentration in the region of the iodide. As the reaction progressed, the concentration of the nitrogen was reduced to about one-half atmosphere; however, at no time during this procedure was any ammonia condensed upon the iodide. When the reaction was completed, as shown by the disappearance in color due to the iodide, ammonia was condensed in the reaction chamber and the contents of the tube were agitated to ensure uniformity of the products. Finally the ammonia was removed by evaporation and the entire system was thoroughly evacuated at room temperature until no change in weight could be observed. The apparatus shown in Fig. 1 was sufficiently small to weigh on an ordinary analytical balance. The following results were obtained with several different preparations.

TABLE I

THE ACTION OF AMMONIA ON GERMANOUS IODIDE

GeI_2, g.	NH_3 added, g.	Ratio moles NH_3/mole GeI_2
1.1723	0.1814	2.97
0.8178	.1276	2.99
0.8712	.1367	3.01
4.7771	.7434	2.99
1.9310	.3000	2.98
1.6961	.2643	2.99

The values given in the above table show that three gram molecules of ammonia are involved in the reaction with one gram molecule of germanous iodide. If the reaction proceeds according to equation (3), the products would consist of one gram molecule of germanous imide and two gram molecules of ammonium iodide. The presence of ammonium iodide in liquid ammonia may be readily detected by a strongly electropositive element, *e. g.*, sodium, which reacts with the acid to liberate hydrogen gas

$$2NH_4I + 2Na = 2NaI + 2NH_3 + H_2 \quad (4)$$

Several such experiments were carried out at $-33.5°$ in which the hydrogen was collected and measured over water in an apparatus similar to that

previously described.[8,9] The results of these experiments are given in Table II.

TABLE II

THE ACTION OF SODIUM ON THE PRODUCTS OBTAINED FROM GERMANOUS IODIDE IN LIQUID AMMONIA

GeI_2, g.	H_2 (found), cc.	H_2 (calcd.), cc.
1.2509	83.0	85.8
0.7560	52.5	51.9
.7777	54.3	53.4
.9855	70.1	67.6

The values given for hydrogen in column 3, Table II, are calculated on the assumption that the reaction proceeds according to equation (3) with the formation of ammonium iodide which, upon the addition of metallic sodium, follows equation (4). No consideration is given in these calculations to the possibility of a reaction occurring between germanous imide and sodium in liquid ammonia. However, it will be noted that the values found for hydrogen (column 2, Table II) agree well with those calculated on the above assumption. From this standpoint it may be assumed that the imide does not react appreciably with sodium to form a sodium salt, GeNNa, with the liberation of hydrogen. Further observations bear out this conclusion. When sodium was added to the solution, a vigorous reaction followed until the solution became permanently blue, due to the presence of an excess of the metal. The solution was allowed to stand for an hour or more, during which time only an inappreciable amount of hydrogen was liberated; practically all of the hydrogen collected in a given experiment was discharged from the solution before the characteristic blue color appeared. It is not possible to state whether the hydrogen liberated after the solution became blue was due to a reaction between the imide and sodium or to a reaction between ammonia and sodium. If the former were taking place, the rate of the reaction must be exceedingly low under the conditions of the experiment, namely, small concentration of sodium and of germanous imide and low temperature, $-33.5°$. Ammono bases of the type corresponding to germanous imide are known to be amphoteric; for example, stannous imide reacts with potassium amide in liquid ammonia to form potassium ammono stannite, SnNK.[10] Germanous imide would be expected to behave similarly; its apparent inactivity with sodium may be accounted for by its extreme insolubility.

Germanous Imide.—The experiments described above show that germanous iodide is completely ammonolyzed in liquid ammonia to germanous imide. In order to obtain the imide in a pure condition, it is

[8] Kraus and Brown, THIS JOURNAL, **52**, 4031 (1930).

[9] Johnson and Fernelius, *J. Chem. Ed.*, **4**, 441 (1929).

[10] Bergstrom, *J. Phys. Chem.*, **32**, 433 (1928).

necessary to remove completely the ammonium iodide which accompanies it in solution. The apparatus shown in Fig. 1 was designed to accomplish this separation. Preliminary experiments indicated germanous imide to be practically insoluble in liquid ammonia. Ammonium iodide is known to be highly soluble in this medium.

After the germanous iodide had reacted with ammonia, in a manner previously described to prevent decomposition, additional ammonia was condensed in the bulb of the reaction chamber until the liquid assumed the position indicated by I. The imide was allowed to settle and then the solution above was siphoned through the Jena glass filter C with stopcock D open. (The Jena glass filter was attached to the Pyrex apparatus by means of an intermediate seal of G702P glass.) Ammonia was again condensed into the bulb through stopcock B, the solution was agitated through boiling with the Dewar flask removed, and finally the supernatant liquid was siphoned through D. This procedure was repeated until the discarded solution failed to give a test for the iodide ion. Finally, the ammonia remaining in the bulb was eliminated by means of the pumps. The imide appeared as a canary yellow powder. Samples for analysis were shaken into tubes E and F, which were then sealed from the reaction chamber.

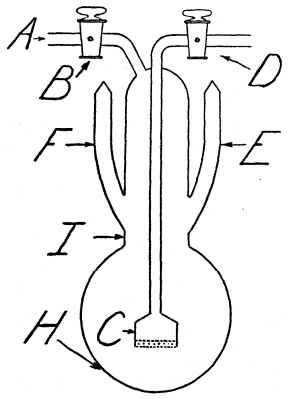

Fig. 1.

It was found necessary to exercise considerable care in the exclusion of air and moisture from the germanous imide in the processes described above. Small amounts of water in the ammonia or the glass line are sufficient to destroy the imide as follows

$$GeNH + 2H_2O = Ge(OH)_2 + NH_3 \qquad (5)$$

Dry oxygen reacts vigorously with the imide with the liberation of sufficient heat to cause the material to glow brightly. Germanic oxide appears to be one of the products of this reaction.

In two preparations of the imide the amount of ammonium iodide separated from the mixture was determined quantitatively. The ammonium iodide solution was allowed to evaporate and then the salt was collected and weighed in the absence of moisture after being heated to 100°. The results are given in Table III.

TABLE III

THE AMOUNT OF AMMONIUM IODIDE SEPARATED FROM GERMANOUS IMIDE

GeI_2, g.	NH_4I (found), g.	NH_4I (calcd.), g.
1.1723	1.0340	1.0400
5.7299	5.1070	5.0810

For the germanium analysis, germanous imide was oxidized to germanic oxide with nitric acid. It was found necessary to allow the imide to react first with water and then to treat the germanous hydroxide, suspended in water, with nitric acid. If the imide is exposed to air, a violent reaction takes place with oxygen with the liberation of considerable heat. Accordingly, a part of the unreacted imide is thermally decomposed to a black substance, presumably germanous nitride, which resists the action of nitric acid. Table IV records the results of the oxidation process.

TABLE IV

THE OXIDATION OF GERMANOUS IMIDE

GeNH, g.	GeO_2 (found), g.	GeO_2 (calcd.), g.
0.0836	0.0992	0.0998
.2456	.2937	.2932
.1904	.2268	.2273

The Kjeldahl method was employed to determine the nitrogen content of germanous imide. A small tube containing a sample was broken and then dropped into a flask of dilute sodium hydroxide solution. The distillate was collected in a known quantity of standard acid solution. It was found difficult to obtain consistent results in this procedure due to the inability to exclude all traces of oxygen during the transfer processes. However, these results, together with those for the germanium analyses, are sufficient to demonstrate the existence of germanous imide in a fairly high state of purity.

TABLE V

THE HYDROLYSIS OF GERMANOUS IMIDE

GeNH, g.	NH_3 (found), g.	NH_3 (calcd.), g.
0.1364	0.0279	0.0265
.1793	.0342	.0348
.1402	.0255	.0272

Properties.—Germanous imide, as prepared by the ammonolysis of germanous iodide in liquid ammonia solution, appears as a light yellow powder. It is insoluble in liquid ammonia. It reacts readily with water or dilute alkali to give germanous hydroxide and ammonia. The imide reacts violently with oxygen with the liberation of considerable quantities of heat. Germanic oxide appears as one product of this oxidation. It is readily oxidized by nitric acid.

Summary

A new method is given for the preparation of germanous iodide, which consists of a reaction between germanous sulfide and concentrated hydrogen iodide solution.

Germanous imide is prepared by the action of ammonia on germanous iodide. A convenient apparatus is described for this preparation and the

separation of ammonium iodide to obtain the imide in a fairly high state of purity.

Some of the properties of germanous imide are described.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATE OF THE FOURTH ORDER REACTION BETWEEN BROMIC AND HYDROBROMIC ACIDS. THE KINETIC SALT EFFECT

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Introduction

While reactions of high order are not common, the reduction in acid solution of bromate or chlorate by a halide,[1] and that of iodate by iodide at very low concentration of iodide,[2] are of the fourth order. Their rates are represented by differential equations of the form

$$-\mathrm{d}(XO_3^-)/\mathrm{d}t = k(XO_3^-)(Y^-)(H^+)^2$$

According to Brönsted,[3] k should decrease rapidly with increasing ionic strength, and the function $k\gamma_n/\gamma^2_{HXO_3}\gamma^2_{HY}$ should be constant at low ionic strengths. Since γ_n, the activity coefficient of a neutral substance, differs but little from unity, the kinetic salt effect may be represented by the equation

$$k/\gamma^2_{HXO_3}\gamma^2_{HY} = \chi \qquad (1)$$

where χ is a true constant.

To study this kinetic salt effect, an investigation of the reduction of bromic acid by hydrobromic acid was undertaken. The reaction

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \qquad (2)$$

was first studied by Judson and Walker,[4] and their conclusion that its rate might be represented by an equation of the above form was later confirmed by Skrabal and Weberitsch.[5] Still later, Bray and Davis[6] investigated the autocatalytic reduction of bromate ion by hydrogen peroxide

$$BrO_3^- + 3H_2O_2 = 3O_2 + Br^- + 3H_2O \qquad (3)$$

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[1] Skrabal, *Z. Elektrochem.*, **30**, 123 (1924); "International Critical Tables," Vol. VII, p. 149.

[2] Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928).

[3] J. N. Brönsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, New York, 1927.

[4] Judson and Walker, *J. Chem. Soc.*, **73**, 418 (1898).

[5] Skrabal and Weberitsch, *Monatsh.*, **36**, 211 (1915).

[6] Bray and Davis, THIS JOURNAL, **52**, 1427 (1930).

and proved that the differential equation expressing its rate was

$$-d(BrO_3^-)/dt = k_1(H_2O_2)(BrO_3^-)(H^+) + k(BrO_3^-)(Br^-)(H^+)^2 \quad (4)$$

The results of the latter investigation gave promise that this indirect method of studying the reduction of bromic acid by hydrobromic acid should yield accurate values of the specific rate. The determination of k by this method has the added advantage that, since bromine is not an end-product, errors due to the accumulation of bromine and the consequent formation of tribromide ion are eliminated.

Experimental Procedure

The experimental procedure of Bray and Davis was closely followed except that perchloric acid was substituted for sulfuric. This substitution abolished two difficulties inherent to sulfuric acid solutions: the obscurity cast upon the interpretation of activity data, and the uncertainty in the hydrogen-ion concentration resulting from the relatively weak second dissociation of that acid.

The experiments were performed in the dark at the three temperatures 25, 45 and 65°. Measured quantities of water, perchloric acid, potassium bromate and hydrogen peroxide, all at the reaction temperature, were placed in the reaction flask in that order. Zero time was taken as the instant the stopcock was closed, immediately after adding the hydrogen peroxide. In the runs in which bromide ion was added, a measured solution of potassium bromide was introduced just preceding the introduction of the hydrogen peroxide solution, and in the same manner.

Considerable care was taken to prevent the discrepancies referred to by Bray and Davis in the gas evolution during the first few minutes of the experiments. Blank experiments performed by adding water to water in the reaction flasks indicated that introducing a solution to the reaction mixture by removing the stopper from the reaction flask, running in the solution from a pipet and then replacing the stopper produced an error which might be as high as two or three cc. extra evolved gas at 25°. This error was presumably due to the introduction of air at room temperature (18–22°) to the reaction flask which was at 25°. It was found that these disturbances could be largely eliminated by adding the solution through a stopcock in the top of the reaction flask, without stopping the shaker. Experiments showed that when the amount of added solution was small (25 cc.) this method completely eliminated initial errors, but that when the amount of added solution was large (150 cc.) some such effect might persist, although of much lesser magnitude. In the experiments at higher temperatures any slight difference in temperature between the added solution and the reaction mixture was sufficient to introduce an initial disturbance, the magnitude of which increased rapidly with the temperature difference and the amount of the added solution.

To check the stoichiometric relations expressed in Reaction 3, 3 moles O_2 produced = 1 mole BrO_3^- used = 3 moles H_2O_2 used, complete analyses were made in several experiments while bromate was still present. In one portion of the solution bromide was determined gravimetrically as silver bromide. The bromide concentration thus found was subtracted from the original bromate concentration to find the bromate concentration of the sample. Another portion of the solution was analyzed iodimetrically for total oxidizing power, and the peroxide concentration was obtained by subtracting the oxidizing power of the bromate from this total. In four experiments carried out in this manner at 25° the ratio of moles O_2 produced to moles BrO_3^- used was found to be 3.00 ± 0.09 and the ratio of moles O_2 produced to moles H_2O_2 used, 1.00 ± 0.02. In three experiments at higher temperatures these ratios were 3.00 ± 0.07 and 1.00 ± 0.04, respectively. All of these results were obtained in 0.1 M (H^+).

This method of analysis was adopted after it had been found that the presence of bromate caused an error in the titration of hydrogen peroxide with permanganate. Thus, in 0.1 M perchloric acid solutions in which the amount of hydrogen peroxide present corresponded to 22.8 cc. of 0.002 M potassium permanganate, 0.05 cc. less permanganate was used when the concentration of bromate was 0.0027 M, and 4.7 cc. less when this concentration was 0.0044 M. This error was overlooked by Bray and Davis, presumably because the bromate concentrations were very low in their titrations.

The Rate Law of the Autocatalytic Reduction. Calculation of the Constants.—In order to test the validity of the rate law, Equation 4, runs were made over as wide a range of hydrogen-ion concentrations as was possible, and a series of experiments was performed (at 25°) in which a small amount of potassium bromide was added to the reaction mixture at the beginning of each run.

Since the concentration of hydrogen ion remains constant throughout each experiment, Equation 4 may be at once reduced to

$$dX/dt = k'(C - X)(D - 3X) + k''(C - X)(X) \qquad (5)$$

or, for added Br^-

$$dX/dt = k'(C - X)(D - 3X) + k''(C - X)(A + X) \qquad (5a)$$

where $k' = k_1(H^+)$, $k'' = k(H^+)^2$ and X, $C - X$, $D - 3X$, represent the instantaneous concentration in moles per liter of bromide ion (formed by reduction of bromate ion), bromate ion and hydrogen peroxide, respectively. A, C, D, are the original concentrations of bromide ion, bromate ion and peroxide.

Integration of Equation 5 or 5a yields

$$\log \frac{X + \alpha}{C - X} = \log \frac{\alpha}{C} + \beta t \qquad (6)$$

where

$$\alpha = \frac{Dk'}{k'' - 3k'} \text{ and } \beta = \frac{Ck'' + (D - 3C)k'}{2.303} \quad (6a)$$

or, for added bromide

$$\alpha = \frac{Ak'' + Dk'}{k'' - 3k'} \qquad \beta = \frac{(A + C)k'' + (D - 3C)k'}{2.303} \quad (6b)$$

If the equations agree with the experimental data, a straight line of slope β and intercept log α/C should result when values of log $(X + \alpha)/(C - X)$ are plotted against t. As both α and β involve k' and k'', a method of approximation similar to that described in detail by Bray and Davis[6] was used. As a first approximation α is assumed equal to 0 (or A if bromide has been added) and values of log $(X/(C - X))$ are plotted against t. As α is relatively small when X is large, a curve is obtained which rises from minus infinity when $X = 0$ and which rapidly approaches a straight line as X increases in value. The intercept of this line yields an approximate value of α, which is then used in plotting values of log $(X + \alpha)/(C - X)$ against t as a second approximation. This process is repeated until no change in α is obtained by further approximations. The results of the work at 25° are summarized in Tables I and II.

TABLE I

EXPERIMENTS AT 25°, WITHOUT ADDED BROMIDE

Run	H^+	Initial (BrO_3^-)	Initial (H_2O_2)	μ	$k_1(10^3)$	k
25	0.0502	0.00500	0.0314	0.0552	29∓5	276±15
21	.0502	.0100	.0327	.0602	31∓9	240±20
23	.0502	.00700	.0327	.0572	30∓7	252±15
8	.0493	.0109	.0251	.0593	47∓8	248±15
Mean				.0580	34	254
13	.104	.00994	.0348	.114	32∓8	216±14
14	.100	.00700	.0331	.107	54∓6	219±16
15	.100	.00700	.0334	.107	31∓4	210±14
16	.100	.00700	.0329	.107	27∓6	200±15
19	.100	.00500	.0334	.105	30∓8	208±20
18	.100	.00500	.0334	.105	25∓5	220±14
17	.100	.00300	.0334	.103	35∓9	230±30
20	.100	.00300	.0334	.103	35∓9	230±30
85	.100	.00500	.0296	.105	35∓8	219±10
86	.100	.00500	.0296	.105	36∓9	223±10
Mean				.106	34	211
134	.200	.00500	.0521	.205	21	187
135	.200	.00500	.0521	.205	23	195
Mean				.205	22	191
132	.300	.00500	.0514	.305	22	172
133	.300	.00500	.0514	.305	25	168
Mean				.305	23	170
128	.500	.00500	.0509	.505	54	144
131	.500	.00500	.0493	.505	42	146
Mean				.505	46	145

TABLE II

EXPERIMENTS AT 25° WITH ADDED BROMIDE

Run	H^+	Initial BrO_3^-	Initial H_2O_2	Initial Br^-	μ	$k_1(10^3)$	k
77	0.0500	0.00500	0.0272	0.00194	0.0569	30	258 ± 10
72	.0500	.00500	.0275	.00194	.0569	120	260 ± 10
71	.0500	.00500	.0275	.00194	.0569	45	255 ± 10
Mean					.0569		257
53	.100	.00500	.0287	.00186	.107	43	210 ± 20
54	.100	.00500	.0287	.00186	.107	143	209 ± 15
59	.100	.00500	.0273	.00186	.107	180	224 ± 15
63	.100	.00500	.0273	.00194	.107	126	225 ± 15
55	.100	.00500	.0264	.000748	.106	36	225 ± 15
57	.100	.00500	.0273	.000748	.106	96	229 ± 15
67	.100	.00500	.0300	.00780	.106	68	229 ± 15
73	.100	.00500	.0272	.00778	.106	85	219 ± 15
74	.100	.00500	.0272	.00778	.106	59	216 ± 14
Mean					.106		220
129[a]	.100	.00500	.0252	.000780	.805	35	141

[a] Run 129 was made in 0.7 N $NaClO_4$ solution.

At a hydrogen-ion concentration below 0.05 N, the reaction is too slow to be measured accurately by oxygen evolution; at values of hydrogen-ion concentration above 0.3 N, slight deviations from the rate law were noted, coincident with the accumulation of appreciable amounts of bromine in the reaction mixture. At all other values of the hydrogen-ion concentration the straight lines obtained by the approximation method were very good, although other pairs of constants properly chosen within the limits specified would satisfy fairly well the actual data in each case.

The agreement between the values of k in Tables I and II, without and with added bromide, is satisfactory: thus at $\mu = 0.06$, the values are almost identical, 254 and 257; and at $\mu = 1.06$, 211 and 220 are within the estimated limits. On the other hand, the error in k_1 is so greatly increased by the presence of bromide that the values in Table II have little if any significance.

The decrease in k with increasing ionic strength will be discussed in a later section and the limiting value at zero ionic strength will be calculated. k_1 also shows a general decrease with increasing ionic strength, but the values are not sufficiently accurate to justify a similar quantitative treatment.

The Effect of Temperature.—The results of the work at 45 and 65° are summarized in Tables III and IV, respectively.

The plotted values of the logarithms of the specific rates against $1/T$ for $\mu = 0.105$ are shown in Fig. 1. From the slopes of these lines, a heat of activation of 16,000 ± 300 cal. was obtained for the fourth order reaction, and an approximate value of 15,000 ± 1000 cal. for the third order reaction.

TABLE III

EXPERIMENTS AT 45°

Run	H^+	Initial BrO_3^-	Initial H_2O_2	μ	$k_1(10^3)$	k
90	0.100	0.005	0.0146	0.105	114∓56	1150±165
91	.100	.005	.0146	.105	112∓50	1100±120
92	.100	.005	.0265	.105	161∓48	1090± 70
93	.100	.005	.0265	.105	198∓81	1140±140
Mean				.105	146	1120
96	.0500	.005	.0564	.055	284∓81	1340±170
97	.0500	.005	.0564	.055	264∓35	1330± 80
Mean				.055	274	1335
98	.025	.005	.0548	.030	308∓35	1550±180
99	.025	.005	.0548	.030	312∓40	1570±140
Mean				.030	310	1560

TABLE IV

EXPERIMENTS AT 65°

Run	H^+	Initial BrO_3^-	Initial H_2O_2	μ	$k_1(10^3)$	k
108	0.0125	0.00500	0.0564	0.0175	1480∓380	10000±600
109	.0125	.00500	.0564	.0175	1520∓350	10200±600
Mean				.0175	1500	10100
104	.0250	.00500	.0449	.0300	1080∓400	8000±500
105	.0250	.00500	.0449	.0300	1000∓300	8280±630
Mean				.0300	1040	8140
106	.0500	.00500	.0414	.055	855∓260	6610±740
107	.0500	.00500	.0414	.055	793∓160	6850±510
Mean				.055	824	6730
111	.100	.00500	.0615	.105	714∓230	5140±650
112	.100	.00500	.0615	.105	745∓260	5070±730
Mean				.105	729	5105
115[a]	.100	.00500	.0464	.106	730	5650

[a] Run 115 had an initial concentration of 0.00078 *M* added bromide.

The Kinetic Salt Effect of the Fourth Order Reaction.—The measurements at 65° were carried to sufficiently low ionic strengths to permit a test of Equation 1 by calculations of the necessary activity coefficients from the theory of Debye and Hückel. The limiting expression for the activity coefficient γ_i of an ion of valence Z is, at 65°[7]

$$\log \gamma_i = -0.6\, Z^2 \sqrt{\mu} \qquad (7)$$

From Equation 7, the logarithm of the activity coefficient product, Equation 1, becomes

$$\log \gamma_{H^+}^2 \gamma_{Br^-} \gamma_{BrO_3^-} = -0.6(1^2 + 1^2 + 1^2 + 1^2)\sqrt{\mu} = -2.4\sqrt{\mu}$$

If k is proportional to this activity coefficient product, a straight line of slope −2.4 will result when values of log k are plotted against $\sqrt{\mu}$. From

[7] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, p. 500.

the plot, Fig. 2, it is evident that such a line is rapidly being approached as the ionic strength decreases.

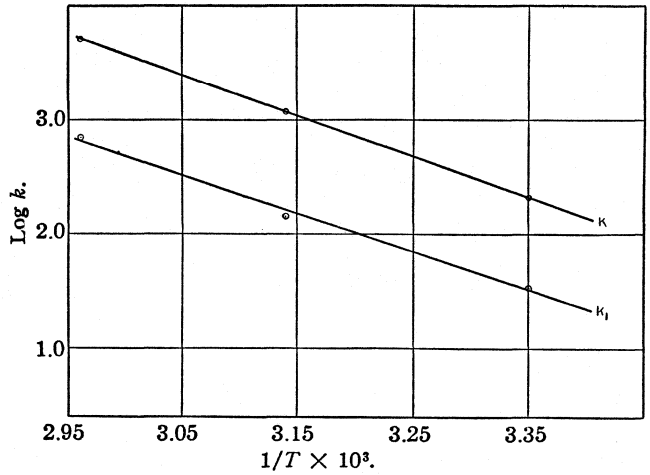


Fig. 1.—Variation of the constants with the temperature.

A further test of Equation 1 may be obtained from the data at 25° by calculating values of χ from the measured activity coefficients of hydrobromic acid. This introduction of activity coefficients should eliminate the observed discrepancy that the values of k for perchloric acid solutions are considerably higher than those obtained by earlier investigators[4,5,6] for sulfuric acid solutions.

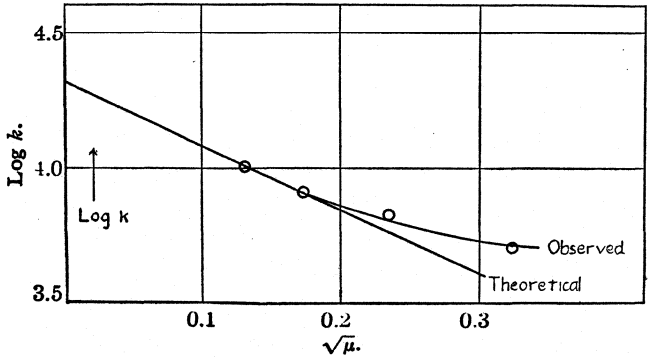


Fig. 2.—Kinetic salt effect at 65°.

In the absence of data for the activity coefficient of bromic acid, γ_{HBrO_3} was assumed to be equal to γ_{HBr}, and Equation 1 was applied in the form

$$k/\gamma^4_{HBr} = \chi \qquad (8)$$

γ_{HBr}, in the presence of perchloric acid, was assumed to have the same value as in a solution of pure hydrobromic acid at the same ionic strength.

Any error introduced by such assumptions as these should not interfere with the accuracy of the extrapolation to zero ionic strength.

Livingston[8] has measured γ_{HBr} in solutions of pure hydrobromic acid, and in certain sulfuric acid solutions, and has suggested a method for calculating it in sulfuric acid solutions to which his measurements do not apply. The work of Harned and James[9] shows that at constant ionic strength γ_{HBr} is lowered when Na^+ or K^+ is substituted for H^+ in a bromide solution. No attempt was made to allow for this effect except in the experiments listed in the last four lines of Table V in which the concentration of Na^+ was high. The activity coefficients of these investigators[8,9] were corrected to agree, at low ionic strengths, with recent values of γ_{HCl} determined by Randall and Young.[10]

The values of the specific rates as determined by Skrabal and Weberitsch,[5] Judson and Walker,[4] Bray and Davis[6] and ourselves, together with the values of γ_{HBr} and χ (Equation 8), are summarized in Table V. This table contains also the results of eight runs which were made to test the effect of the addition of the inert salt, $NaClO_4$, upon the value of χ. The details of these are given in Table Va.

TABLE V

SUMMARY OF DATA FOR THE FOURTH ORDER REACTION AT 25°

Experimenter	Run	μ	k	γ_{HBr}	$\chi = \frac{k}{\gamma_{HBr}^4}$	Acid
Judson and Walker	11	0.912	63	0.562	632	HBr, $HBrO_3$
Skrabal and Weberitsch	2	.251	80	.629	512	H_2SO_4
Skrabal and Weberitsch	6	.141	95	.670	472	H_2SO_4
Skrabal and Weberitsch	8	.306	72	.609	525	H_2SO_4
Skrabal and Weberitsch	9	.110	120	.756	367	H_2SO_4
Skrabal and Weberitsch	10	.150	103	.664	531	H_2SO_4
Skrabal and Weberitsch	11	.116	167	.700	696[a]	H_2SO_4
Skrabal and Weberitsch	12	.216	156	.721	586[a]	H_2SO_4
Skrabal and Weberitsch	13	.209	159	.748	510[a]	H_2SO_4
Skrabal and Weberitsch	15	.066	148	.738	500[a]	H_2SO_4

[8] Livingston, THIS JOURNAL, **48**, 45 (1926). A lower limit for the values of γ_{HBr} in sulfuric acid solutions is given which holds when the ionic fraction of the sulfuric acid is 0.6 or greater. In only three of the experiments summarized in Table V was this condition not fulfilled: Runs 11, 12, 13, of Skrabal and Weberitsch. In these three runs γ_{HBr} was calculated from the following equation of Livingston

$$\gamma_{u'} = \gamma_{u\ pure} \frac{m'_{\pm}}{m_{\pm}}$$

where $\gamma_{u'}$ is the desired activity coefficient; $\gamma_{u\ pure}$ is the activity coefficient in a strong electrolyte at the given ionic strength; $m'_{\pm}$ is the effective mean molality calculated assuming the first dissociation of H_2SO_4 to be complete and the second dissociation constant to have an average value of 3×10^{-2} at these ionic strengths; and $m_{\pm}$ is the mean molality calculated assuming the second dissociation to be complete.

[9] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

[10] Randall and Young, THIS JOURNAL, **50**, 989 (1928).

TABLE V (*Concluded*)

Experimenter	Run	μ	k	γ_{HBr}	$\chi = \frac{k}{\gamma_{HBr}^4}$	Acid
Bray and Davis	1A	0.156	98	0.661	515	H_2SO_4
Bray and Davis	1B	.162	98	.661	515	H_2SO_4
Bray and Davis	2A	.190	100	.653	550	H_2SO_4
Bray and Davis	2B	.190	101	.653	555	H_2SO_4
Bray and Davis	3A	.185	97	.653	535	H_2SO_4
Bray and Davis	3B	.365	76	.601	585	H_2SO_4
Bray and Davis	4A	.365	76	.601	585	H_2SO_4
Bray and Davis	4B	.545	66	.581	580	H_2SO_4
Young and Bray	21	.0602	240	.820	530	$HClO_4$
Young and Bray	23	.0572	252	.822	553	$HClO_4$
Young and Bray	8	.0593	248	.820	547	$HClO_4$
Young and Bray	13	.114	216	.789	553	$HClO_4$
	Mean of runs					
Young and Bray	14, 15, 16	.107	210	.792	533	$HClO_4$
Young and Bray	18, 19, 85, 86	.105	217	.793	549	$HClO_4$
Young and Bray	128, 131	.505	145	.772	408	$HClO_4$
Young and Bray	132, 133	.305	170	.766	492	$HClO_4$
Young and Bray	134, 135	.205	191	.771	540	$HClO_4$
Young and Bray	120, 121	.305	156	.753	485[b]	$HClO_4$
Young and Bray	122, 123	.405	165	.752	516[b]	$HClO_4$
Young and Bray	124, 125	.175	188	.771	532[b]	$HClO_4$
Young and Bray	126, 127	.805	144	.787	375[b]	$HClO_4$

[a] Experiment performed at 26° corrected to 25°.

[b] $NaClO_4$ added. For details see Table Va.

TABLE Va

EXPERIMENTAL RESULTS AT 25° IN THE PRESENCE OF $NaClO_4$

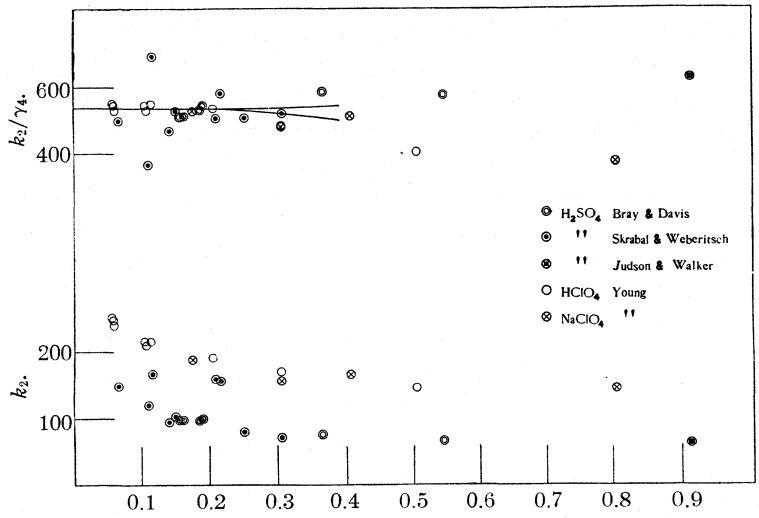
Run	H^+	BrO_3^-	H_2O_2	$NaClO_4$	μ	k
120	0.100	0.00500	0.0135	0.200	0.305	159 ± 19
121	.100	.00500	.0135	.200	.305	154 ± 15
Mean						156
122	.100	.00500	.0562	.300	.405	165 ± 30
123	.100	.00500	.0562	.300	.405	165 ± 10
Mean						165
124	.100	.00500	.0536	.070	.175	190 ± 17
125	.100	.00500	.0536	.070	.175	187 ± 14
Mean						188
126	.100	.00500	.0540	.700	.805	145 ± 11
127	.100	.00500	.0540	.700	.805	144 ± 5
Mean						144

The values of k are plotted against the ionic strength in Fig. 3; in Fig. 4 are plotted values of χ on a corresponding scale. From this plot it is evident that the introduction of the measured activity coefficients of hydrobromic acid in the manner prescribed by Brönsted does eliminate a pronounced trend in the measured rate constants at ionic strengths less than 0.2 and does, in the same region, reconcile the measurements in

sulfuric acid to those in perchloric. It may be added that the specific effect of potassium ion on the activity of hydrobromic acid is of the nature to counteract the decrease in χ at higher ionic strengths; and that in perchloric acid solutions the use of the activity coefficients of Harned and James does in fact give values of χ which are constant to $\mu = 0.5$.

Extrapolation to $\mu = 0$ of the sulfuric acid results leads to a value of χ_0 between 500 and 560. This result agrees satisfactorily with the more accurate extrapolation of the perchloric acid values, $\chi_0 = 540 \pm 15$.

Fig. 4.



Variation of k and χ with ionic strength.

Fig. 3.

Mechanism of the Autocatalytic Reduction.—As was pointed out above, in the runs in which the hydrogen-ion concentration was 0.3 *M* or greater, slight deviations from the rate law were observed which seemed to be correlated with the appearance of appreciable amounts of bromine in the solution during the latter parts of the experiments.

This accumulation of bromine increases fairly rapidly with the acid concentration, so that at 0.5 *M* hydrogen ion, sufficient bromine is present to be measured accurately. The determination of the bromine concentrations at various times was undertaken in order to compare the observed rate of oxygen evolution (Reaction 3) with that calculated for the reaction

$$Br_2 + H_2O_2 = O_2 + 2H^+ + 2Br^- \qquad (9)$$

which, according to Bray and Livingston,[11] obeys the law

[11] (a) Bray and Livingston, THIS JOURNAL, **45**, 1251 (1923); (b) Livingston and Bray, *ibid.*, **45**, 2048 (1923); (c) Livingston, *ibid.*, **48**, 53 (1926); (d) Bray and Livingston, *ibid.*, **50**, 1654 (1928).

$$\frac{dO_2}{dt} = \chi_2 \frac{(Br_2)(H_2O_2)}{(H^+)(Br^-)\gamma^2_{HBr}} \quad (10)$$

At an acid concentration of 0.5 *M*, duplicate runs were made having initial concentrations of 0.00503 *M* bromate ion and 0.0455 *M* hydrogen peroxide. In one of these, the bromine concentration was determined from time to time by extraction with carbon tetrachloride, running the extractions into slightly acidic solutions of potassium iodide and titrating the liberated iodine with a 0.01 *N* thiosulfate solution. The results of these titrations, together with the calculated concentrations of bromine corrected for tribromide,[12] are given in the third and fourth columns of Table VI. In the other of the duplicate runs the evolved oxygen was measured frequently, and the concentrations of bromide ion, bromate ion, and hydrogen peroxide were calculated in the usual manner. Since the stoichiometric relationships for the formation of bromine must be those of Equation 2, these concentrations were corrected as follows: from the bromide ion concentration, $^5/_3$ that of the total bromine was subtracted; from the bromate, $^1/_3$ that of the bromine; and from the hydrogen ion, twice that of the bromine. These corrected concentrations form the last four columns of Table VI.

TABLE VI

CONCENTRATIONS AT VARIOUS TIMES

Millimoles per Liter

Time, minutes	Br^- uncorrected	Br_2	Br_2 corrected for Br_3^-	Br^- corrected	BrO_3^-	H^+	H_2O_2
0	0	0	0	0	5.03	500	45.5
28	2.39	...	...	2.39	2.64	500	38.9
32	2.92	0.11	0.10	2.74	2.08	500	36.6
35	3.39	.19	.18	3.07	1.59	500	35.2
39	3.94	.36	.34	3.34	0.98	499	33.6
44	4.43	.40	.37	3.76	.48	499	32.1
49	4.76	.27	.25	4.31	.19	500	31.2
53	4.91	...	...	4.91	.12	500	30.8

The observed rates of evolution of oxygen, obtained by taking tangents to the oxygen time curve at the times given in Table VI, form the first row of Table VII. (The units are moles per minute from 250 cc. of solution.) The corresponding rates of oxygen evolution from Reaction 9, calculated from[13]

$$V_o = \frac{dO_2}{dt} = \frac{0.0275}{4} \frac{(Br_2)(H_2O_2)}{(H^+)(Br^-)}$$

[12] The bromine concentration was corrected for tribromide using the value of 16.2 [Lewis and Randall, THIS JOURNAL, **38**, 2348 (1916)] for the equilibrium constant of the reaction $Br_2 + Br^- \rightleftarrows Br_3^-$.

[13] The value of the specific rate, $\chi_2 = 0.0275$ at $\mu = 0.5$, is based on the steady state measurements and χ_2 values given in Ref. 11 (b) (c) (d).

are given in the second row of Table VII. It is evident that this reaction fails to account for much of the oxygen formed, and does not provide for the oxidation of enough hydrogen peroxide.

For comparison with these results, there are listed in the fifth and third rows of the table the corresponding rates of the third and fourth order reactions

$$V_a = (0.03/4)(H_2O_2)(BrO_3^-)(H^+)$$

and

$$V_b = (220/4)(BrO_3^-)(Br^-)(H^+)^2$$

and in the fourth row the sum, $V_b + V_c$. The values of V_a are negligible in comparison with those of V_b or V_c. An examination of the remaining data in the table leads at once to the following conclusion. During the reduction of one mole of BrO_3^- by Br^- in the presence of hydrogen peroxide, there is formed one mole of oxygen in addition to that due to Reaction 9.

TABLE VII

RATES OF OXYGEN EVOLUTION AT VARIOUS TIMES

Moles $\times 10^{-4}$ per Min. from 250 Cc.

	Time	32	35	39	44	49
1	dO_2/dt (observed)	1.21	1.06	0.72	0.63	0.38
2	dO_2/dt due to reduction of Br_2 by $H_2O_2 = V_c$	0.18	0.26	.40	.37	.23
3	Rate of the fourth order reaction $= V_b$	.783	.670	.449	.247	.113
4	Sum of Rows 2 and 3 $= V_b + V_c$	.96	.93	.85	.62	.34
5	Rate of the third order reaction $= V_a$	.0029	.0020	.0012	.0006	.0002

A mechanism for the autocatalytic reduction of bromate ion by hydrogen peroxide may now be postulated with a considerable degree of surety. In agreement with other investigators, we shall assume that the most probable rate-determining steps in the third and fourth order reactions are

$$BrO_3^- + H_2O_2 + H^+ \xrightarrow{V_a} O_2 + HBrO_2 + H_2O \qquad (a)$$

and

$$BrO_3^- + Br^- + 2H^+ \xrightarrow{V_b} HBrO + HBrO_2 \text{ (or } H_2Br_2O_3) \qquad (b)$$

Bray and Livingston have furnished almost conclusive evidence that the rate-determining step in the reduction of bromine by hydrogen peroxide, Reaction 9, is

$$HBrO + H_2O_2 \xrightarrow{V_c} O_2 + H^+ + Br^- + H_2O \qquad (c)$$

and that the hydrolysis equilibrium is maintained during this reaction. The empirical conclusion stated in the preceding paragraph requires that some product of the fourth order reaction (b), other than HBrO, reacts as rapidly as it is formed, with production of oxygen. Consequently, the next step may be written

$$HBrO_2 + H_2O_2 \xrightarrow{V_d} O_2 + HBrO + H_2O \qquad (d)$$

$$(\text{or } H_2Br_2O_3 + H_2O_2 \longrightarrow O_2 + 2HBrO + H_2O)$$

where $V_d = V_b$. Equation 3 is the sum (a) + (b) + (c), or (b) + (d) + 2(c).

The results presented in this section have thus led to the conclusion that, under the conditions of these experiments, hydrogen peroxide, rather than hydrobromic acid, acts as the reducing agent at every stage of Reaction 3 except the first step of the reduction of bromate ion by bromide ion.

Summary

The rate of the autocatalytic reduction of bromate ion by hydrogen peroxide may be expressed by the equation

$$[-d(BrO_3^-)/dt] = k_1 (H_2O_2)(BrO_3^-)(H^+) + k (BrO_3^-)(Br^-)(H^+)^2$$

over hydrogen-ion concentrations ranging at 25° from 0.05 *M* to 0.5 *M* and at 65° from 0.0125 *M* to 0.105 *M*.

The heat of activation of the fourth order reaction, calculated in the usual manner, is 16,000 ± 300 calories; that of the third order reaction, 15,000 ± 1000 calories.

The expression for the kinetic salt effect of the fourth order reaction

$$\frac{k}{\gamma_{HBr}^2 \gamma_{HBrO_3}^2} = x$$

is the limiting law at 65°.

The rate law for the fourth order reaction in perchloric and sulfuric acid solutions of ionic strengths less than 0.2 is

$$-d(BrO_3^-)/dt = 540 \pm 15(BrO_3^-)(Br^-)(H^+)^2\gamma_{HBr}^4 \text{ at } 25°$$

A mechanism is given for the autocatalytic reduction of bromate ion by hydrogen peroxide, in which the reduction takes place in steps and hydrogen peroxide acts as the reducing agent for the intermediates HBrO and $HBrO_2$ (or $H_2Br_2O_3$). Definite evidence is presented in support of this mechanism.

BERKELEY, CALIFORNIA

[Contribution from the William G. Kerckhoff Laboratories of the Biological Sciences, California Institute of Technology]

THERMAL DATA. I. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF SEVEN ORGANIC COMPOUNDS CONTAINING NITROGEN

By Hugh M. Huffman and Henry Borsook

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We have recently begun in this Laboratory a systematic study of some of the thermal properties of physiologically important organic compounds. These investigations are to include studies of low temperature heat capacities and heats of combustion. The data thus obtained may be utilized to calculate the entropies and free energies of the compounds by means of the third law of thermodynamics and the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$. In this paper are presented the low temperature specific heat data for the following seven compounds: *d*-alanine, *l*-asparagine, *l*-asparagine hydrate, *l*-aspartic acid, *d*-glutamic acid, creatine and creatinine. We have also included the corresponding entropies and free energies calculated from these data by means of the third law of thermodynamics.

Materials

d-Alanine.—This material was placed at our disposal for this investigation by the Hoffmann-La Roche Laboratories, Nutley, New Jersey. It was subjected to several crystallizations from water by adding a large excess of alcohol. The resulting material gave theoretical values for total nitrogen. The specific rotation of the hydrochloride was, α_D^{20} 10.1°.

l-Asparagine Hydrate.—Material obtained from Merck was subjected to a number of fractional crystallizations by rapidly cooling the hot aqueous solution to prevent racemization. The Kjeldahl analysis gave the theoretical results within the error of the method. A solution, having a volume of 25 cc. at 20°, containing 10% hydrochloric acid and 2.5236 g. of the monohydrate gave the rotation α_D^{20} 27.0°.

l-Asparagine Hydrate.—The hydrated acid described above was dried in an oven at 100–110° to a constant weight.

l-Aspartic Acid.—An Eastman product was recrystallized seven times. The sample gave the theoretical values for nitrogen and free amino groups. A solution containing in 25 cc. at 20°, 2.2903 g. of this acid, and 3 mole equivalents of hydrochloric acid gave a rotation α_D^{20} 26.42°.

d-Glutamic Acid.—This material was prepared from Ajinomoto according to the method of Schmidt and Foster.[1] The final product gave the theoretical values for nitrogen and free amino groups. A solution containing in 25 cc. at 20°, 1.269 g. of the acid and 0.2483 g. of hydrochloric acid gave the rotation α_D^{20} 31.1.

Creatine.—A Pfanstiehl product was subjected to several fractional crystallizations. The final product gave the theoretical values for nitrogen.

Creatinine.—A very pure Pfanstiehl product was further purified by the methods of Edgar and Hinegardner.[2] The resulting product gave the theoretical values for nitrogen.

[1] Schmidt and Foster, *J. Exp. Biol. Med.*, **18**, 205 (1920–1921).

[2] Edgar and Hinegardner, *J. Biol. Chem.*, **56**, 881 (1923).

Method and Apparatus

In principle the method of Nernst was employed with an aneroid calorimeter to determine the "true" specific heats. The details of the method and apparatus have been described elsewhere,[3] so that only a brief description is necessary.

In brief it consists of supplying a measured amount of heat electrically to a copper calorimeter which contains the substance under investigation. The change in temperature is measured by a calibrated copper–constantan thermocouple. All electrical measurements are made on a White double potentiometer in conjunction with a sensitive galvanometer. Time measurements are made with an accurately calibrated stop watch.

To promote rapid attainment of thermal equilibrium, the compound under investigation is compressed into dense pellets and these are spaced in the calorimeter by means of thin copper disks.

In view of the accuracy of the various measurements involved, the error in the specific heats is probably less than 1%.

The specific heat data in terms of the 15° calorie[4] and with all weights reduced to a vacuum basis appear in Table I.

TABLE I

SPECIFIC HEATS

d-Alanine: Crystalline

Temp., °K.	84.4	89.2	96.2	104.2	111.7	119.5	134.6
C_p per g.	0.121	0.127	0.135	0.146	0.154	0.163	0.180
Temp., °K.	149.2	165.4	179.9	200.1	219.9	239.8	260.0
C_p per g.	0.194	0.209	0.222	0.241	0.258	0.275	0.292
Temp., °K.	275.1	276.3	281.2	289.6	296.8		
C_p per g.	0.306	0.306	0.310	0.318	0.324		

l-Asparagine

Temp., °K.	85.1	89.3	95.4	102.5	110.8	119.8	134.7
C_p per g.	0.109	0.114	0.120	0.128	0.136	0.145	0.158
Temp., °K.	149.9	170.3	190.4	208.8	230.3	252.1	276.2
C_p per g.	0.171	0.188	0.204	0.219	0.236	0.254	0.273
Temp., °K.	282.1	290.2	296.5				
C_p per g.	0.277	0.284	0.289				

l-Asparagine Hydrate

Temp., °K.	90.4	94.1	108.3	140.1	169.4
C_p per g.	0.120	0.125	0.141	0.175	0.206
Temp., °K.	199.9	239.3	276.2	286.2	296.7
C_p per g.	0.236	0.274	0.309	0.317	0.328

[3] Parks, THIS JOURNAL, **47**, 338 (1925).

[4] The factor 0.2390 was used for converting joules to calories.

TABLE I (*Concluded*)

l-Aspartic Acid

Temp., °K.	88.2	91.7	98.2	109.1	123.8	139.6	159.9	179.9
C_p per g.	0.112	0.116	0.123	0.133	0.146	0.159	0.175	0.190
Temp., °K.	199.8	220.3	249.4	278.1	283.2	287.3	293.9	
C_p per g.	0.205	0.220	0.242	0.262	0.266	0.269	0.274	

d-Glutamic Acid

Temp., °K.	90.8	95.3	101.6	108.4	117.1	130.4	145.4	159.8
C_p per g.	0.114	0.119	0.126	0.133	0.141	0.153	0.166	0.177
Temp., °K.	179.6	200.3	220.4	250.2	275.9	280.3	286.2	294.6
C_p per g.	0.192	0.210	0.224	0.246	0.266	0.269	0.274	0.281

Creatine

Temp., °K.	86.9	91.8	97.2	112.9	126.6	140.3	159.8	179.8
C_p per g.	0.123	0.128	0.134	0.150	0.164	0.176	0.193	0.212
Temp., °K.	200.6	220.4	239.7	258.6	277.2	282.3	289.7	296.3
C_p per g.	0.230	0.248	0.265	0.280	0.295	0.300	0.306	0.312

Creatinine

Temp., °K.	86.8	90.0	95.1	104.9	115.8	130.2	149.9	170.7
C_p per g.	0.124	0.128	0.134	0.143	0.154	0.166	0.181	0.196
Temp., °K.	189.7	210.6	229.5	275.8	282.6	289.8	296.5	
C_p per g.	0.210	0.226	0.240	0.276	0.281	0.287	0.292	

Discussion

Entropies of the Compounds.—Using the data in Table I we have calculated the molal entropies at 298.1°K. for these compounds. In these calculations we have used the extrapolation method of Kelley, Parks and Huffman[5] to calculate the entropy at 90°K. For the entropy change between 90 and 298°K. the usual method of graphical integration was employed. The results of these calculations appear in Table II; column 2 is the entropy increment from 0 to 90°K., column 3 the entropy change between 90 and 298°K. from the experimental values, and column 4 the entropy at 298°K.

TABLE II

ENTROPIES OF THE COMPOUNDS

Substance	$S_{90°}$	$\Delta S_{90-298.1°}$	$S_{298.1°}$
d-Alanine	8.88	22.77	31.6
l-Asparagine	11.90	29.84	41.7
l-Asparagine hydrate	13.57	37.46	51.0
l-Aspartic acid	12.21	29.28	41.5
d-Glutamic acid	13.00	32.73	45.7
Creatine	13.31	31.99	45.3
Creatinine	13.38	26.66	40.0

In several cases we are now able to determine the effect of substituting an amino group for hydrogen and the hydroxyl group in the molecule. If

[5] Kelley, Parks and Huffman, *J. Phys. Chem.*, **33**, 1802 (1929).

we consider succinic acid, aspartic acid and asparagine, we find that the last two may be derived from the first by the successive change of a hydrogen and an hydroxyl to amino groups. The entropies of these compounds at 298° are, respectively, 42.0, 41.5 and 41.7 E. U.[6] Since the extreme difference in these values is within the probable error, we feel justified in stating that there is no change in the entropy of a compound for substitutions of this type.

In two cases we have been able to obtain the effect of lengthening the carbon chain. We find a difference of 5.5 E. U. between *d*-alanine and glycine[7] and a difference of 4.2 E. U. between glutamic acid and aspartic acid. These effects are of the same order of magnitude as found by Parks and Huffman and their collaborators in studies of various organic compounds.

The Free Energies.—We have also calculated the free energies of these seven compounds from the fundamental thermodynamic equation $\Delta F = \Delta H - T\Delta S$. The essential data are given in Table III. With the

TABLE III

THERMAL DATA AT 298.1°K.

The 15° cal. is used throughout and all weights are reduced to vacuum.

Substance	Heat of combustion at constant pressure, cal.	ΔH_{298}, cal.	ΔS_{298}, E. U.	ΔF_{298}, cal.
d-Alanine	387,200	−134,600	−153.5	− 88,800
l-Asparagine	463,100	−187,100	−207.7	−125,200
l-Asparagine hydrate	459,400	−259,100	−254.2	−183,300
l-Aspartic acid	384,700	−231,300	−193.9	−173,500
d-Glutamic acid	542,200	−236,400	−222.3	−170,200
Creatine	555,200	−129,200	−218.2	− 64,100
Creatinine	563,200	− 52,800	−167.6	− 2,900

exception of creatine we have used the heats of combustion as given in the "International Critical Tables"[8] corrected to 25°. For creatine we have used the value of Emery and Benedict,[9] since the value for creatinine appearing in the " I. C. T." is also that of these workers. Hence the results of the free energy calculations should be on a more comparable basis. These values were then employed in conjunction with 68,310 cal.[10] and 94,240 cal.,[11] respectively, for the heats of combustion of hydrogen and graphitic carbon. The values of ΔS, the entropy of formation, were obtained by subtracting from the S_{298} values the corresponding values of the elements contained therein. We have used for the entropies of the elements the

[6] Parks and Huffman, THIS JOURNAL, **52**, 4381 (1930).

[7] Parks and Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, 1932.

[8] "International Critical Tables," Vol. V, p. 167.

[9] Emery and Benedict, *Am. J. Physiol.*, **28**, 301 (1911).

[10] Rossini, *Bur. Standards J. Research*, **6**, 34 (1931).

[11] Roth and Naeser, *Z. Electrochem.*, **31**, 461 (1925).

values 1.3,[12] 15.6,[13] 22.9[14] and 24.5[15] E. U. per gram atom, respectively, for carbon, hydrogen, nitrogen and oxygen.

In view of the accuracy of the measurements involved, we feel that the uncertainty in the $T\Delta S$ term cannot in any case exceed ± 300 calories. The accuracy with which the heats of combustion of carbon and hydrogen are now known should preclude any great uncertainty due to their use even in the largest molecules considered. Consequently we feel that the accuracy of the free energy values is limited largely by the accuracy of the combustion data. A study of these values where more than one worker has burned the compound will show differences from 2000 to 4000 calories per mole.

Summary

1. The heat capacities of seven nitrogen-containing organic compounds have been measured over the temperature range 90 to 298°K.

2. The entropies of these seven compounds have been calculated from the heat capacity data.

3. The free energies of these compounds have been calculated and their accuracy was found to have been limited largely by the accuracy of the combustion data.

[12] Lewis and Gibson, THIS JOURNAL, **39**, 2581 (1917).

[13] Giauque, *ibid.*, **52**, 4816 (1930).

[14] Giauque, private communication.

[15] Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

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

DESULFURIZATION OF THIOUREAS BY BROMATE AND IODATE SOLUTIONS

BY HUBERT H. CAPPS AND WILLIAM M. DEHN

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In preparing thioureas for the purpose of studying desulfurization effects on them by bromate and iodate solutions, it was observed that certain bases, though closely related, either do or do not react with phenyl mustard oil or with thiocyanic acid to yield the corresponding thioureas. For example, while *m*-nitroaniline[1] easily yields phenyl-*m*-nitrophenylthiourea, the corresponding thioureas could not be formed with ortho- or with para-nitroaniline, either by direct heating or in solvents. By direct heating the *p*-nitroaniline, however, gave thiocarbanilide and di-*p*-nitrophenylthiourea[2]

[1] Brückner, *Ber.*, **7**, 1235 (1874); Losanitsch, *ibid.*, **14**, 2365 (1881); Kjellin, *ibid.*, **36**, 197 (1903).

[2] For similar product formed by heating 3-nitrothiocarbanilide, see Elbs and Schlemmer, *J. prakt. Chem.*, [2] **27**, 480 (1883).

but no mono-*p*-nitrothiocarbanilide. Also 3-nitro-*o*-toluidine, which differs but little from *m*-nitroaniline, gave no thiourea.

Furthermore, while phenyl mustard oil and phenyl isocyanate react exothermically with piperidine to give phenylpiperidylthiourea[3] and phenylpiperidylurea, piperidine thiocyanate could not be isomerized to piperidylthiourea, even when heated at 220°. This is remarkable in view of the fact that piperidine cyanate easily yields piperidylurea.[4] The play of affinity in these and other cases is very selective[5] and theories of steric hindrance, relative alkalinities, etc., are inapplicable to account for these negative results.

Frequently with unsymmetrical thioureas and less often with unsymmetrical ureas, it was observed both in the literature and in experiments that the melting points are variable, depending upon the solvent used, upon the thermal conditions involved in their preparation, and upon the method of making the melting point determinations. This variability was especially observed by Kjellin, who showed that two molecules of the unsymmetrical thiourea frequently undergo intermolecular double decomposition[6] so as to yield two different symmetrical thioureas

$$2RNHCSNHR' \longrightarrow RNHCSNHR + R'NHCSNHR'$$

TABLE I

MELTING POINTS OF THIOUREAS

X of Ph-NH-CS-NHX	Lit. m. p.	1st m. p.	2d m. p.	3d m. p.	4th m. p.	5th m. p.	Oil in m. p. tube
p-Bromophenyl	158	167	154	150	148	148	+
p-Chlorophenyl	152	158	155	153	153		+
2,5-Dichlorophenyl		168	154	140	130	125	+
2,4-Dichlorophenyl	157	168	130	120			+
p-Tolyl	142	172	140	160	160		−
p-Ethoxy	129	144	122	122	124	122	+
2,4-Dimethylphenyl	125.5	133	Did not resolidify				
	126	134					
4-Hydroxy-2-methylphenyl		177	Did not resolidify				
β-Naphthyl	157	167	169	167	165	164	+
2-Hydroxy-4-methylphenyl	110	117	112	102	Did not resolidify		−

[3] Gebhardt, *Ber.*, **17**, 3040 (1884).

[4] Cahours, *Ann. chim.*, [3] **38**, 84 (1853).

[5] Aminization of ortho and para but not meta of chloro, bromo, hydroxy or alkyloxy nitrobenzenes and the easy hydrolysis of ortho and para but not the meta nitroanilines are examples of selective affinities that are converse to the above thioureas. Because the hydrochloride of *m*-nitroaniline is less easily hydrolyzed than the hydrochloride of the ortho and para nitroanilines, and the hydrochloride of piperidine is the least hydrolyzed, and it is apparent that relative alkalinities are not involved.

[6] Elbs and Schlemmer, *Ber.*, **36**, 194 (1903), give another type of decomposition: $2RNHCSNHR' \longrightarrow RNCS + R'NCS + R'NH_2 + RNH_2$, whose products can unite to form the two symmetrical thioureas. The fact that thioureas isomerize more readily than ureas and these decompose in accordance with this reaction, accounts for the greater thermal sensitiveness of the thiourea over that of the ureas.

TABLE II

MELTING POINT OF UREAS

X of Ph-NH-CO-NHX	Lit. m. p.	1st m. p.	2d m. p.	3d m. p.	4th m. p.	5th m. p.	Oil in m. p. tube
2,5-Dichlorophenyl		200.5		200	201		
2,4-Dichlorophenyl		206.5	206				
p-Tolyl	213–231	212	208	204	205	203	—
o-Tolyl	196	196	196	196	196	196	—
Methyl	150	151	150	150		151	—
Allyl	113	111	108	117	119	107	
	115.5	117	117	107	116	107	—

In the tables are given data of successive melting points on the same samples in the same capillary tube.

Though it has long been known[7] that alcohol unites with mustard oils to yield thiocarbanilic esters, it has been most commonly used as the solvent in the preparation of thioureas from phenyl mustard oil and bases. This alcohol often accounts for the variability of products. We have employed cold toluene solutions as the most successful condition for the preparation of thioureas.[8]

It was found that certain thioureas are smoothly desulfurized by iodate solution. For example, all thioureas of the types $RNHCSNH_2$ and $RNHCSNHR'$ except phenylbenzylthiourea were thus desulfurized, but thioureas of types $RR'NCSNH_2$ and $R_2NCSNHR$ and R_2NCSNR_2 were entirely negative. It was found that bromate was as effective as iodates, in alkaline solutions, for the purpose of such desulfurization and that with either desulfurizations are smoother than with lead, mercury or silver compounds, since heating alone yields either the cyanamide or the urea which can be filtered off and crystallized from organic solvent so as to obtain pure and substantially quantitative yields. The progress of desulfurization can easily be followed by the lead test. Whereas thiocarbanilide is desulfurized in a few minutes, some of the thioureas required many hours of heating before the product gave no test for sulfur.

The thioureas, the bromate or the iodate, and sodium hydroxide in equal weights were heated[9] in sufficient water for such time as was necessary to give negative tests with lead solution. The precipitate was filtered off, washed with water and finally recrystallized from toluene or other solvent. With thioureas of the type $RNHCSNH_2$, forming, of course, the cyanamide,

[7] Hofmann, *Ber.*, **2**, 74 (1869); **3**, 772 (1870); Bamberger, *ibid.*, **15**, 2164 (1882); Fromm, *ibid.*, **42**, 1957 (1909).

[8] Since thiocyanic acid does not blacken when heated with alkaline lead solutions, and thioureas do, it is useful in checking the formation of such thioureas.

[9] In preparing the ureas from the thioureas, a decomposition into base and thiocyanate took place to some extent, the former being detected by odor and the latter by ferric solutions. Neither phenyl mustard oil nor the original thiourea give the red color with ferric solution; *o*-tolylcyanamide gives a red color upon heating; this disappears upon cooling.

TABLE III

NEW THIOUREAS

R′ of	M. p., °C.	Crystal form	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
Type $C_6H_5NHCSNHR'$						
2,5-Dichlorophenyl	168	Needles	9.43	9.32		
o-Phenetidyl	145	Prisms	10.29	10.46		
4-Hydroxy-2-methylphenyl	177	Prisms			12.40	12.78
2,4-Dichlorophenyl	168	Prisms	10.00	10.62		
Type $H_2NCSNHR'$						
p-Methoxyphenyl	210	Prisms			17.58	17.62
2,5-Dichlorophenyl	185	Prisms	32.10	31.94	14.49	14.52
Type R′NHCSNHR						
2,4-Xylyl-*o*-tolyl	162	Needles			11.85	11.88

TABLE IV

NEW UREAS FROM THIOUREAS

Thiourea	Desulfurizing reagent	M. p., °C.	Crystal form	Calcd.	Found
Phenyl-2,4-dichlorophenyl	$KBrO_3$	208	Prisms	Cl, 25.24	Cl, 24.93
Phenyl-2-4-dimethylphenyl	KIO_3	226	Tablets	N, 12.06	N, 11.67
o-Tolyl-*p*-chlorophenyl	$NaBrO_3$	212	Prisms	Cl, 13.61	Cl, 13.82

TABLE V

KNOWN UREAS FROM KNOWN THIOUREAS

X of PhNH-CS-NHX	Lit. m. p.	M. p., °C.	Crystal form	Desulfurizing reagent
p-Bromophenyl		238	Plates	KIO_3
p-Chlorophenyl		238		KIO_3
p-Ethoxyphenyl	161–162	162–185		$KBrO_3$
2,4-Dimethylphenyl		226	Tablets	
p-Tolyl		212		$KBrO_3$
β-Naphthyl		220–221	Prisms	KIO_3
o-Tolyl		195		KIO_3
		196	Needles	$KBrO_3$
Phenyl-HOC_2H_4-		237	Needles	$KBrO_3$
		122–123	Plates	KIO_3
o-Ethyloxyphenyl		175		KIO_3
Allyl		117		$KBrO_3$
Methyl		151		$KBrO_3$
$(m\text{-}NO_2C_6H_4NH)_2CS$	233	238		$KBrO_3$

TABLE VI

KNOWN CYANAMIDES FROM KNOWN THIOUREAS

X of $XNHCSNH_2$	Desulfurizing reagent	M. p., °C., lit.	M. p., °C., found	Crystal form
2,4-Dimethylphenyl	$NaBrO_3$	109–110	117	
o-Tolyl	$NaBrO_3$	77	76.5	
β-Naphthyl	$NaBrO_3$	102	104–106	Plates
α-Naphthyl	$NaBrO_3$	135	126	Plates
p-Bromophenyl	$NaBrO_3$	112	112	Needles

after filtering, the alkali solutions were acidified with acetic acid, when the cyanamide separated either as an oil or as a solid.

Summary

Bromate in alkaline solution is an efficient reagent for desulfurization of thioureas. Owing to decomposition by heat thioureas often give varied melting points; they are best recrystallized from toluene.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

QUINAZOLINES. IV. ALCOHOLYSIS IN THE QUINAZOLINE SERIES AND THE PREPARATION OF SOME MIXED DIETHERS OF QUINAZOLINE

BY N. A. LANGE AND F. E. SHEIBLEY

RECEIVED MAY 9, 1932 PUBLISHED NOVEMBER 5, 1932

In the course of some experiments with 2,4-dichloroquinazoline it was observed that one of the two chlorine atoms present in this compound undergoes substitution more readily than the other, and that under proper conditions monochloroquinazolines only are formed. By converting these monochloro derivatives into known compounds, the location of the entering groups was ascertained and the more reactive chlorine atom assigned to the 4-position.[1]

When warm alcoholic solutions of 2,4-dichloroquinazoline are treated with potassium cyanide or other salts of weak acids, 2-chloro-4-ethoxyquinazoline is formed. In order to explain this it was assumed that in such solutions of 2,4-dichloroquinazoline there exists an equilibrium between the chlorine at the 4-position and the solvent, thus

$$C_8H_4N_2Cl_2 + C_2H_5OH \rightleftharpoons C_8H_4N_2ClOC_2H_5 + HCl$$

and that with conditions providing for the speedy removal of the hydrogen chloride formed, as does the presence of salts of weak acids, the reaction to the right is favored.[2] This mechanism is not limited to the alcohols, however, for on merely shaking 2,4-dichloroquinazoline with aqueous sodium hydroxide, 2-chloro-4-ketodihydroquinazoline results.[3]

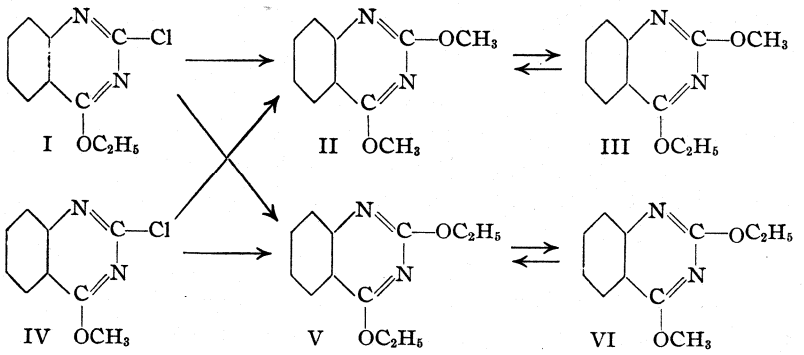
The formation of 2,4-diethoxyquinazoline (V) from 2-chloro-4-ethoxyquinazoline (I) and alcoholic sodium ethylate was described in an earlier paper.[4] This and the corresponding reaction between 2-chloro-4-methoxyquinazoline (IV) and methyl alcoholic sodium methylate to give 2,4-dimethoxyquinazoline (II) indicated that mixed diethers of the types III and VI might be prepared by treating 2-chloro-4-ethoxy- and 2-chloro-4-

[1] Lange, Roush and Asbeck, THIS JOURNAL, **52**, 3696 (1930).

[2] Lange and Sheibley, *ibid.*, **53**, 3867 (1931).

[3] British Patent 287,179.

[4] THIS JOURNAL, **52**, 3700 (1930).

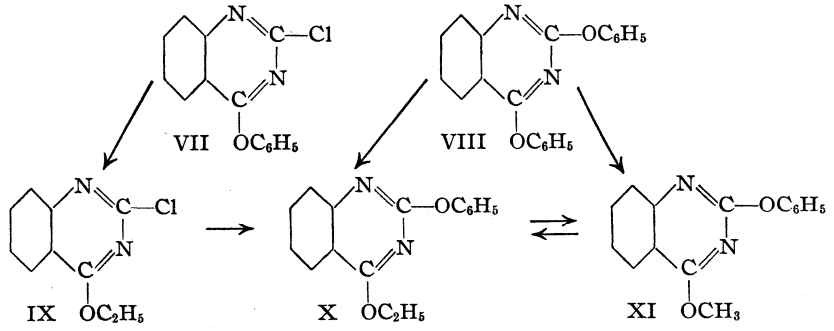


methoxyquinazolines (I and IV) with sodium methylate and sodium ethylate, respectively. Preliminary experiments in this direction, however, soon indicated that the characteristic reactivity of the 4-position in quinazoline was not by any means confined to halogen substituents only. 2-Chloro-4-methoxyquinazoline (IV) was allowed to react with sodium ethylate in alcohol, but the product was 2,4-diethoxyquinazoline (V) instead of the expected 2-ethoxy-4-methoxy derivative (VI). Similarly, sodium methylate in methyl alcohol converted 2-chloro-4-ethoxyquinazoline (I) into 2,4-dimethoxyquinazoline (II). These unexpected results suggested that perhaps in alcoholic solutions of 4-alkoxyquinazolines there exists an equilibrium between the 4-alkoxy group and the solvent, similar in form to the expression already proposed for 2,4-dichloroquinazoline, and such that under alkaline conditions the alcohol present in decided excess almost wholly determines the nature of the product.

From the views just presented it was reasonable to infer that 2,4-diethoxyquinazoline (V), say, on treatment with sodium methylate, would give the desired 2-ethoxy-4-methoxyquinazoline (VI). This was found to be the case, and a corresponding treatment of 2,4-dimethoxyquinazoline (II) with sodium ethylate resulted in the formation of the isomeric 2-methoxy-4-ethoxyquinazoline (III). These mixed quinazoline dialkyl ethers are colorless crystalline solids with properties intermediate between those of diethoxy and dimethoxyquinazolines, and possess the characteristic pleasant fruit-like odor which is especially pronounced in the case of the dimethoxy derivative. The alcoholysis leading to their formation is reversible, for on treating them with sodium dissolved in the alcohols corresponding with their 2-substituents, the initial dialkoxy compounds were again obtained. Thus 2-ethoxy-4-methoxyquinazoline (VI) and sodium ethylate in alcohol gave 2,4-diethoxyquinazoline (V), and 2-methoxy-4-ethoxyquinazoline (III) in methyl alcohol in the presence of sodium methylate was transformed into 2,4-dimethoxyquinazoline (II).[5]

[5] Compare Johnson and Guest, THIS JOURNAL, **32**, 1280 (1910); also Reid, *Am. Chem. J.*, **45**, 487 (1911).

A corresponding behavior was observed with 4-phenoxyquinazolines. The product of the action of alcoholic sodium ethylate on 2-chloro-4-phenoxyquinazoline (VII) was 2-chloro-4-ethoxyquinazoline (IX) and not the mixed diether, 2-ethoxy-4-phenoxyquinazoline. A similar treatment of 2,4-diphenoxyquinazoline (VIII)[6] produced the now expected mixed diether, 2-phenoxy-4-ethoxyquinazoline (X), which was also obtained by adding 2-chloro-4-ethoxyquinazoline (IX) to sodium dissolved in molten phenol. The failure of phenol, under these conditions, to replace the 4-ethoxy group with a phenoxy group is in accord with the thesis put forward previously[7] to the effect that sodium phenate, in alcoholic solutions of 2,4-dichloroquinazoline, does not act as an acid remover as do sodium alcoholates, but reacts directly with the 4-chlorine atom, splitting out sodium chloride and forming 2-chloro-4-phenoxyquinazoline. By employing methyl alcohol and acting on 2,4-diphenoxyquinazoline (VIII) with sodium methylate, the analogous 2-phenoxy-4-methoxyquinazoline (XI) was prepared. This substance, treated with alcoholic sodium ethylate, reverted to the known (from IX) 2-phenoxy-4-ethoxyquinazoline (X), which action is also reversible, the ethoxy derivative (X) giving the methoxy derivative (XI) again, through the action of sodium methylate.



When the treatment with sodium alcoholates leading to these changes is prolonged, hydrolysis ensues and alkali-soluble derivatives of 4-keto-dihydroquinazoline result. These products are being studied and will be described in a subsequent communication. In a search for water-soluble substances, a di-β-hydroxy derivative of 2,4-diethoxyquinazoline was prepared and is included as a matter of record.

All melting points given in this paper are corrected.

Experimental Part

The alcoholysis of the chloro-alkoxyquinazolines (I, IV) was effected by warming them almost to the boiling point in an alcoholic solution of sodium alcoholate, then al-

[6] U. S. Patent 1,758,792.

[7] Lange and Sheibley, THIS JOURNAL, 53, 3868 (1931).

lowing the solution to stand at room temperature overnight, filtering from the precipitated sodium chloride and pouring the filtrate into water. Warming on the steam-bath for an hour an alcoholic solution of sodium alcoholate and dimethoxy- or diethoxyquinazoline and then precipitating the product by pouring into water gave the mixed dialkoxy derivatives (III, VI) formed by alcoholysis of the group in position 4. Such mixed diethers are hydrolyzed to benzoylene urea by boiling their alcoholic solutions with a few drops of concentrated hydrochloric acid. 2-Chloro-4-phenoxyquinazoline was converted into 2-chloro-4-ethoxyquinazoline by allowing a mixture of the former and sodium alcoholate in alcohol to stand overnight at room temperature and then warming slightly, the ethoxy derivative (IX) crystallizing out directly on cooling. When, however, this reaction mixture was heated immediately instead of first being allowed to stand overnight, impure diethoxyquinazoline (V) and not 2-chloro-4-ethoxyquinazoline resulted. The 2-phenoxy-4-alkoxyquinazolines (X, XI) were prepared by warming on the steam-bath a mixture of 2,4-diphenoxyquinazoline and sodium alcoholate in alcohol for one to two hours, or until all of the diphenoxyquinazoline had dissolved and no solid separated on cooling, after which the solution was poured into water and allowed to coagulate. The compounds obtained by alcoholysis, their properties and the yields of the crude precipitated products obtained are given in Table I.

Preparation of 2-Phenoxy-4-ethoxyquinazoline (X) from 2-Chloro-4-ethoxyquinazoline (IX).—Ten grams of phenol in which 0.4 g. of sodium had been dissolved was treated with 1.8 g. of 2-chloro-4-ethoxyquinazoline, and the mixture warmed on a steam-bath for two hours. After standing overnight it was poured into about 100 cc. of water, sodium hydroxide solution was added to dissolve the excess phenol, and the heavy oil which had separated soon became solid. This was filtered, dried and weighed 2.2 g. Crystallization from alcohol gave small yellow-tinged tabular crystals, m. p. 107–108°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.15; H, 5.30. Found: C, 72.58; H, 5.43.

Preparation of 2,4-Diphenoxyquinazoline (VIII).—About 30 g. of warm molten phenol was treated with 0.8 g. of sodium. After all of the sodium had reacted, the mixture was heated to 130° in an oil-bath and 3 g. of 2,4-dichloroquinazoline added slowly with stirring. It was then heated at 170° for one hour and allowed to stand overnight, when it solidified. The solid mass was stirred with 200 cc. of water, and strong sodium hydroxide solution added until the excess phenol had dissolved and the residual oil solidified. The product was filtered and washed, first with dilute acetic acid and then with water, and weighed 4.1 g. after drying. Crystallized from acetone followed by a recrystallization from glacial acetic acid, it formed small rhomb-shaped crystals, m. p. 160–161°, which are sparingly soluble in alcohol, and very sparingly soluble in ether. On boiling with dilute hydrochloric acid (1:1) it is decomposed into phenol and benzoylene urea. Boiling with alcoholic aniline does not affect it.

Anal. Calcd. for $C_{20}H_{14}O_2N_2$: C, 76.40; H, 4.49. Found: C, 76.09; H, 4.63.

Preparation of $\overline{N{=}C(OCH_2CH_2OH)C_6H_4N{=}C}OCH_2CH_2OH$, 2,4-Di-β-hydroxyethoxyquinazoline.—This compound is fairly soluble in water and glycol, rendering its isolation difficult. Two grams of 2,4-dichloroquinazoline was added to 0.5 g. of sodium dissolved in 25 cc. of freshly distilled glycol, and the mixture was heated on a steam-bath for two hours. After diluting with 150 cc. of water the solution was made acid with acetic acid, and filtered from any oily droplets which had separated. About 25 g. of salt was stirred into the filtrate, ammonia was added in slight excess over the acidity, and the resulting brine heated on the steam-bath for one hour. On aspirating air over the surface of this liquid for some days, white crystalline crusts separated; these were removed and the aspirating of air over the surface of the mother liquors was continued. The total solids thus obtained were dried and combined, and extracted with about 100

TABLE I

TRANSFORMATIONS OF 2,4-QUINAZOLINE ETHERS BY ALCOHOLYSIS

Starting material Quinazoline	G.	Sodium, g.	Abs. alc., cc.	Water, cc.	Product formed Quinazoline	G.	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Chloro-4-ethoxy-(I)	3	0.4	30 Me	150	2,4-Dimethoxy-(II)[a]	2.2	75	$C_{10}H_{10}O_2N_2$	63.12	63.26	5.30	5.15
2-Chloro-4-methoxy-(IV)	3	.4	30 Et	150	2,4-Diethoxy-(V)[a]	2.7	55	$C_{12}H_{14}O_2N_2$	66.02	66.51 66.45	6.47	6.45 5.99
2,4-Dimethoxy-(II)	1	.15	25 Et	80	2-Methoxy-4-ethoxy-(III)[b]	0.95	57– 58	$C_{11}H_{12}O_2N_2$	64.67	65.02	5.93	6.05
2,4-Diethoxy-(V)	1	.15	25 Me	80	2-Ethoxy-4-methoxy-(VI)[c]	0.9	61– 62	$C_{11}H_{12}O_2N_2$	64.67	64.61	5.93	5.86
2-Chloro-4-phenoxy-(VII)	1.9	.2	10 Et	0	2-Chloro-4-ethoxy-(IX)[d]	1.5	90– 92	$C_{10}H_9ON_2Cl$*	57.55	58.07	4.35	4.63
								* Calcd.: Cl, 17.0. Found: C, 17.2				
2,4-Diphenoxy-(VIII)	1	.1	30 Et	100	2-Phenoxy-4-ethoxy-(X)[e]	0.6	107–108	$C_{16}H_{14}O_2N_2$	72.15	...	5.30	..
2,4-Diphenoxy-(VIII)	1	.1	30 Me	100	2-Phenoxy-4-methoxy-(XI)[f]	0.85	139.5	$C_{15}H_{12}O_2N_2$				
								Calcd.: N, 11.11. Found: N, 11.30				

[a] Further identified by mixed melting points with known specimens of dimethoxy- and diethoxyquinazolines.

[b] Fine white matted needles from dilute alcohol. The substance depresses the melting point of diethoxyquinazoline and is converted into dimethoxyquinazoline on warming with methyl alcoholic sodium methylate.

[c] Flat glistening needles from dilute alcohol. This substance also depresses the melting point of diethoxyquinazoline into which it is again converted on warming with alcoholic sodium ethylate.

[d] This compound is difficult to purify when prepared by this method. Its identity was established by mixed melting points with known specimens of chloroethoxyquinazoline, and by its conversion into 2-phenoxy-4-ethoxyquinazoline.

[e] Colorless, minute glistening prisms from alcohol. Mixed with the product from chloroethoxyquinazoline and sodium phenate the melting point was unchanged. Treatment with sodium methylate converts the substance into 2-phenoxy-4-methoxyquinazoline. The same product (X) was also obtained when alcoholic potassium hydroxide was substituted for sodium ethylate.

[f] Microscopic hair-like needles from acetone or alcohol, sparingly soluble in the latter. On warming for fifteen minutes with a slight excess of sodium ethylate in absolute alcohol, 2-phenoxy-4-ethoxyquinazoline is formed.

cc. of boiling alcohol. The mixture resulting was allowed to stand and the insoluble residue of salt removed by filtration. The inspissated alcoholic extract, on standing, slowly deposited glistening granular crystals, m. p. 153–154°. The substance is fairly soluble in water on warming, to a solution having a bitter taste, and from which it may be recrystallized.

Anal. Calcd. for $C_{12}H_{14}O_4N_2$: C, 57.57; H, 5.64. Found: C, 57.81; H, 6.03; C, 58.18; H, 5.99; C, 58.02; H, 5.28.

Preparation of $\overline{N{=}C(OCH_2CH_2OCOCH_3)C_6H_4N{=}C}OCH_2CH_2OCOCH_3$, the Diacetyl Derivative of 2,4-Di-β-hydroxyethoxyquinazoline.—This acetylation was effected by boiling 1.9 g. of the dihydroxy derivative with an excess of acetic anhydride in the presence of anhydrous sodium acetate for two hours, then pouring into water and neutralizing the acidity with sodium carbonate when, after standing in cold water for an hour, the separated oil solidified. It was filtered, washed with water and crystallized from alcohol or dilute alcohol, yielding 1.4 g. of crystals, m. p. 65–66°.

Anal. Calcd. for $C_{16}H_{18}O_6N_2$: C, 57.46; H, 5.43. Found: C, 57.31; H, 5.34.

Summary

Mixed 2,4-diethers of quinazoline have been prepared by acting on 2,4-dialkoxyquinazolines with sodium alcoholates in alcohols other than those used in obtaining the original dialkoxy compounds. The replacement of an alkoxy (OR) by a different alkoxy (OR′) takes place only at the 4-position, the 2-substituent being unaffected. The transposition is reversible, the mixed diethers being readily converted into the respective dialkoxy derivatives again by employing the proper alcohols. The reaction has been extended to 4-phenoxyquinazolines, these being easily transformed into 4-alkoxy compounds which are further transformable, except that in this case the replacement of phenoxy by alkoxy is irreversible. The following new quinazolines have been prepared: 2-methoxy-4-ethoxy-, 2-ethoxy-4-methoxy-, 2-phenoxy-4-methoxy-, 2-phenoxy-4-ethoxy- and 2,4-di-β-hydroxyethoxyquinazoline and its diacetyl derivative.

CLEVELAND, OHIO

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

THE SYNTHESIS OF VINYLETHYLMALONIC ESTER AND INCIDENTAL COMPOUNDS

BY ARTHUR C. COPE AND S. M. MCELVAIN

RECEIVED JUNE 6, 1932 PUBLISHED NOVEMBER 5, 1932

Attempts to introduce the vinyl group indirectly into monosubstituted malonic esters and barbituric acids have been reported by Voorhees and Skinner.[1] Further attempts to introduce the vinyl group directly into malonic ester through the reaction of vinyl bromide with the sodium derivative of phenylmalonic ester also have been reported.[2] All of these efforts were unsuccessful. The present paper reports the results of further work in this direction which has resulted in the successful synthesis of vinylethylmalonic ester. However, the properties of this ester, described below and in the following paper, seem to preclude any hope of obtaining the corresponding barbituric acid from it by any of the procedures ordinarily used for the conversion.

Two methods of synthesis of vinylethylmalonic ester seemed possible. The first of these involved the preparation of the quaternary salt (II) and the decomposition of the corresponding base by distillation into the vinylethylmalonic ester. The preparation of the salt (II) was to be accomplished through the reaction of trimethylamine with ethyl (β-bromoethyl)-malonic ester (I). When this reaction was tried it was found that conditions which produced a satisfactory rate of reaction gave tetramethylammonium bromide rather than the desired salt (II). The malonic ester was isolated in the form of the hydrochloride of ethyl (β-dimethylaminoethyl)-malonic ester (III). The course which the reaction had taken is illustrated by the equations

$$(CH_3)_3N + BrCH_2CH_2\text{—}\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{C}}(COOC_2H_5)_2 \longrightarrow (CH_3)_3\overset{\displaystyle Br}{\overset{\displaystyle |}{N}}CH_2CH_2\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{C}}(COOC_2H_5)_2 \longrightarrow$$

(I) (II)

$$CH_3Br + (CH_3)_2NCH_2CH_2\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{C}}(COOC_2H_5)_2(CH_3)_3N + CH_3Br \longrightarrow (CH_3)_4NBr$$

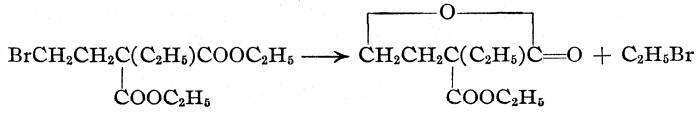
(III)

If the reactants were allowed to stand in ether solution for several weeks, a small quantity of a salt, which bromine analysis showed to be mainly (90%) (II), precipitated. However, the yield was so low and the time of formation so extended that the method was abandoned as impractical. In addition to the above difficulty it was found that the bromo ester

[1] Voorhees and Skinner, THIS JOURNAL, 47, 1124 (1925).

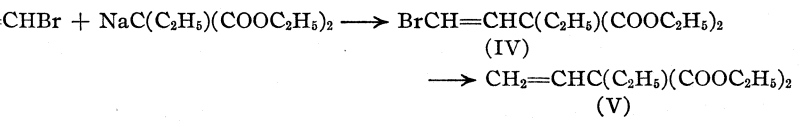
[2] Vanderveer Voorhees, Ph.D. Dissertation, University of Wisconsin, 1924.

(I) has a decided tendency to decompose on distillation into ethyl bromide and α-ethyl-α-carbethoxybutyrolactone.[3]



This decomposition takes place to a slight extent during distillation under pressures of 1–3 mm. Distillation at atmospheric pressure converts the bromo ester smoothly and completely into the lactone and ethyl bromide.

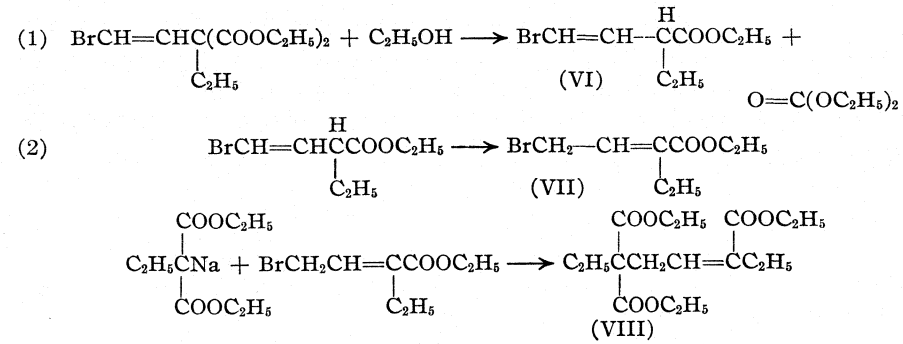
The second and successful method of synthesis of vinylethylmalonic ester involved the reaction of symmetrical dibromomethylene with sodioethylmalonic ester, followed by the reduction of the resulting ethyl (β-bromovinyl)-malonic ester (IV) with zinc dust and alcohol at 170° to vinylethylmalonic ester (V). These reactions may be illustrated thus



The yield of the bromovinyl ester (IV) amounted to 25% of the theoretical, while the yield of vinylethylmalonic ester from the reduction of the bromo ester was 54%. In marked contrast to ethyl (β-bromoethyl)-malonic ester (I), ethyl (β-bromovinyl)-malonic ester (IV) shows no tendency to lose ethyl bromide and change into a lactone; in fact it distils (264–266°) at atmospheric pressure without the slightest decomposition. The vinylethylmalonic ester was characterized by analyses, the amount of hydrogen absorbed in a quantitative catalytic hydrogenation and the conversion of this reduction product, diethylmalonic ester, into di-*p*-nitrobenzyl diethylmalonate, which was compared with an authentic specimen.

The reaction for the preparation of the bromovinyl ester (IV) is somewhat more complicated than is shown above. Under the most favorable conditions of reaction there was obtained along with (IV) an approximately equal quantity of a high boiling, bromine-free *tricarboxylic* ester. This compound was shown to be 3,6,6-tricarbethoxyoctene-3 (VIII), which had been formed from the bromovinyl ester (IV) by the reactions

[3] This compound corresponds in its physical properties to the compound reported as ethyl (β-hydroxyethyl)-malonic ester by Shonle, Keltch and Swanson, THIS JOURNAL, **52**, 2440 (1930). They obtained their hydroxy ester by the ethylation of β-hydroxyethylmalonic ester. It is probable that this latter compound was also the lactone rather than the hydroxy ester since decomposition during the distillation of the reaction product of ethylene chlorohydrin and sodiomalonic ester was noted. This supposition is strengthened by earlier observations of the instability of β-hydroxyethylmalonic ester by Traube and Lehmann, *Ber.*, **32**, 720 (1899) and Cretcher, Koch and Pittinger, THIS JOURNAL, **47**, 3083 (1925).



The characterization of (VIII) as described below was completed long before it was possible to find an explanation for its formation. The origin of the necessary alcohol for reaction (1) was at first a mystery since the reaction between dibromoethylene and sodioethylmalonic ester had been carried out in absolute ether and this sodio derivative had been prepared by the action of powdered metallic sodium on the ethylmalonic ester in ether. However, an investigation of this latter reaction showed that only 77% of the theoretical quantity of hydrogen was evolved, hence 23% of the sodium used had reduced the malonic ester instead of forming the sodium derivative. This amount of reduction is capable of producing the alcohol necessary for the formation of the triester (VIII). The validity of the above reactions is shown also by the following facts, (a) a considerable amount of ethyl carbonate was isolated from the reaction, (b) ethyl (β-bromovinyl)-malonic ester (IV) reacts vigorously and, within a few minutes, completely with an equivalent of sodium ethoxide in alcohol to form ethyl α-ethyl-γ-ethoxycrotonate, $C_2H_5OCH_2CH{=}C(C_2H_5)COOC_2H_5$, and sodium bromide; the speed of this reaction definitely points to a shift in the double bond of the bromo ester (VI) to the more reactive allyl type (VII). The identity of this substituted ethyl crotonate was established by reduction and comparison of the reduction product with an authentic specimen of ethyl α-ethyl-γ-ethoxybutyrate.

The triester (VIII) was characterized by reduction to 3,6,6-tricarbethoxyoctane and by the conversion of this latter ester through saponification and decarboxylation into α,α'-diethyladipic acid.

Several attempts to condense vinylethylmalonic ester with urea by means of sodium ethoxide in alcoholic solution were made. However, the only product isolated from the reaction mixture was α-ethylcrotonamide,[4] $CH_3CH{=}C(C_2H_5)CONH_2$. The formation of this compound is due to the alcoholysis of the vinylethylmalonic ester, the rearrangement of the resulting unsaturated ester to ethyl α-ethylcrotonate and the reaction of this latter ester with urea (or ammonia) to form the above amide.

[4] Von Auwers, *Ann.*, **432**, 76 (1923).

The marked readiness with which the vinylethylmalonic ester undergoes alcoholysis, together with its susceptibility to cleavage by sodium ethoxide, as described in the following paper, would seem to indicate that the synthesis of vinylethylbarbituric acid could not be effected through this ester.

Experimental

Mono-ethylmalonic ester was kindly furnished in liberal quantities by Mr. H. A. Shonle of the Lilly Research Laboratories, to whom the authors wish to acknowledge their indebtedness, not only for this and other valuable materials, but for his interest and many valuable suggestions.

Ethyl (β-Bromoethyl)-ethylmalonate and α-Ethyl-α-carbethoxy Butyrolactone.—The bromo ester was prepared by a procedure used by Shonle,[5] which involved the reaction of 2 moles of ethylene bromide with 1 mole of sodio-ethylmalonic ester prepared from ethylmalonic ester and powdered sodium under benzene. The yield of product boiling at 128–130° (3 mm.), n_D^{25} 1.4541, amounted to 35–40%. If the distillation of this product is not carried out at quite low pressures and superheating avoided, there is a considerable evolution of ethyl bromide (with a resultant rise in pressure) and the distillate shows a halogen content much lower than the value calculated for the bromo ester. When such material is distilled under atmospheric pressure ethyl bromide is evolved rapidly and the distillate, which is α-ethyl-α-carbethoxybutyrolactone, contains no bromine.

This lactone[6] boils at 265–267° (740 mm.); 135–138° (9 mm.); n_D^{25} 1.44421; d_{25}^{25} 1.1045; M_D calcd. 45.16, observed 44.87. Saponification equivalent, calcd. 93, found 95.5.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.02; H, 7.58. Found: C, 58.06; H, 7.85.

Reaction of Ethyl (β-Bromoethyl)-ethylmalonate with Trimethylamine.—A solution of 29.6 g. (1 mol) of the bromo ester and 6.5 g. (1.1 mol) of trimethylamine in 25 cc. of absolute alcohol was sealed in a bomb tube and heated at 130° for eighteen hours. After this time the tube was opened and the contents diluted with ether. The precipitated salt showed a bromine content of 51.55% (calcd. for tetramethylammonium bromide, 51.30%). The ether–alcohol solution from which this salt had precipitated was evaporated to dryness and the residue taken up in dry ether. The hydrochloride of ethyl (β-dimethylaminoethyl)-ethylmalonate was precipitated with dry hydrogen chloride. After recrystallization the hydrochloride melted at 147–148°. Voorhees[2] records a similar melting point for this compound after recrystallization but states that after sublimation it melts at 154°.

Anal. Calcd. for $C_{13}H_{26}O_4NCl$: Cl, 12.01. Found: Cl, 12.00.

When the above reaction was carried out in alcohol at 100° for eighteen hours, a salt containing 29.86% bromine was obtained (calcd. for the quaternary salt (II), 23.0%). When a solution of the reactants in dry ether was allowed to stand for several weeks a small yield of a salt containing 26.17% bromine was obtained.

Ethyl (β-Bromovinyl)-ethylmalonate.—To 115 g. (5 moles) of powdered sodium, covered with 3 liters of absolute ether in a 5-liter three-necked flask carrying a dropping funnel, a mercury-seal stirrer and a reflux condenser, was added slowly 940 g. (5 moles) of ethylmalonic ester. When all of the sodium had reacted, 1860 g. (10 moles) of sym-

[5] Private communication.

[6] The physical constants reported for ethyl (β-hydroxyethyl)-malonic ester[3] are b. p. 128–131° (6 mm.), n_D^{20} 1.4444. No analyses were given.

metrical dibromoethylene[7] was added and the ether refluxed with stirring for six hours on a steam-bath. Then the reaction mixture was stirred at room temperature for ninety hours. After this time the ethereal solution was washed with dilute hydrochloric acid and a 10% salt solution. The ether was then removed by distillation and the residue fractionated through a Widmer column. The boiling points and amounts of the fractions collected were

Fraction	Compound	B. p., °C.	Weight, g.	Recovery or yield, %
1	Dibromoethylene	107–111	1008	54.1
2	Diethyl carbonate	124–126	62	7.1
3	Ethylmalonic ester	106–110 (25 mm.)	119	12.7
4	Ethyl (β-bromovinyl)-malonic ester	117–120 (1 mm.)	362	24.8
5	3,6,6-Tricarbethoxyoctene-3	152–155 (1 mm.)	251	30.7

Intermediate fractions between 3 and 4 and 4 and 5 amounted to 39 g. and 48 g., respectively; 123 g. of a non-distillable residue remained. Ethyl (β-bromovinyl)-malonic ester (fraction 4) had the following constants: n_D^{25} 1.46195; d_{25}^{25} 1.2645; M_D calcd. 63.95; observed, 63.89.

Anal. Calcd. for $C_{11}H_{17}O_4Br$: Br, 27.27. Found: Br, 27.32.

The bromovinyl ester was further characterized by catalytic reduction to diethylmalonic ester; 12 g. in 30 cc. of alcohol absorbed 2 moles of hydrogen in fifteen minutes in the presence of 0.1 g. of Adams' platinum catalyst. The reduction product was converted into di-*p*-nitrobenzyl diethylmalonate,[8] m. p. 90–91°.

The bromovinyl ester may be distilled at atmospheric pressure without any noticeable decomposition, b. p. 264–266°. With alkali it gives immediately an intense red color. This color reaction is a convenient test for the purity of fraction 5, since pure 3,6,6-tricarbethoxyoctene-3 remains colorless in the presence of alkali.

When the condensation between dibromoethylene and sodioethylmalonic ester was carried out in benzene instead of ether, the chief product was the bromine-free fraction 5, although a small amount of the bromovinyl ester (fraction 4) was obtained. Besides the unfavorable ratio of reaction products, this condition of reaction has a further disadvantage. At the reflux temperature of benzene, the dibromoethylene is decomposed by the alkali present into bromoacetylene, which ignites spontaneously when it comes in contact with air at the top of the reflux condenser.

Ethyl Vinylethylmalonate.—A solution of 25 g. of ethyl (β-bromovinyl)-malonic ester in 60 cc. of 95% alcohol was placed in the glass liner of a steel bomb[9] and 10 g. of zinc dust added. The liner was then placed in the bomb under an initial pressure of 1200 lb. of nitrogen and the bomb heated with shaking at 170° for ten hours. After the removal of the zinc by filtration, the combined alcoholic solutions from eight such runs were distilled under diminished pressure to remove the alcohol. The residue was then taken up in ether and the resultant solution washed with dilute hydrochloric acid and dried over anhydrous sodium sulfate. After removal of the ether the material was fractionated. That portion of the distillate (46 g.) which boiled above 124° (24 mm.) was again treated as described above with zinc and alcohol in the bomb and the resultant product combined with the low boiling (below 124° (24 mm)) portion from the first distillation and the combined product redistilled through a Widmer column. The yield of vinyl ethylmalonic ester from the reduction of 200 g. of the bromovinyl ester was 79 g. (54%); b. p. 122–124 (30 mm.); n_D^{25} 1.4341; d_{25}^{25} 1.0110; M_D calcd., 56.07; observed, 55.15.

[7] *Chem. Zentr.*, [II] **84**, 1375 (1913).

[8] Lyman and Reid, THIS JOURNAL, **39**, 711 (1917).

[9] *Cf.* Adkins and Cramer, *ibid.*, **52**, 4349 (1930).

Molecular weight (in benzene). Found: 212.4; calcd., 214.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.64; H, 8.47. Found: 61.80; 8.47.

The vinylethylmalonic ester was definitely characterized by quantitative catalytic reduction with Adams' platinum catalyst; 0.4150 g. of ester required for complete reduction 43.48 cc. (100.06%) of hydrogen. The reduction product, diethylmalonic ester, was converted into di-*p*-nitrobenzyl diethylmalonate.[8]

3,6,6-Tricarbethoxyoctene-3.—This ester (fraction 5 in the preparation of the bromovinyl ester, see above) on redistillation boiled at 150–152° (2 mm.) or 304–306 (740 mm.); n_D^{25} 1.45212; d_{25}^{25} 1.0534; molecular weight in benzene and dioxane 320, 321.2. Zeisel determination showed 2.90 ethoxyl groups per mole. Saponification equivalent with 0.2 *N* potassium hydroxide (sodium hydroxide does not give complete saponification due to the separation of an insoluble, resinous material) 107.8; calcd., 109.3; M_D calcd., 85.56; observed, 84.28.

Anal. Calcd. for $C_{17}H_{28}O_6$: C, 62.13; H, 8.53. Found: 61.80, 8.51.

This triester slowly decolorized a solution of bromine in carbon tetrachloride, but could not be reduced catalytically over a platinum catalyst. Over nickel, however, at 175° and 2500 lb. pressure it absorbed 1 mole of hydrogen after a second addition of fresh catalyst. Over the copper–chromium oxide catalyst[10] at 175° and 2500 lb. pressure it readily absorbed 1 mole of hydrogen to give an 80% yield of 3,6,6-tricarbethoxyoctane.

3,6,6-Tricarbethoxyoctane.—This ester boiled at 154–156 (2 mm.); n_D^{25} 1.44421; d_{25}^{25} 1.0337; M_D calcd., 85.95; obs., 85.08. Saponification equivalent (0.2 *N* alcoholic KOH) 109; calcd., 110.

Anal. Calcd. for $C_{17}H_{30}O_6$: C, 61.82; H, 9.09. Found: C, 61.77; H, 8.91.

A portion of this ester was saponified with alcoholic potassium hydroxide and the resultant acid, after removal of the alcohol, decarboxylated by refluxing with 20% sulfuric acid. The α,α'-diethyladipic acid was extracted from the acid solution with ether and after three recrystallizations from water melted at 136–136.5°[11] and had a neutral equivalent of 103.4. In order to establish definitely the identity of this adipic acid, it was prepared from 3,3,6,6-tetracarbethoxyoctane which was obtained by the ethylation of ethylbutane-1,1,4,4-tetracarboxylate[12] by Lean's procedure.[11] By saponification and decarboxylation of this tetracarbethoxyoctane a mixture of the racemic and meso-α,α'-diethyladipic acids was obtained. Recrystallization from water gave the less soluble meso acid which melted at 136–136.5° and gave no depression when mixed with the diethyladipic acid obtained from the tricarbethoxyoctane.

The above data established the structure of the high boiling bromine-free fraction (V) and the isolation of ethyl carbonate from the reaction mixture indicated that the carbethoxy group was removed by alcoholysis. The alcohol necessary for a cleavage must be formed in the reaction, as all of the starting materials were dry and free from alcohol. The most probable source of the necessary alcohol seemed to be the initial reaction of powdered sodium with ethyl monoethylmalonate, as under these conditions ester reduction or acyloin condensation, which would produce alcohol or sodium ethoxide, could take place. The acyloin condensation as a side reaction would also explain the large residue obtained on fractionating the mixture.

The measurement of the quantity of hydrogen evolved in the reaction of an excess of ethyl monoethylmalonate with a weighed quantity of powdered sodium was used to determine the extent of these side reactions. The normal reaction giving the sodium

[10] Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

[11] Lean, *J. Chem. Soc.*, **65**, 1009 (1894).

[12] Noyes and Kyriakides, THIS JOURNAL, **32**, 1058 (1910).

enol ester evolves a molecular equivalent of hydrogen, while none is formed in the side reactions.

An apparatus similar to that employed by Moureu and Mignonac[13] for differentiating amines by the Grignard reagent was used. Approximately 1.5 g. of freshly cut sodium was weighed under mineral oil, powdered under xylene, and washed into a 500-cc. 3-necked round-bottomed flask with 60 cc. of anhydrous ether. The flask was fitted with a mercury-seal stirrer, separatory funnel, and reflux condenser, the latter protected by a calcium chloride tube which was attached to a delivery tube leading to an inverted 1-liter graduate over water. The flask was immersed to a definite level in a water-bath at 40° and, after the formation of air bubbles due to the refluxing ether had ceased, the delivery tube was placed under the graduate and a small portion of ethyl monoethylmalonate introduced through the separatory funnel. The water-bath was then removed and the ester added at such a rate as to keep the solution refluxing. Toward the end of the reaction the water-bath was replaced and the final gas volume read after the reaction ceased. The accuracy of the method was shown by the fact that ethyl alcohol gave about 103% of the theoretical amount of hydrogen when it was used instead of the malonic ester. By this procedure the average of several runs using both ether and benzene as media showed that when an excess of ethyl malonic ester was allowed to react with sodium only 77% of the theoretical amount of hydrogen was evolved. The remaining hydrogen equivalent must have been utilized for reduction which would produce the necessary alcohol (or sodium ethoxide) for the cleavage of the ethyl (β-bromovinyl) malonic ester into ethyl α-ethyl-γ-bromocrotonate (VII).

Reaction of Ethyl (β-Bromovinyl)-malonic Ester with Alcoholic Sodium Ethoxide.—To an alcoholic solution of sodium ethoxide prepared by dissolving 3.93 g. (1 atom) of sodium in 125 cc. of absolute alcohol was added 50 g. (1 mole) of the bromovinyl ester. An intense red color developed immediately, sodium bromide was precipitated, and the reaction was sufficiently vigorous to cause the alcohol to reflux for about five minutes. When this initial reaction subsided the alcohol was refluxed for an additional five minutes. The sodium bromide was then filtered off and the alcohol removed from the filtrate by distillation under diminished pressure. The residue was taken up in ether, washed with water, dried with anhydrous sodium sulfate, and distilled. A small forerun of ethyl carbonate followed by 23.6 g. (75%) of ethyl α-ethyl-γ-ethoxycrotonate was obtained, b. p. 96–99° (14 mm.), n_D^{25} 1.42800, d_{25}^{25} 0.9441; M_D calcd. 51.29; observed, 50.83. Molecular weight (in benzene): 185.4; calcd., 186. Zeisel determination gave 2.03 ethoxyl groups per mole. A sample titrated with standard bromine solution absorbed 99.3% of the calculated amount.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.46; H, 9.75. Found: 64.25, 9.61.

This ester appears to be quite unstable and gradually changes on standing into a number of products which were not investigated further. For example, a sample which originally boiled at 96–99° (14 mm.) distilled, after standing for five months, over a range of 75–140° (14 mm.). The fact that this distillate was distinctly acid would indicate that the change in the ester had involved an oxidation. Freshly prepared ester was used for the determination of the physical constants given above and in the following reduction experiment.

Over a copper–chromium oxide catalyst[10] and at 2500 lb. pressure this ester absorbed considerably more than the theoretical quantity of hydrogen before reaching 150°. Distillation of the reduction product from 12 g. of the unsaturated ester gave 2.8 g. of ethyl diethylacetate, b. p. 150–152°, 2.5 g. of an intermediate fraction boiling at 50–90° (14 mm.) and 2.0 g. of ethyl α-ethyl-γ-ethoxybutyrate.

[13] Moureu and Mignonac, *Compt. rend.*, **158**, 1624 (1914).

Ethyl α-Ethyl-γ-ethoxybutyrate, b. p. 90–92° (14 mm.); n_D^{25} 1.41525; d_{25}^{25} 0.9182; M_D calcd. 51.68; observed 51.35.

Anal. Calcd. for $C_{10}H_{20}O_3$: C, 63.77; H, 10.71. Found: C, 63.67; H, 10.55.

The physical properties of the above ester correspond to those of ethyl α-ethyl-γ-ethoxybutyrate prepared from ethylmalonic ester through reaction of β-ethoxyethyl bromide, followed by saponification, decarboxylation and esterification of the monocarboxylic acid. The yields, properties and analyses of the intermediates and final ethyl α-ethyl-γ-ethoxybutyrate of this synthesis are summarized in the following table.

	Compound	Yield, %	B. p., °C.	n_D^{25}	d_{25}^{25}
1	Ethyl (β-ethoxyethyl)-ethylmalonate	63	142–3 (17 mm.)	1.42925	1.0069
2	α-Ethyl γ-ethoxybutyric acid	86	138–9 (18 mm.)	1.42775	0.9774
3	Ethyl α-ethyl-γ-ethoxybutyrate	82	90–92 (14 mm.)	1.41520	.9179

	Coumpound	M_D calcd.	M_D observed	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
1	Ethyl (β-ethoxyethyl)-ethylmalonate	67.36	66.85	$C_{13}H_{24}O_6$	59.95	59.78	9.29	9.12
2	α-Ethyl γ-ethoxybutyric acid	42.31	42.22	$C_8H_{16}O_3$	59.95	60.13	10.07	10.15
3	Ethyl α-ethyl-γ-ethoxybutyrate	51.68	51.48	$C_{10}H_{20}O_3$	63.77	63.74	10.71	10.78

Reaction of Vinylethylmalonic Ester with Urea in Alcoholic Sodium Ethoxide Solution.—To a solution of 3.45 g. (3 atoms) of sodium in 50 cc. of absolute alcohol were added 10.7 g. (1 mol) of vinylethylmalonic ester and 4.5 g. (1.5 mol) of urea and the resultant solution was refluxed for eighteen hours. The ester gave a deep red color with warm sodium ethoxide solution although no color developed with cold 10% sodium hydroxide (the latter behavior is characteristic of ethyl β-bromovinylethylmalonate) The alcohol was then distilled under diminished pressure, the residue dissolved in water and the alkaline solution extracted with ether. On acidification of the aqueous solution a very small quantity of an oily precipitate was formed which showed no signs of crystallization even after long standing. The water was finally distilled and the brown residue (NaCl + some organic material) extracted with absolute ethanol in a Soxhlet extractor. A very small quantity of an oil was thus separated which could not be crystallized from any of the usual solvents. Distillation of the ether extract of the alkaline solution gave 2.2 g. of a product that boiled at 145–147° (22 mm.) and which solidified on cooling. After recrystallization from naphtha it melted at 113–114°. This product was identified as α-ethylcrotonamide by comparison with an authentic specimen of this amide prepared by the procedure of von Auwers.[4]

Summary

The synthesis of vinylethylmalonic ester is reported and it is shown that on account of the ease with which it is cleaved this ester cannot be converted into a barbituric acid by the usual method.

The following new compounds, incidental to the synthesis of vinylethylmalonic ester, are reported: α-ethyl-α-carbethoxybutyrolactone, ethyl (β-bromovinyl)-ethylmalonate, 3,6,6-tricarbethoxyoctene-3, 3,6,6-tricarbethoxyoctane, ethyl α-ethyl-γ-ethoxycrotonate, ethyl α-ethyl-γ-ethoxy-

butyrate, ethyl (β-ethoxyethyl)-ethylmalonate, α-ethyl-γ-ethoxybutyric acid.

MADISON, WISCONSIN

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

THE CLEAVAGE OF DISUBSTITUTED MALONIC ESTERS BY SODIUM ETHOXIDE

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In the preceding paper the marked susceptibility of β-bromovinylethyl malonic ester and vinylethylmalonic ester to cleavage into the corresponding acetic esters and ethyl carbonate by means of alcoholic sodium ethoxide is pointed out. The isolation of α-ethyl crotonamide from the attempted preparation of vinylethylbarbituric acid parallels the results reported by Dox and Thomas[1] in their unsuccessful attempts to prepare diphenylbarbituric acid from diphenylmalonic ester. That the susceptibility of the malonic ester to cleavage was the cause of the failure of the synthesis in the latter case is shown by an experiment performed in the present work in which diphenylmalonic ester was split quantitatively into diphenylacetic ester and ethyl carbonate in thirty minutes by refluxing with alcoholic sodium ethoxide. This cleavage is simply a reversal of the type of acetoacetic ester condensation which Lux[2] has applied to the synthesis of malonic ester from ethyl carbonate and ethyl acetate

$$O{=}C(OC_2H_5)_2 + CH_3COOC_2H_5 \xrightarrow{NaOC_2H_5} CH_2(COOC_2H_5)_2 + C_2H_5OH$$

If there is any analogy to the cleavage of the acetoacetic ester type, it would be expected from the work of Dieckmann[3] that the disubstituted malonic esters would be more readily cleaved by alcoholic sodium ethoxide than the monosubstituted or unsubstituted malonic esters. Experiments with diethyl- and monoethylmalonic esters reported in the experimental part of the paper indicate that such is the case.

It seemed likely that barbituric acids might be prepared from these more sensitive disubstituted malonic esters by condensing them with urea by means of dry, alcohol-free sodium ethoxide.[4] Preliminary experiments with diethylmalonic ester showed that such a condensation took place at 170°, the theoretical quantity of alcohol being distilled out of the reaction mixture in eight to ten minutes, and a yield of 55–65% of barbital obtained. Under similar conditions both vinylethylmalonic ester and diphenylmalonic

[1] Dox and Thomas, THIS JOURNAL, **45**, 1811 (1923).

[2] Lux, *Ber.*, **62**, 1824 (1929).

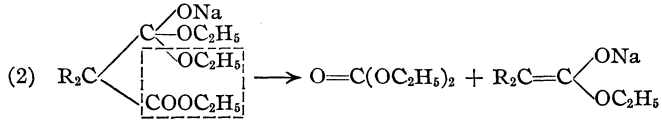
[3] Dieckmann, *ibid.*, **33**, 2678 (1900).

[4] *Cf. Friedländer*, **7**, 655 (1903).

ester gave high yields of alcohol but in the case of the former ester a gummy, alkali-insoluble material was the main product obtained from the reaction mixture. The diphenylmalonic ester reaction yielded principally diphenylacetamide, the product obtained by Dox and Thomas from the reaction in alcoholic solution.

It was evident from these results, as well as from the discrepancy in the yields of alcohol and barbital in the case of diethylmalonic ester, that sodium ethoxide itself will cleave these disubstituted malonic esters. An investigation in this direction showed that in the main two distinctly different types of reaction take place, (1) the decomposition of the malonic ester directly into the disubstituted acetic ester, carbon monoxide, carbon dioxide and relatively small amounts of ethylene, diethyl ether, alcohol, and the disubstituted acetic acids; (2) the cleavage of the malonic ester into ethyl carbonate and presumably the sodium enolate of the disubstituted acetic ester, although definite evidence of the presence of this latter compound was obtained only in the case of diphenylmalonic ester. These reactions which are probably preceded by the formation of the sodium ethoxide addition product with a carbethoxy group of the malonic ester may be illustrated as follows

(1) $R_2C(COOC_2H_5)_2 + NaOC_2H_5 \longrightarrow R_2CHCOOC_2H_5 + CO + CO_2 + C_2H_4$, etc.

(2) 

The temperature necessary to bring about the above reactions as well as the extent to which each of them takes place is dependent upon the nature of the substituent R groups. The pertinent data obtained from the malonic esters studied are summarized in Table I. The nature and amounts of the gaseous products were determined only in the case of

TABLE I

THE CLEAVAGE OF DISUBSTITUTED MALONIC ESTERS BY SODIUM ETHOXIDE

Substituents	Temp. of reaction, °C.	Yield of ethyl carbonate, %	Yield of $R_2CHCOOC_2H_5$, %	Yield of ether, %	Recovered malonic ester, %
Diethyl	220–230	16	67	8	12
Ethyl, isoamyl	220–230	12	66	9	5
Ethyl, methyl-*n*-propylcarbinyl	220–230	4	64	11	6
Phenyl, ethyl[a]	120 (24 mm.)	58	38	0	4
Vinyl, ethyl[a]	100 (14 mm.)[b]	38	..	0	35
Diphenyl[a]	100 (20 mm.)	90	0	0	0

[a] The reactions of these esters were run under diminished pressure in order that the ethyl carbonate might distil as it was formed.

[b] At this temperature and pressure the recovered vinylethylmalonic ester distilled over unchanged with the ethyl carbonate.

diethylmalonic ester and consequently are not included in this table. The amount of reaction (1) was determined by the yield of the disubstituted acetic ester which distilled out of or was extractable from the reaction mixture by ether. The amount of reaction (2) was determined by the yield of redistilled ethyl carbonate. Obviously, these values are minima and since some if not all of the diethyl ether, which was obtained in some cases, may have been formed from the ethyl carbonate,[5] the yields of ether are included in the data.

It is evident from the above data that the dialkylmalonic esters as a group react mainly according to reaction (1), while diphenylmalonic ester reacts entirely according to reaction (2). Phenylethylmalonic ester is, as might be expected, intermediate between these two extremes, showing considerable amounts of both types of reactions. Vinylethylmalonic ester appears to show only reaction (2) but since the volatility of this ester prevents any large amount of reaction from taking place no definite conclusions may be drawn on this point. It is significant that of the disubstituted malonic esters which were studied, those containing a double bond in the β,γ-position relative to the carbethoxy groups are cleaved by sodium ethoxide at a relatively low temperature and mainly into ethyl carbonate.

The preparative value of these reactions should be mentioned. Dialkylacetic esters may be prepared directly from the reaction of dry sodium ethoxide on dialkylmalonic esters in a few minutes and in quite good yields. Although the yields are somewhat higher when the dialkylmalonic ester is split to the dialkylacetic ester by alcoholic sodium ethoxide (see experimental part), special equipment is required for this reaction. The cleavage of diphenylmalonic ester by sodium ethoxide is a novel and most satisfactory method for the preparation of the sodium enolate of diphenylacetic ester in a pure state.[6] This enolate was characterized by its conversion (in 81% yields) into ethyl diphenylacetic ester[6] through reaction with ethyl iodide. No evidence of the existence of stable enolates of the other disubstituted acetic esters was obtained. It may be that the higher temperatures necessary for reaction caused their decomposition or polymerization in the cases of the dialkylmalonic esters. However, with ethylphenylmalonic ester it is seen from the above data that a considerable yield of ethyl carbonate was obtained and that the reaction temperature was but slightly higher than that required for diphenylmalonic ester. Attempts to demonstrate the presence of this enolate by benzylating it to

[5] *Cf.* Geuther, *Centr.*, **39**, 635 (1868). The observation of Geuther that carbon dioxide, ethyl alcohol and sodium carbonate are formed by the decomposition of sodium ethyl carbonate explains the presence of small amounts of alcohol obtained in the above reactions. It is possible that some of the ether might be formed from the reaction of sodium ethoxide with sodium ethyl carbonate.

[6] *Cf.* the preparation of the potassium enolate from diphenylacetic ester by Staudinger and Meyer, *Helv. Chim. Acta*, **5**, 656 (1922).

the known ethylphenylbenzylacetic ester gave no isolable quantities of the latter compound. It would seem that since the association of the disubstituted acetic ester enolate with ethyl carbonate is so apparent in the case of the diphenyl compound, their transitory existence must be assumed in the other instances. This assumption is substantiated by the fact that in these instances the extent of tar formation parallels the yield of ethyl carbonate.

Experimental

Materials Used.—Sodium ethoxide was prepared by the reaction of powdered sodium with a 1% excess of absolute alcohol in dry ether.[7] The purity of the product was established by analysis for sodium. Diethylmalonic ester was purified by washing with hot 25% potassium hydroxide[8] and distillation. Monoethylmalonic ester, ethyl isoamylmalonic ester and ethyl methyl-*n*-propylcarbinylmalonic ester were kindly furnished by Mr. H. A. Shonle of The Lilly Research Laboratories, Indianapolis, Indiana. Ethyl phenylmalonic ester was supplied in liberal quantities by Dr. V. H. Wallingford of the Mallinckrodt Chemical Works, St. Louis, Missouri. Each of these esters was fractionated before use. Vinylethylmalonic ester is described in the preceding paper.

Diphenylmalonic ester was prepared by the following modification of the procedure of Dox and Thomas.[1] To a cooled solution of 90 g. of oxomalonic ester in 270 g. of benzene was added 180 g. of 100% sulfuric acid (prepared by the addition of the calculated quantity of fuming sulfuric acid to the ordinary concentrated acid). The mixture was stirred and heated gradually in a water-bath to 65–70° and held at that temperature for seven hours. It was then poured onto ice, the benzene layer separated, and the acid aqueous solution extracted with benzene. The benzene extracts were combined, washed with water and sodium bicarbonate solution and then distilled. After removal of the benzene, 41 g. of diphenylmalonic ester, b. p. 192–194° (5 mm.), which solidified to a solid, m. p. 57–60°, was obtained. One recrystallization of this product from 175 cc. of alcohol gave 30 g. of product, m. p. 62–63°. The high purity of this product was proved by saponification of a 1-g. sample in an aqueous-alcoholic sodium hydroxide solution, followed by acidification with dilute sulfuric acid and absorption of the carbon dioxide evolved in ascarite. From 1 g. of the ester (m. p. 62–63°), 0.1418 g. of carbon dioxide (100.5%) was obtained. Material melting at 60–62° was found to be 98.3% pure by this method.

The procedure described by Dox and Thomas[1] was found in the present work to give a lower melting (58–59°) product.

Barbituric Acid Synthesis with Dry Sodium Ethoxide.—A mixture of 10 g. (1 mol) of diethylmalonic ester, 4.2 g. (1.7 mol) of urea and 9.5 g. (3 mols) of sodium ethoxide was heated in a two-necked 100-cc. flask, fitted with a mercury-seal stirrer and a condenser set for distillation, by an oil-bath to 170°. In twelve minutes 9.3 g. (109%) of ethyl alcohol had distilled out of the reaction mixture. The residue was decomposed with dilute hydrochloric acid and the diethylbarbituric acid recrystallized once from hot water. The yield was 5.55 g. (65%).

When this procedure was followed using vinylethylmalonic ester instead of diethylmalonic ester 101% of the calculated quantity of alcohol distilled out in ten minutes. The residue was only partially soluble in alkali, and this soluble portion gave a red gum on acidification. The major portion of the reaction was an alkali-insoluble

[7] *Cf.* Houben–Weyl, 1922, Vol. II, p. 578.

[8] Michael, *J. prakt. Chem.*, **72**, 551 (1905).

resinous material. From 5 g. of diphenylmalonic ester 68% of the expected alcohol was obtained in twelve minutes. From the residue 0.62 g. of diphenylacetic acid and 1.31 g. of diphenylacetamide, m. p. 168–169°, were isolated.

The Cleavage of Substituted Malonic Esters with Alcoholic Sodium Ethoxide. 1. Diphenylmalonic Ester.—To a solution of 0.46 g. (1 atom) of sodium in 50 cc. of absolute alcohol was added 6.24 g. (1 mol) of diphenylmalonic ester. After refluxing this solution for thirty minutes, the alcohol was removed under diminished pressure, the residue treated with water and then extracted with ether. After drying, the ether extract was distilled; 4.33 g. (81%) of ethyl diphenylacetate, b. p. 186–189° (20 mm.), m. p. 60–61°, was obtained. This product showed no depression of melting point when mixed with an authentic specimen.

2. Diethylmalonic Ester.—A solution of 11.5 g. (1 atom) of sodium in 200 cc. of absolute alcohol and 108 g. (1 mole) of diethylmalonic ester were placed in the brass liner of a steel bomb and heated for six hours at 250° under an initial hydrogen pressure of 1000 pounds. The contents of the bomb were then filtered with suction and the solid material (sodium carbonate or sodium ethyl carbonate) was washed with ether. These washings were added to the filtrate. Fractionation of this solution yielded 58.9 g. (82%) of ethyl diethylacetate, b. p. 147–150°, and 12 g. (11%) of unchanged diethylmalonic ester.

3. Monoethylmalonic Ester.—When the above procedure was repeated using 94 g. of monoethylmalonic ester and 2 equivalents of sodium ethoxide, 30 g. (52%) of ethyl butyrate and 19.5 g. (21%) of the unchanged malonic ester were obtained.

The Cleavage of Disubstituted Malonic Esters by Dry Sodium Ethoxide.—The experiments with the dialkylmalonic esters were all carried out in the same manner except that the nature and amounts of the gaseous products of the reaction were determined only in the case of diethylmalonic ester. A description of the procedure used for the latter compound will suffice for this type.

A mixture of 108 g. (1 mole) of diethylmalonic ester and 34 g. (1 mole) of sodium ethoxide was placed in a 500-cc. Claisen flask, fitted with a mercury-seal stirrer and connected to a distillate receiver. This receiver was connected through a trap surrounded by a mixture of ice and hydrochloric acid to a graduated carboy filled with a saturated salt solution which served as a gas receiver. The flask was immersed in an oil-bath which was heated rapidly to 220–230° and kept at that temperature for thirty minutes. During this time 70 g. of distillate and 6 liters of gas were collected. The receiver was then changed, the stirrer in the reaction flask replaced by a solid stopper and a vacuum applied to the reaction flask. An additional 14 g. of distillate was thereby collected. An analysis of the collected gas showed that yields of 14% of ethylene and 25% of carbon monoxide had been obtained. Fractionation of the combined distillates through a Widmer column gave the following products: 3.0 g. (8%) ether, b. p. 35–38°; 1.45 g. ethyl alcohol, b. p. 77–79°; 9.5 g. (16%) ethyl carbonate, b. p. 126–128°; 48.2 g. (67%) ethyl diethylacetate, b. p. 147–150°; 12 g. (12%) diethylmalonic ester. The residue in the reaction flask on acidification yielded large quantities of carbon dioxide and a small amount of diethylacetic acid. A quantitative determination of the carbon dioxide on a smaller run showed that it was formed to the extent of 35% of the theoretical.

Ethyl α-ethyl-ϑ-methylcaproate (I) and ethyl α-ethyl-β-methylcaproate (II), which were obtained from ethylisoamylmalonic ester and ethylmethyl-*n*-propylcarbinylmalonic ester, respectively, as well as the acid (III) obtained from the saponification of (II), are new compounds. Their properties and analyses are given in Table II.

In the case of diphenylmalonic ester 12.4 g. (1 mole) of the ester and 2.7 g. (1 mole) sodium ethoxide were placed in a 100-cc. two-necked flask connected by one neck

TABLE II

PHYSICAL PROPERTIES AND ANALYSES

Compound	Formula	B. p., °C.	d_{25}^{25}	n_D^{25}	M_D Calcd.	M_D Found	Analyses % C Calcd.	H Calcd.	C Found	H Found
I[a]	$C_{11}H_{22}O_2$	197–198	0.8560	1.41481	54.60	54.59	70.90	11.91	70.70	11.78
II	$C_{11}H_{22}O_2$	197–198	.8671	1.41885	54.60	54.36	70.90	11.91	70.95	11.97
III	$C_9H_{18}O_2$	230–232	.9087	1.43015	45.23	45.16	68.29	11.47	68.19	11.40

[a] This ester was also characterized by conversion to the corresponding amide, m. p. 109–110°. Tiffeneau, *Bull. soc. chim.*, **33**, 183 (1923), reports this amide as melting at 106–108°.

to a distillate receiver surrounded by solid carbon dioxide–ether mixture and carrying in the other neck a stirrer fitted with machined conical bearings which allowed for its operation under diminished pressure. The flask was heated in an oil-bath for forty minutes at 100° under 20 mm. pressure. The distillate was ethyl carbonate which on redistillation boiled at 125–126° and weighed 4.25 g. (90%). The residue in the reaction flask was insoluble in ether, but was decomposed by ether containing dry hydrogen chloride into sodium chloride and pure diphenylacetic ester, m. p. 60–61°.

Vinylethylmalonic ester (10.7 g.) and an equivalent of sodium ethoxide after ten minutes at 100° and 14 mm. pressure gave a distillate which upon fractionation was separated into 2.23 g. (38%) of ethyl carbonate and 3.82 g. (35.4%) of unchanged vinylethylmalonic ester. The organic portion of the residue was entirely polymerized material from which nothing definite could be isolated.

Ethylphenylmalonic ester (66 g.) reacted readily at 120° with an equivalent of sodium ethoxide and after thirty minutes under 24 mm. pressure a distillate was obtained which on redistillation gave 17.2 g. (58%) of ethyl carbonate. The temperature of the oil-bath was then raised to 200°, whereupon 24.7 g. of distillate came over. Fractionation of this distillate yielded 18.4 g. (38%) of ethyl α-phenylbutyrate, b. p. 117–119° (17 mm.), and 2.5 g. (4%) of ethylphenylmalonic ester.

Alkylation Experiments with the Ester Enolates.—The residue remaining after the distillation of ethyl carbonate from the above described reaction of diphenylmalonic ester and sodium ethoxide at 100° was treated with 25 cc. of ethyl iodide and refluxed for fifteen hours. This reaction mixture was then taken up in ether, washed with water, dried and distilled. The yield of ethyl ethyldiphenylacetate, b. p. 186–188° (15 mm.), was 8.66 g. (81%). Two grams of this ester yielded on saponification 1.7 g. (95%) of ethyl diphenylacetic acid,[6] which after one recrystallization melted at 173–174°.

The red, viscous residue that remained after the reaction of ethylphenylmalonic ester with sodium ethoxide at 120° was treated with an excess of benzyl chloride instead of raising the temperature to remove any undistilled ethyl α-phenylbutyrate as described above. This mixture was heated under reflux for sixteen hours at 160–170°. When the reaction product was fractionated 15 g. (31%) of ethyl α-phenylbutyrate, 22 g. of higher boiling material and 24 g. of tar were obtained. However, saponification of the higher boiling material gave no trace of α-phenyl-α-benzylbutyric acid which has been described[9] as a solid melting at 140°.

Summary

The cleavage of certain substituted malonic esters by alcoholic sodium ethoxide and by dry sodium ethoxide is reported. It is shown that with the former reagent these esters are cleaved smoothly into the substituted acetic esters. With the latter reagent the disubstituted malonic esters

[9] Blondeau, *Ann. chim.*, [10] **3**, 5 (1924).

undergo in the main two types of cleavage, (1) into the disubstituted acetic esters and simpler decomposition products and (2) into ethyl carbonate and the sodium enolate of the disubstituted acetic esters. The nature of the substituent groups determines the readiness and manner in which these malonic esters are cleaved.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE CONDENSATION OF CERTAIN PHENOLS WITH SOME ALIPHATIC ALDEHYDES[1]

BY WILTON C. HARDEN AND E. EMMET REID

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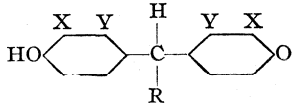
Recently there have been many studies of the bactericidal power of series of substituted phenols and phenol derivatives. Johnson and his co-workers.[2] Dohme, Cox and Miller[3] and Leonard[4] have studied the alkyl resorcinols. Other reports in this field have been made by Hampil,[5] Schaffer and Tilley,[6] Rettger and his co-workers,[7] and Klarmann.[8]

The bactericidal properties of the alkyl phenols have been studied by Schaffer and Tilley,[6] Rettger, Plastridge and Valley,[9] and the alkyl cresols by Coulthard, Marshall and Pyman.[10] Klarmann and his collaborators[11] have made an extensive investigation of the mono ethers of dihydric phenols, and recently Read and Miller[12] have reported on certain substituted phenols.

The present investigation is concerned with several series of di-(hydroxyphenyl)-alkyls of the general type  These were all prepared by the Baeyer reaction[13] which has been used by

[1] From the Ph.D. dissertation of Wilton C. Harden, Johns Hopkins University, 1932.

[2] Johnson and Hodge, THIS JOURNAL, **35**, 1014 (1913); Johnson and Lane, *ibid.*, **43**, 348 (1921).

[3] Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

[4] Leonard, *J. Am. Med. Assoc.*, **83**, 2205 (1924).

[5] Hampil, *J. Infectious Diseases*, **43**, 25 (1928).

[6] Schaffer and Tilley, *J. Bacteriology* **12**, 303 (1926); **14**, 259 (1927).

[7] Rettger, Valley and Plastridge, *Zentr. Bakt. Orig.*, **110**, 80 (1929).

[8] Klarmann, THIS JOURNAL, **48**, 791 (1926); **48**, 2358 (1926); Klarmann and Von Wowern, *ibid.*, **51**, 605 (1929).

[9] Rettger, Plastridge and Valley, *Zentr. Bakt. Orig.*, [I] **111**, 287 (1929).

[10] Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

[11] Klarmann, THIS JOURNAL, **53**, 3397 (1931); **54**, 298 (1932); **54**, 1204 (1932).

[12] Read and Miller, *ibid.*, **54**, 1195 (1932).

[13] Baeyer, *Ber.*, **5**, 280, 1096 (1872).

many investigators.[14] In the first four series, R varies from H to C_6H_{13}. Series I. Derivatives of phenol, X and Y = H: five of these have been previously reported. Series II. Derivatives of *o*-cresol, X = CH_3, Y = H: all except the first mentioned are new compounds. Series III. Derivative of *m*-cresol, X = H, Y = CH_3: all are new. Series IV. Derivatives of resorcinol, X = H, Y = OH: all of these except the first member are new. Series V. Condensation products of chloral with various phenols, R = CCl_3, X and Y = H or CH_3. Series VI. Miscellaneous: compounds made for purpose of comparison.

The bromo derivatives of the members of the first four series have been prepared for a better characterization of the compounds. These proved to be practically insoluble even in dilute alcohol and so could not be studied. The solubilities of the members of the first four series in water and 25% alcohol were determined. Their bactericidal power was tested against *Staphylococcus aureus*, strain no. 209. The compounds were, in general, dissolved in 25% alcohol, although in some cases stronger concentrations of alcohol were necessary. The technique employed consisted of the United States Department of Agriculture method, which is essentially as follows: 0.5 cc. of standard culture is added to 5 cc. of diluted antiseptic. Transfers are made with a 4-mm. platinum loop made from No. 23 B. and S. gage wire. The culture medium used was a sterile nutrient, beef extract broth, 10 cc. being used in each sub-culture tube. All dilutions were made with sterile distilled water.

The toxicities of the compounds of Series I, II and IV toward goldfish, *Carassius aureus*, and seedlings of *Lupinus albus* were determined.

Results

All the compounds of Series I, II, III and V are white crystalline solids which dissolve clear in the calculated amount of alkali solution to form the disodium salts. The compounds of Series IV and Compound No. 34 of Series VI could not be obtained colorless. Solutions of their sodium salts are dark red and oxidize to give tarry precipitates in the course of several hours.

The properties are shown in Tables I and II. In Figs. 1, 2 and 3 the solubilities, the melting points and bactericidal power of the compounds of Series I, II, III and IV are plotted against the number of carbon atoms in the side chain.

It will be noted that in all four series the solubilities in water decrease as the molecular weight of the side chain increases. In the case of 25% alcohol there are several exceptions. It will also be noted that in the case

[14] Lunjac, *Chem. Centr.*, **1**, 1650 (1904); II, 550 (1908); Zincke, *Ann.*, **302**, 237 (1898); Städel, *ibid.*, **194**, 329 (1878); **330**, 66 (1904); Claus and Trainer, *Ber.*, **19**, 3004 (1886); Auwers and Rietze, *Ann.*, **356**, 153 (1907); Fabinyl, *Ber.*, **11**, 283 (1878); Eberhardt, *ibid.*, **27**, 1804 (1824).

TABLE I

Comp. No.	R	M. p., °C.	Soly. in water, g./100 cc.	Soly. in 25% alcohol g./100 cc.	Maximum killing dilution, *S. aureus*	Ratio killing dilution to solubility	Toxicity to goldfish 1:30,000, killing time in minutes	Toxicity to *Lupinus albus* 1:30,000, % of normal growth
			Series I. Phenol					
1	H, *p-p'*	158	0.3950	0.780	300	2.34	100	70
2	H, *o-p'*	115	.2074	.937	450	4.24	100	70
3	CH_3	122	.0330	.671	1,200	8.05	65	70
4	C_2H_5	129	.0207	.1348	1,500	2.02	90	39
5	C_3H_7	137	.0165	.1744	3,500	6.10	50	14
6	C_4H_9	120	.0058	.0768	9,500	7.30	30	21
7	C_5H_{11}	110.5	.0037	.0388	12,500	4.86	25	14
8	C_6H_{13}	120[a]	.0005	.0120	14,000	1.68	20	39
			Series II. *o*-Cresol					
9	H	127	0.0560	0.0729	250	0.18	20	78
10	CH_3	100	.0489	.336	1,000	3.37	22	52
11	C_2H_5	94	.0259	.0784	3,500	1.99	38	40
12	C_3H_7	135	.0118	.0460	6,500	3.00	50	35
13	C_4H_9	97	.0022	.0226	7,500	1.70	60	46
14	C_5H_{11}	78	.0005	.0044	10,000	0.43	55	50
15	C_6H_{13}	85		.0035	24,500	0.86	55	43
			Series III. *m*-Cresol					
16	H	113	0.0445	0.0765	250	0.10		
17	CH_3	128	.0354	.1040	2,000	2.08		
18	C_2H_5	140	.0226	.0364	16,000	5.82		
19	C_3H_7	145	.0073	.0130	1,000	0.14		
20	C_4H_9	149	.0047	.0147	1,000	.14		
21	C_5H_{11}	152	.0018	.0112	20,000	2.23		
22	C_6H_{13}	156	.0007	.0071	20,000	1.42		
			Series IV. Resorcinol					
23	H	250	0.0534	0.0904	2,000	1.80	90	72
24	CH_3	do not	.0118	.0284	4,000	1.34	25	51
25	C_2H_5	melt	.0090	.0163	8,000	1.30	68	88
26	C_3H_7	at	.0091	.0101	10,000	1.00	50	86
27	C_4H_9	300° C.	.0081	.0091	2,000	0.19	75	93
28	C_5H_{11}		.0056	.0068	3,000	.20	300	85
29	C_6H_{13}		.0028	.0030	Satd. sol. does not kill	..	Alive after 24 hrs.	95

[a] Lunjac, *Chem. Centr.*, I, 1650 (1904), gives m. p. of 103°. The m. p. of 120° was checked after repeated crystallizations from different solvents.

of the derivatives of the lower aldehydes the order of solubility is as follows: phenol > *o*-cresol > *m*-cresol > resorcinol, while with the higher members this order is reversed. These curves serve to show the slight influence which the position and nature of such substituents as methyl and hydroxyl exert on the solubility of such compounds and the relatively large influence

TABLE II

Series V Condensations Using Chloral				Series VI Miscellaneous				
Comp. No.	Phenol used	M. p., °C.	Maximum killing dilution, *S. aureus*	Comp. No.	Aldehyde	Phenol	M. p., °C.	Maximum killing dilution, *S. aureus*
30	Phenol	199–200	1,350	33	Formaldehyde	Salicylic acid	239[a]	8000
31	*o*-Cresol	121–122	10,000	34	Formaldehyde	Pyrogallol	240[b]	2000
32	*m*-Cresol	162–163	10,000	35	Formaldehyde	Thymol	150	6000
36	Thymol	193.5	10,000					

[a] Methylene di-salicylic acid, German Patents 243,086, 499,070, also Madsen *Arch. Pharm.*, **245**, 44 (1907) and others.

[b] See Baeyer, *Ber.* **5**, 1096 (1872); Caro, *ibid.*, **25**, 947 (1892); Kahl, *ibid.*, **31**, 144 (1898).

of the length of the side chain. In Series I, II and III the melting points show an alternating effect; in Series I and II the net effect is a lowering of the melting point as the series advances; in Series III the opposite is the case. There seems to be no general relation between the melting point of the parent compound and the melting point of its bromine derivative, in some cases one is higher, in other cases the other.

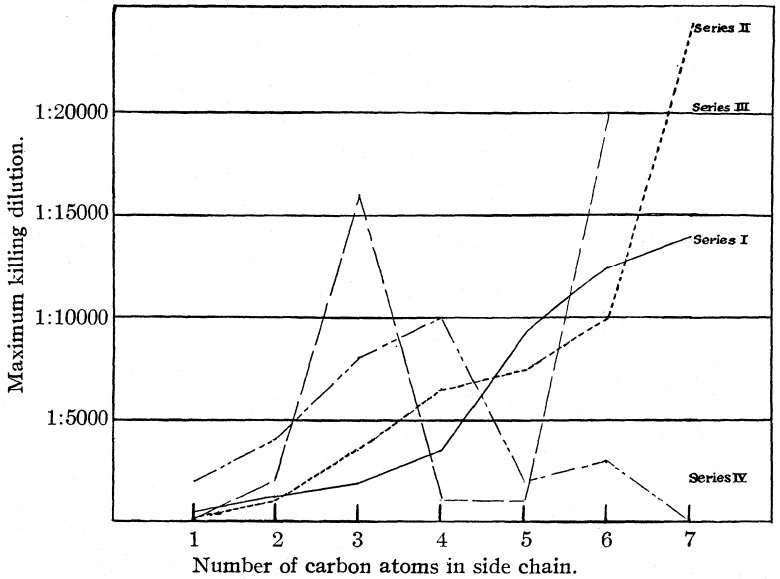


Fig. 1.—Germicidal power *in vitro:* test organism, *staphylococcus aureus.*

It will be seen that, in general, germicidal activity increases with increase in the length of the aliphatic chain. This is in accord with the results found by other investigators for similar series.[15] Since the degree of in-

[15] Walker and co-workers, *J. Chem. Soc.*, 514–520 (1931); Dohme, Cox and Miller, THIS JOURNAL, **48**, 1688 (1926); Leonard, *J. Am. Med. Assoc.*, **83**, 2005 (1924); Schaef-

solubility is also directly proportional to the length of the side chain, it follows that the least soluble compounds are in general the *most* germicidal. This is rather to be expected for in such compounds the determining factor seems to be not the substituent groups themselves but their effect on the distribution coefficient. The germicidal activity is thus a function of the lipoid solubility and hence inversely proportional to the solubility in water.

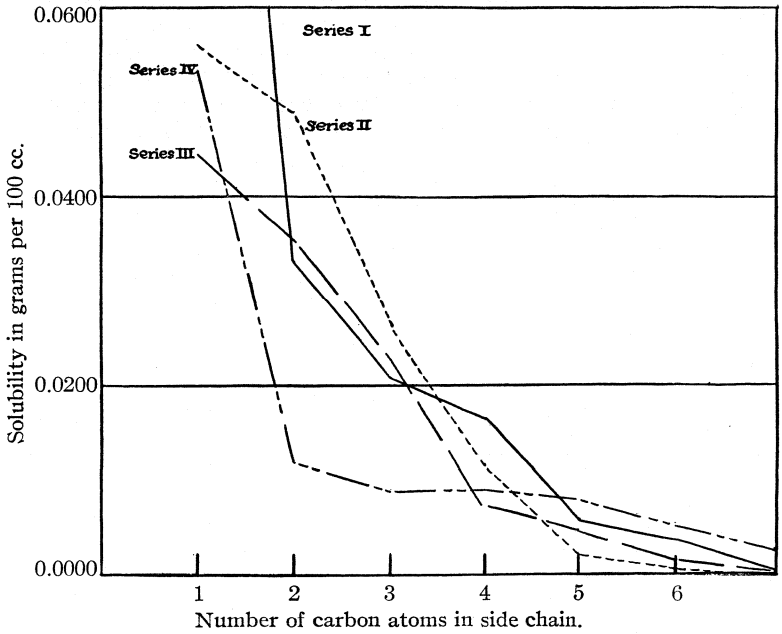


Fig. 2.—Solubilities in water at 25°.

Exceptions to these general statements are found in Compounds 19 and 20 of Series III and in the case of Series IV where germicidal activity reaches a maximum with the butyl compound and then falls off. No explanation is offered for this phenomenon.

To show that in these compounds, as in all phenolic germicides, germicidal activity is due in large part to the free hydroxyl groups, the dibenzoate of Compound No. 8 and the tetraacetate of Compound No. 26 were prepared. These compounds showed absolutely no germicidal action even in saturated solutions, while their parent compounds killed the test organism in dilutions of 1:14,000 and 1:10,000, respectively. This is in accord with the findings of other investigators in similar cases.[16]

fer and Tilley, *J. Bacteriology*, **14**, 259 (1927); Johnson, THIS JOURNAL, **35**, 1014 (1913), and others.

[16] Klarmann, Shternov and Von Wowern, *J. Bacteriology*, **17**, 440 (1929); Klarmann, Gatyas and Shternov, THIS JOURNAL, **53**, 3398 (1931).

Experimental

Materials Used.—The phenol used in preparing the compounds of Series I was Merck's "Reagent Grade," used without purification. The ortho and meta cresols in Series II and III were obtained from the Eastman Kodak Company and were redistilled before use. The resorcinol in Series IV was the ordinary resublimed resorcinol of commerce. All the aldehydes, with the exception of capron-aldehyde, were obtained from the Eastman Kodak Company. Considerable difficulty was experienced in finding a method to give satisfactory yields of capron-aldehyde. Finally hexyl alcohol was prepared by a Bouveault–Blanc[17] reduction of the ethyl ester of caproic acid using anhydrous butyl alcohol as the solvent. Some normal hexyl alcohol was also obtained from Kahlbaum. The alcohol was catalytically dehydrogenated, using a special catalyst. Single runs gave as high as 20% yields of capron-aldehyde and after repeated fractionations and redehydrogenations, an over-all yield of 80% was obtained.

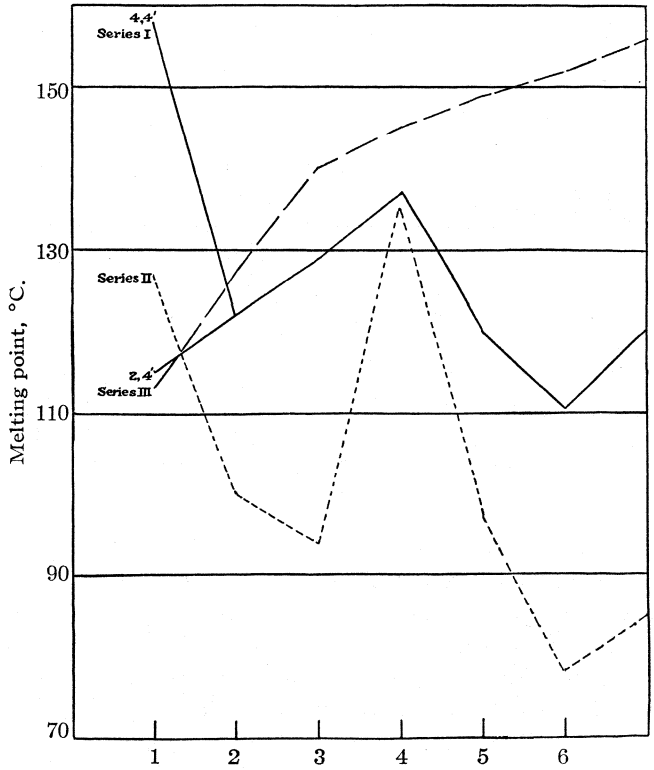


Fig. 3.—Melting points.

Preparation of Compounds of Series I.—The compounds of this series were prepared by two general methods. The first two members were prepared by one method and the remaining six by the other method. 2,4′- and 4,4′-dihydroxydiphenylmethane have been isolated as inter-

[17] Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 666 (1904).

mediate steps in the formation of Bakelite and other phenolic resins and have also been prepared[18] from diaminodiphenylmethane.[19] They were prepared by us simultaneously according to the technique of Morgan.[20] Molecular quantities of phenol and para formaldehyde were dissolved in alcohol (200 cc. of alcohol per mole) and 1 to 2 cc. of concentrated hydrochloric acid added. The solution was allowed to stand at room temperature for several hours and finally warmed slightly for one hour. Alcohol and excess phenol were removed by steam distillation and the resulting resins repeatedly extracted with boiling water. These aqueous extracts upon concentration yielded first plates of the 4,4′-compound and on further concentration and cooling, needles of the 2,4′-isomer. These were repeatedly crystallized from water.

The remaining members of this series were all prepared by the second general method, namely, that used by Zincke and Lunjac.[21] A typical example is the preparation of Compound No. 3, dihydroxydiphenylethane.

Eighty-five grams of phenol was placed in a 500-cc. three-necked flask, equipped with mechanical stirrer, and well cooled in crushed ice; 10.0 g. of acetaldehyde was added slowly from a dropping funnel. When all the aldehyde had been added, 0.5 cc. of hydrochloric acid (sp. gr. 1.19) was added and stirring continued for three hours. The temperature was kept below 5°. At the end of three hours, the flask was stoppered and placed in the ice box overnight. The mass of fine, white crystals was then sucked dry on a Buchner funnel and washed with cold benzene. The crystals were then suspended in water and steam distilled until *all* phenol was removed. The resulting product was crystallized from a mixture of benzene and petroleum ether; yield 15.0 g., 28%; melting point 122°.

The compounds of Series II and III were prepared in a similar manner, except that in the case of Series III the time of condensation was shortened to about one-half hour. Much difficulty was experienced in obtaining them in the crystalline form. The lower members were crystallized from water, but the higher ones at first resisted all efforts. Finally they were dissolved in ether, after steam distillation had removed the residual cresol and aldehyde. The ether solution was then dried with sodium sulfate, filtered, and the ether removed by distillation. The resulting product was a heavy tar or resin which was dissolved in the least possible amount of hot xylene or toluene and poured into a Petri dish. This was placed in a vacuum desiccator for some weeks with occasional stirring. Eventually small groups of crystals began to form and finally the whole mass crystallized. These fine crystals were removed by filtration and washed with petroleum

[18] Baekeland, *J. Ind. Eng. Chem.*, **5**, 510 (1913).

[19] Haase, *Ann.*, **283**, 163 (1894).

[20] Morgan, *J. Soc. Chem. Ind.*, **49**, 245 (1930).

[21] Zincke, *Ann.*, **303**, 255 (1898); Lunjac, *Chem. Centr.* I, 1650 (1904).

ether. It was found that the crystals, once formed, could be recrystallized with comparative ease.

The first member of Series IV, like that of Series I and II, has been previously prepared.[22] The entire series was prepared using the technique devised by Caro,[23] who first condensed resorcinol and formaldehyde. Three parts of resorcinol and one part of aldehyde were dissolved in twenty parts of dilute hydrochloric acid and the solution stirred mechanically for several hours or until a precipitate had formed. With the lower aldehydes the solution was kept cool, but with the higher members the 1 to 5 hydrochloric acid was made by dilution with alcohol, and the solution was warmed, and in some cases even boiled on the water-bath. The precipitates thus formed were crystallized from suitable solvents. Repeated crystallizations were necessary to free the products from red dyes formed by side reactions. The tetrabromo compounds were prepared with some difficulty, apparently due to oxidation.

Series V. Condensations with Chloral.—In view of some of the interesting bacteriological and pharmacological properties exhibited by the compounds of the first four series, it was thought that condensations using trichloroacetaldehyde or chloral might also yield interesting products. Many workers[24] have studied various condensations of chloral and chloral hydrate but only two of these may be considered modified Baeyer reactions.

TABLE III

ANALYTICAL DATA

Series I. Phenol

Comp. No.	R	Formula	Bromine derivative	M. p., °C.	Bromine, % Found	Calculated
1	H, *p-p'*	$C_{13}H_{12}O_2$	$C_{13}H_8Br_4O_2$	226	62.00–61.98	61.98
2	H, *o-p'*	$C_{13}H_{12}O_2$	$C_{13}H_8Br_4O_2$	193	61.84–61.64	61.98
3	CH_3	$C_{14}H_{14}O_2$	$C_{14}H_{10}Br_4O_2$	140	60.30–60.12	60.34
4	C_2H_5	$C_{15}H_{16}O_2$	$C_{15}H_{12}Br_4O_2$	150	59.05–59.10	58.79
5	C_3H_7	$C_{16}H_{18}O_2$	$C_{16}H_{14}Br_4O_2$	152	57.05–57.20	57.31
6	C_4H_9	$C_{17}H_{20}O_2$	$C_{17}H_{16}Br_4O_2$	Tar	Tetrabromodiacetate m. p. 168°	
					48.55–48.87	48.75
7	C_5H_{11}	$C_{18}H_{22}O_2$	$C_{18}H_{18}Br_4O_2$	Tar	Tetrabromodiacetate m. p. 129°	
					47.73–47.42	47.73
8	C_6H_{13}	$C_{19}H_{24}O_2$	$C_{19}H_{20}Br_4O_2$	Tar	Tetrabromodiacetate m. p. 111°	
					46.78–47.02	46.75

[22] Morgan, *J. Soc. Chem. Ind.*, **49**, 236; Traubenberg, *Z. angew. Chem.*, **36**, 515 (1903).

[23] Caro, *Ber.*, **25**, 947 (1892).

[24] Chattaway and co-workers, *Chem. Abstracts*, **21**, 1980 (1927); **22**, 1965 (1928); **22**, 2946 (1928); **23**, 599 (1929); Prats, *Rev. Acad. Ciene Madrid*, **24**, 307 (1927); Chattaway and Farinholt, *J. Chem. Soc.*, 1737, 1828 (1931).

TABLE III (*Concluded*)

Comp. No.	R	Formula	Bromine derivative	M. p., °C.	Bromine, % Found	Calculated
			Series II. *o*-Cresol			
9	H	$C_{15}H_{16}O_2$	$C_{15}H_{14}Br_2O_2$	173.5		
10	CH_3	$C_{16}H_{18}O_2$	$C_{16}H_{16}Br_2O_2$	77		
11	C_2H_5	$C_{17}H_{20}O_2$	$C_{17}H_{18}Br_2O_2$	111		
12	C_3H_7	$C_{18}H_{22}O_2$	$C_{18}H_{20}Br_2O_2$	104		
13	C_4H_9	$C_{19}H_{24}O_2$	$C_{19}H_{22}Br_2O_2$	Oil	Dibromodiacetate m. p. 150° 30.34–30.40	30.39
14	C_5H_{11}	$C_{20}H_{26}O_2$	$C_{20}H_{24}Br_2O_2$	Oil	Dibromodiacetate m. p. 121° 29.41	29.02
15	C_6H_{13}	$C_{21}H_{28}O_2$	$C_{21}H_{26}Br_2O_2$	Oil[a]		
			Series III. *m*-Cresol			
16	H	$C_{15}H_{16}O_2$	$C_{15}H_{12}Br_4O_2$	185	58.70	58.80
17	CH_3	$C_{16}H_{18}O_2$	$C_{16}H_{14}Br_4O_2$[b]	207	57.29	57.12
18	C_2H_5	$C_{17}H_{20}O_2$	$C_{17}H_{16}Br_4O_2$[c]	121	55.39	55.91
19	C_3H_7	$C_{18}H_{22}O_2$	$C_{18}H_{18}Br_4O_2$	142	54.29	54.57
20	C_4H_9	$C_{19}H_{24}O_2$	$C_{19}H_{20}Br_4O_2$	Oil m. p. 78°	Tetrabromodiacetate 46.56	46.75
21	C_5H_{11}	$C_{20}H_{26}O_2$	$C_{20}H_{22}Br_4O_2$[d]	119	52.19	52.09
22	C_6H_{13}	$C_{21}H_{28}O_2$	$C_{21}H_{24}Br_4O_2$	67	50.81	50.92
			Series IV. Resorcinol			
23	H	$C_{13}H_{12}O_4$	$C_{13}H_8O_4Br_4$	...	58.16	58.36
24	CH_3	$C_{14}H_{14}O_4$	$C_{14}H_{10}O_4Br_4$	...	56.80	56.90
25	C_2H_5	$C_{15}H_{16}O_4$	$C_{15}H_{12}O_4Br_4$	...	55.90	55.52
26[e]	C_3H_7	$C_{16}H_{18}O_4$	$C_{16}H_{14}O_4Br_4$	...	54.18	54.20
27	C_4H_9	$C_{17}H_{20}O_4$	$C_{17}H_{16}O_4Br_4$	...	52.94	52.90
28	C_5H_{11}	$C_{18}H_{22}O_4$	$C_{18}H_{18}O_4Br_4$	...	51.55	51.74
29	C_6H_{13}	$C_{19}H_{24}O_4$	$C_{19}H_{20}O_4Br_4$	...	50.10	50.60

[a] The dibromodiacetate and the dibromodibenzoate were both oils. The dibromodi(nitrobenzoate) was prepared, m. p. 215°, % bromine found, 20.69; calcd., 20.81; nitrogen found, 3.47%, calcd., 3.64.

[b] Dibromo derivative, m. p. 189°; % bromine found, 40.70; calcd., 40.22.

[c] Tetrabromodiacetate, m. p. 81°; % bromine found, 48.63; calcd., 48.74.

[d] Tetrabromodiacetate, m. p. 142°; % bromine found, 45.56; calcd., 45.81.

[e] Tetraacetate prepared, m. p. 250°.

Ter Meer[25] has reported dihydroxydiphenyltrichloroethane made by condensing phenol and chloral. This compound is also described by Elbs.[26] The method of Elbs has been used in the present investigation.

Table VI. Miscellaneous Condensations

The compounds of this series which are shown in Table VI were prepared in order to study particularly their germicidal activity. They were prepared by various modifications of the Baeyer reaction.

[25] Ter Meer, *Ber.* **7**, 1201 (1874).

[26] Elbs, *J. prakt. Chem.*, [2] **47**, 60 (1850).

TABLE IV

ANALYTICAL DATA

Series V. Condensations with Chloral

Comp. No.	Phenol	Formula	M. p., °C.	Chlorine, % Found	Calculated
30	Phenol	$C_{14}H_{11}Cl_3O_2$	199–200	33.35	33.57
31[a]	*o*-Cresol	$C_{16}H_{15}Cl_3O_2$	121–122	30.81	30.80
32	*m*-Cresol	$C_{16}H_{15}Cl_3O_2$	162–163	30.51	30.80
33	Thymol	$C_{22}H_{27}Cl_3O_2$	193.5	24.82	24.79

[a] Crystallizes from benzene with one mole of benzene of crystallization; m. p. 91°; % bromine found, 25.03, 24.97; chlorine calcd. for $C_{16}H_{15}Cl_3O_2 \cdot C_6H_6$, 25.12.

The authors wish to express their thanks to Dr. H. A. B. Dunning for his coöperation in the testing of these compounds in the Research Laboratories of Hynson, Westcott and Dunning, Inc., and to Dr. David I. Macht, Mr. W. Eric Drake and Mr. Grant Spurrier for their valuable assistance.

Conclusions

Thirty-five compounds have been prepared by the Baeyer reaction. They are of the general type $R_1—\underset{R_2}{\overset{H}{C}}—R_1$ where R_1 is a phenol or substituted phenol and R_2 may be hydrogen or an alkyl from C_1 to C_6. Bromine derivatives of twenty-nine of them have been prepared. In all, sixty-seven compounds have been made and examined, fifty of which are not previously described in the literature.

These compounds have been tested bacteriologically and pharmacologically. Many of them show marked germicidal activity *in vitro*. The toxicity for animal and plant organisms has been tested and will be reported in more detail elsewhere.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

MODE OF FORMATION OF DISUBSTITUTED MALONIC ESTER DERIVATIVES[1]

BY MAX S. DUNN, C. E. REDEMANN AND S. LAURITSEN

RECEIVED JUNE 13, 1932 PUBLISHED NOVEMBER 5, 1932

Disubstituted malonic ester derivatives may be formed by three mechanisms according to the hypotheses which have been proposed. These reactions, using benzyl chloride as the halogen compound, are given in the accompanying chart.

Consecutive Reaction Mechanism

$$\underset{\text{I}}{CH_2(COOC_2H_5)_2} \xrightarrow{NaOC_2H_5} \underset{\text{II}}{C_2H_5OOCCH{=}C(ONa)(OC_2H_5)} \xrightarrow{C_6H_5CH_2Cl} \underset{\text{III}}{CH(CH_2C_6H_5)(COOC_2H_5)_2} \xrightarrow{NaOC_2H_5}$$

$$\underset{\text{IV}}{C_2H_5OOC.C(CH_2C_6H_5){=}C(ONa)(OC_2H_5)} \xrightarrow{C_6H_5CH_2Cl} \underset{\text{V}}{C(CH_2C_6H_5)_2(COOC_2H_5)_2}$$

Disodium Malonic Ester Mechanism

$$\text{II} \xrightarrow{NaOC_2H_5} C(ONa)(OC_2H_5){=}C{=}C(ONa)(OC_2H_5) \xrightarrow{2C_6H_5CH_2Cl} \underset{\text{V}}{C(CH_2C_6H_5)_2(COOC_2H_5)_2}$$

Leuchs Mechanism

$$\text{II} + \text{III} \longrightarrow \text{IV} \longrightarrow \text{V}$$

The consecutive reaction mechanism is probably the principal one for sodium alcoholate solutions which favor the establishment of the necessary equilibria.[2] The hypothesis that disubstituted products may be formed through the agency of disodium malonic ester is still used by some authors despite the molecular weight experiments of Vorländer and von Schilling[3] and the spectroscopic investigations of Macbeth and Stewart,[4] which point to the non-existence of the disodium compound.

Support for the latter view and for the reactions postulated by Leuchs is obtained from the experiments reported in the present paper.

With equal molar proportion of reactants it is well known that the yield of disubstituted ester is much lower with aliphatic than with aromatic halides. In this connection Nef has stated that "the more negative the group introduced into the molecule the higher will be the proportion of the

[1] Presented at the Pasadena meeting of the American Association for the Advancement of Science, June, 1931. Financial assistance in this work has been received from the research funds of the University of California.

[2] Conrad and Guthzeit, *Ber.*, **15**, 2841 (1882); Nef, *Ann.*, **266**, 52 (1891).

[3] Vorländer and von Schilling, *Ber.*, **32**, 1876 (1899).

[4] Macbeth and Stewart, *J. Chem. Soc.*, Proc., **29**, 11 (1913).

disubstituted product." In our experiments with benzyl chloride, using methyl or ethyl alcohol as the solvent, mono- and dibenzylmalonic ester were formed in approximately a 2 to 1 molar ratio. With no solvent the ratio was increased. In this case the yield was lower than in the other experiments due to the formation of a crust of sodium malonic ester on the sodium[5] and to the condensation of two or three molecules of sodium malonic ester to give side reaction products.[6] The highest ratio (12.5 to 1) of mono and di-ester resulted when toluene was used as the liquid medium and the reaction mixture allowed to stand for forty-two days at room temperature.

By a quantitative study of the reaction between sodium and malonic ester in toluene evidence was obtained showing that an equal number of moles of sodium and malonic ester was used in bringing the reaction to completion and that only half the available sodium was utilized. Hence it may be concluded that no appreciable quantity of disodium malonic ester was formed under these conditions.

Clean, bright sodium was prepared by heating the commercial product in boiling toluene. Toluene was purified by refluxing it for three and a half hours with metallic sodium, after which it was fractionally distilled. This treatment was necessary to remove a reddish, gelatinous precipitate which formed when C. P. toluene was refluxed with sodium. Malonic ester, b. p. 103–104° (27 mm.) and sp. gr. 1.052, was used.

In each experiment 30 cc. of toluene, 2.00 cc. (0.013 mole) of malonic ester and about 0.7 g. (0.03 mole) of sodium, freshly purified and accurately weighed in toluene, were refluxed under anhydrous conditions in an oil-bath. The reaction mixture was chilled with ice, the liquid decanted and the residual sodium washed with three portions of toluene. The clean sodium was then dissolved in alcohol, diluted with water to a known volume and duplicate 25-cc. portions titrated with 0.1043 *N* sulfuric acid.

The results obtained from a series of such experiments are given in the table below. Since obvious quantitative difficulties are involved in handling metallic sodium, the final values are somewhat in excess of the theoretical.

Time of heating in minutes	Mole of sodium used	Molal ratio of sodium and malonic ester
5	0.00291	0.22
10	.00329	.26
20	.00468	.36
30	.00839	.64
50	.01137	.86
105	.01387	1.05
180	.01445	1.10

Further experiments, designed to test the postulates of Leuchs, were performed using toluene as the liquid medium in order that secondary reactions, initiated by sodium, might be avoided. Definite evidence was obtained for the formation of malonic ester from sodium malonic ester and benzylmalonic ester and of dibenzylmalonic ester from sodium benzyl-

[5] Conrad, *Ber.*, **12**, 749 (1879).

[6] Willstätter, *ibid.*, **32**, 1272 (1899); Baeyer, *ibid.*, **18**, 3454 (1885).

malonic ester and benzyl chloride. Hence it may be concluded that in toluene, and perhaps to some extent in alcoholic solutions, disubstituted derivatives of malonic ester are formed according to this hypothesis.

All substances used in these experiments were highly purified. Sodium malonic ester was prepared as a pale yellow powder by refluxing 23 g. of sodium and 160.5 g. of malonic ester in 1 liter of dry toluene until the sodium had disappeared. Then the toluene was removed by distillation and the residual material heated to 100° (11.5 mm.) for forty-five minutes to drive off the malonic ester. The residue of dry sodium malonic ester and 248.1 g. of added benzylmalonic ester were heated for three hours on a boiling water-bath and the resulting brown solution distilled *in vacuo*. The yield of product, b. p. 90–110° (33 mm.), was 81.5 g. After three additional fractionations at 98–100° (27 mm.), 37.4 g. of material, assumed to be pure malonic ester, was obtained. Equivalent weight values for this substance, found by saponification for thirty minutes with 1 *N* alcoholic potassium hydroxide, were 81.2, 81.5, 81.8 and 79.9 or an average value of 81.2 (calcd. 80.0).

The residual sodium benzylmalonic ester, from which the malonic ester had been completely removed, was refluxed for seven hours in an oil-bath with 126 g. of benzyl chloride and 500 cc. of toluene. The resulting mixture was filtered and the filtrate distilled *in vacuo*. The yield of product, b. p. 220–241° (27 mm.), was 99 g. Refractionation yielded 34 g. of viscous, golden oil, b. p. 233–243° (26 mm.). This product was assumed to be dibenzylmalonic ester since it was identical in appearance and boiling range with a highly purified, known sample of this ester. The unknown oil, saponified by heating it for two hours with 1 *N* alcoholic potassium hydroxide, gave on titration (with thymolphthalein) 178.8 and 170.3 (calcd. 170) as equivalent weight values. Difficulty was experienced in obtaining sharp end-points in titrating the solution due to its deep yellow color.

The assumption that benzylmalonic ester could be formed directly from malonic ester and benzyl chloride and that benzylmalonic ester and benzyl chloride react to give dibenzylmalonic ester is untenable as shown by the following experiments.

One mole each of purified benzyl chloride and malonic ester were refluxed with 235 cc. of anhydrous toluene for ten hours. During this time there was no visible sign of any reaction. Toluene, obtained as the first fraction in the vacuum distillation of the mixture, contained no detectable acid. The remaining liquid distilled completely below 200° (760 mm.). The boiling point of pure benzylmalonic ester is 297–300° (760 mm.).

One mole each of purified benzyl chloride and benzylmalonic ester were refluxed with 250 cc. of anhydrous toluene for ten hours. No evidence of a reaction was noted. On vacuum distillation the liquid distilled completely below 200° (25 mm.). The boiling point of pure dibenzylmalonic ester is 235–240° (28 mm.).

Summary

1. The molal ratios of mono- and dibenzylmalonic ester, formed when equal molal quantities of sodium, malonic ester and benzyl chloride react, were found to be approximately 2 to 1 for methyl and ethyl alcohols, 1.2 to 1 with no solvent and ranging from 2.1 to 1 to 12.5 to 1 with toluene.

2. It was concluded from a quantitative study of the reaction between sodium and malonic ester in toluene that no appreciable quantity of disodium malonic ester was formed under the experimental conditions.

3. The view of Leuchs, that disubstituted derivatives of malonic ester may be formed directly from the reactants, is supported by our experiments.

Los Angeles, California

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

THE REACTIONS OF ANHYDRACETONEBENZIL WITH CERTAIN HALOGEN COMPOUNDS

BY C. F. H. ALLEN AND E. W. SPANAGEL

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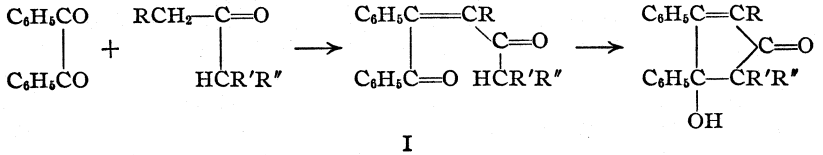
It has been shown by Japp and his co-workers[1] that benzil condenses with many aliphatic ketones; the primary product is an α,β-unsaturated ketone. If the latter still contains a hydrogen atom in the alpha position to the carbonyl group, it usually cannot be isolated but undergoes an intramolecular addition to form a cyclic ketone (I).

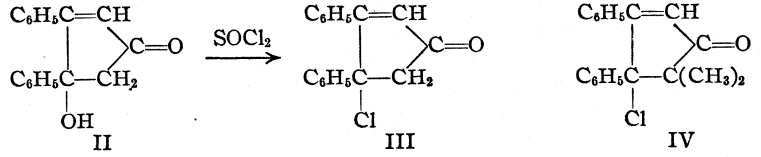


I

The ring compounds have been shown to be derivatives of cyclopentanone.

Gray[2] prepared the two isomeric benzal derivatives (XVI) of anhydracetonebenzil (II), both of which gave the same acetate when treated with acetic anhydride and sulfuric acid, and used this series of reactions as evidence for the presence of an OH group in the starting material. Because of the tendency for this substance (II) to lose water with the usual acylating and dehydrating agents, it does not form esters, although tertiary alcohols generally form halides rather than esters when treated with acid halides.

We have treated anhydracetonebenzil (II) and its dimethyl derivative (XX) (formula I, R′ and R″ = CH_3) with acetyl chloride and have obtained chlorides (III, IV). Since thionyl chloride acted in a similar manner to give the same substances it would seem conclusive evidence that there is a tertiary hydroxyl group as shown by the formula.



II III IV

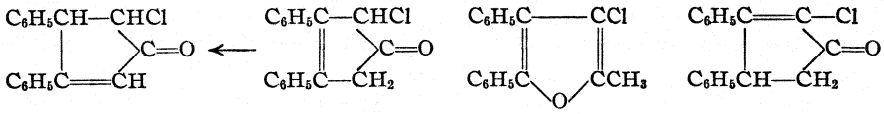
However, by the action of hydrogen chloride on anhydracetonebenzil, Japp prepared a chloride isomeric with ours, of which he was unable to determine the constitution, so it was necessary for us to account for the second chloride and determine the structures of both.

All the possible structures are represented by formulas III, V, VI, VII, VIII. Since the chlorides have a carbonyl group, the chlorofuran VII is

[1] Japp and co-workers, *J. Chem. Soc.*, (a) **47**, 11 (1885); (b) **51**, 420 (1887); (c) **57**, 662 (1890); (d) **71**, 1138 (1897); (e) **75**, 1017 (1899); (f) **79**, 1024 (1901); (g) **85**, 1473 (1904); (h) *Ber.*, **18**, 179 (1885); (i) **21**, 2933 (1888).

[2] Gray, *J. Chem. Soc.*, **95**, 2131 (1909).

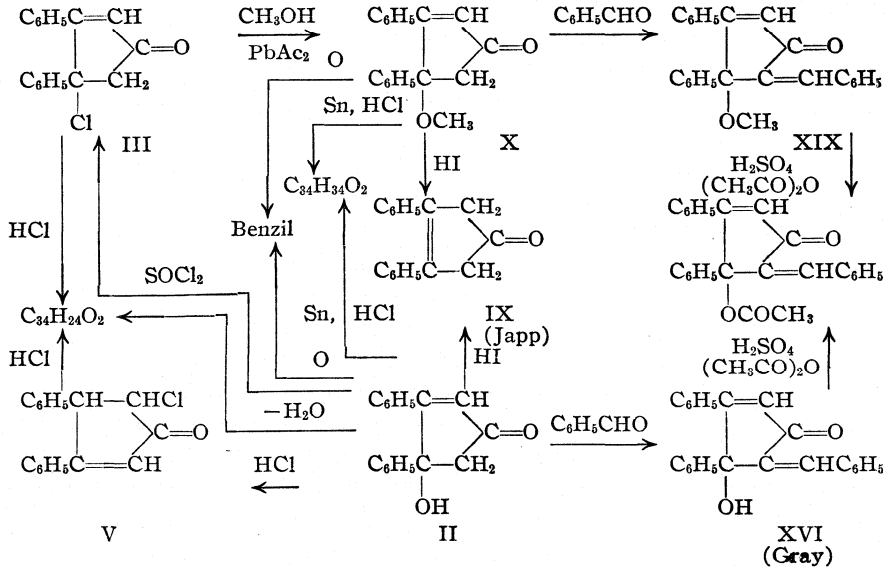
excluded. Formula VI seems improbable, *a priori*, because, having hydrogen between two unsaturated linkages, the hydrogen could shift and, doubtless, would do so, resulting in V.



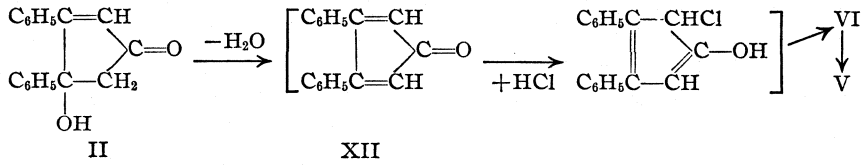
V VI VII VIII

Our chloride formed a methyl ether when treated with potassium, lead or silver acetates in absolute methanol. This ether still contained the five-membered ring since it formed the same reduction products as anhydracetonebenzil (*e. g.*, hydrogen iodide gave a cyclopentenone (IX) and stannous chloride a bimolecular reduction product); oxidation gave benzil. It formed an oxime, and condensed with benzaldehyde to give a pair of geometrical isomers (XIX), showing that the CH_2 was still next to the carbonyl group. It gave a dibromosubstitution product with sodium hypobromite.

Both chlorides (Japp's and ours) on treatment with basic reagents lost hydrogen chloride and gave the same bimolecular product, $C_{34}H_{24}O_2$ (the structure of this will be taken up later; it is also formed from anhydracetonebenzil and dehydrating agents). Barring molecular rearrangements, only substances represented by formulas III and V could lose hydrogen chloride to give the same substance; accordingly our chloride is best represented by formula III and Japp's must be V. Additional evidence in favor of V for Japp's chloride is the non-formation of a benzal derivative. These reactions may be summarized by the flow sheet



Since alkaline reagents act alike on both chlorides and remove hydrogen chloride, a structure of a cyclopentadieneone (XII) can be written as possible for the primary product; in view of the ease with which cyclopentadiene polymerizes, it is not surprising that the ketone does. Now when anhydracetonebenzil is treated with hydrogen chloride without taking precautions, only the chlorine-free bimolecular product, $C_{34}H_{24}O_2$, is found; *i. e.*, the hydrogen chloride acts as a dehydrating agent. In view of this, Japp's chloride is probably formed by addition of hydrogen chloride to the ends of the conjugated system in the cyclopentadieneone (before it polymerizes), followed by the usual shift of enolic hydrogen on a double bond.



II XII

β,β-Dimethylanhydracetonebenzil (XX), which has no alpha hydrogen and cannot be dehydrated, did not give a chloride with hydrogen chloride. Also substance (III) gave a mixture of the bimolecular compound and Japp's isomer (V) when treated with hydrogen chloride. These reactions are in agreement with the proposed mechanism.

By the use of hydrogen bromide we have made a bromide that behaves like Japp's chloride in all respects, and loses hydrogen bromide with alkaline reagents to give the same bimolecular product; it is, therefore, represented by formula V (Br for Cl).

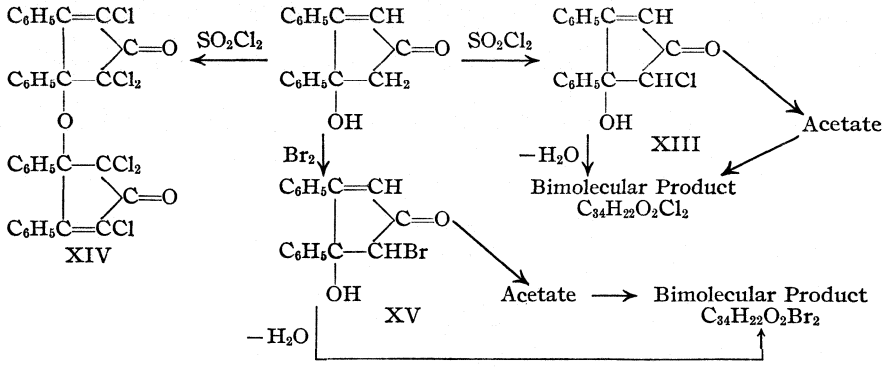
The only known cyclopentadieneone, which has been made by Dilthey,[3] is a tetraphenyl (two remaining H in XII replaced by C_6H_5); it does not polymerize, probably because of the hindrance of the additional phenyl groups.

In the absence of a solvent, phosphorus trichloride dehydrated anhydracetonebenzil and gave the bimolecular product, $C_{34}H_{24}O_2$; in dry benzene it formed the chloride (III). This same chloride was also obtained by the use of phosphoryl chloride and anhydrous aluminum chloride in benzene. Arsenic trichloride showed no action. Sulfur chloride reacted vigorously but gave intractable oils and gums.

Sulfuryl chloride gave two products; one was formed by a simple substitution of one hydrogen in the alpha position, yielding a monochloroanhydracetonebenzil (XIII). The other was a bimolecular hexachloride, for which the most probable formula is represented by (XIV). Formula (XIII) is preferred to one having the chlorine on the doubly bound carbon by analogy with the dimethyl homolog (XX), which does not react at all

[3] Dilthey and Quint, *J. prakt. Chem.*, [2] **128**, 149(1930).

with sulfuryl chloride, and because the chlorine is active enough to be removed readily by alkaline reagents.

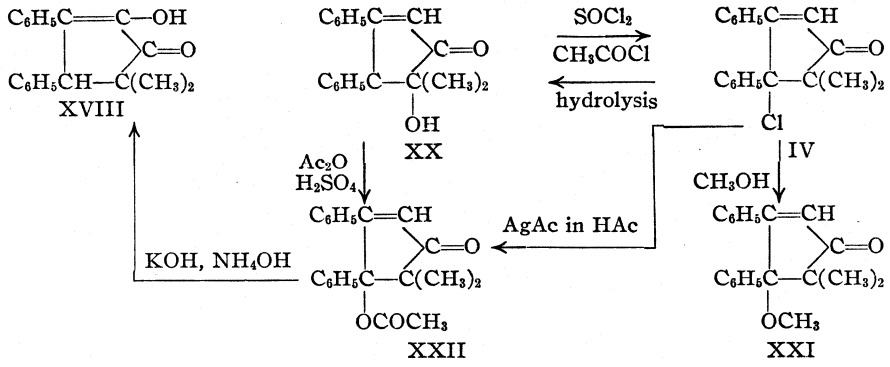


The monochloro ketone (XIII) was dehydrated under the same conditions as anhydracetonebenzil and formed a bimolecular product with essentially the same properties as $C_{34}H_{24}O_2$, but containing two chlorine atoms.

Japp brominated anhydracetonebenzil and obtained a monobromo substitution product for which he gave a melting point of 172° but wrote no formula. On trying to repeat his work, we also obtained a monobromo substitution product, but the melting point was 198°—we have been able to get but one and never any other melting point. Now if a formula (XV) is assigned to this substance, it is evident that two stereoisomers can exist—this may account for the variation. On dehydration this bromo ketone gave a bimolecular compound with the characteristic properties of $C_{34}H_{24}O_2$, but containing two bromine atoms. Therefore, by analogy, the structures of the bromo and chloro ketones and the bimolecular products are similar.

In the dimethyl series a few new relations have been established. With acetyl and thionyl chlorides, dimethylanhydracetonebenzil (XX) formed the chloride (IV). The latter regenerated the hydroxy compound with potassium hydroxide, and potassium or silver acetates in alcoholic solution, but with silver acetate in acetic acid gave the same acetate (XXII) that had been previously prepared by Gray[2] from the hydroxy compound, acetic anhydride, and sulfuric acid. The acetate, on hydrolysis with alcoholic potash, did not regenerate the hydroxy compound from which it was made, but the isomer (XVIII).[2] The latter was not affected by acetyl or thionyl chlorides. Neither of the hydroxyl compounds (XX, XVIII) was affected by concentrated sulfuric acid.

The chloride (IV) readily formed a methyl ether (XXI). These reactions are summarized in the following outline



Experimental

A. Reactions with Anhydracetonebenzil, (II). (a) The Chloride (III).—A mixture of 20 g. of anhydracetonebenzil[1e] and 40 cc. of acetyl chloride was stirred mechanically at room temperature until the solid had dissolved (eight hours). On spontaneous evaporation, 14 g. (65%) of a yellowish solid remained; after repeated crystallization from *n*-butyl ether it formed rods, m. p. 121°.

Anal. Calcd. for $C_{17}H_{13}OCl$: Cl, 13.2. Found: Cl, 13.4.

The chloride is sparingly soluble in petroleum ether and readily soluble in the other usual organic solvents. In alcoholic solution it reacted with the solvent and a bimolecular product, $C_{34}H_{24}O_2$, identical with the one described by Japp,[1b] separated. The latter substance was also formed by the action of heat or light on the chloride; it formed cubes from benzene, m. p. 199–200° with gas evolution.

This chloride was also prepared from anhydracetonebenzil and thionyl chloride, phosphorus trichloride, phosphoryl chloride and anhydrous aluminum chloride, in benzene solution by refluxing 1 g. of the ketone, 2 g. of the chloride, and 10 cc. of dry benzene for ten minutes, pouring into 100 cc. of water, separating the upper layer, washing and drying over calcium chloride. The solvent was evaporated from the filtered solution and the residue dissolved in ether; on slow spontaneous evaporation, 0.5 g. of the chloride crystallized. The yields were of this order except with the aluminum chloride, where a large amount of oily by-product resulted. In the absence of a solvent phosphorus trichloride acted only as a dehydrating agent to give the bimolecular product. Arsenic trichloride showed no action under any of the conditions tried. Sulfur chloride gave only unmanageable oils.

(b) The Chloride (V) (Japp's).—This was made as previously described[1b] as well as by the action of hydrogen chloride on the chloride (III). It melted at 128°.

Dry hydrogen chloride was bubbled through a solution of 0.5 g. of the chloride (III) in 10 cc. of ether until absorption ceased. The solvent was allowed to evaporate spontaneously after twelve hours; a residue composed of oil and two kinds of crystals was separated into the starting material and the bimolecular product, $C_{34}H_{24}O_2$. From the oil a few milligrams of the chloride (V) was isolated. All these substances were identified by means of mixed melting points.

The chloride was recovered unchanged after boiling with pyridine or either alcoholic or acetic acid solutions of silver and potassium acetate. Alcoholic potash, however, removed hydrogen chloride and the bimolecular product resulted. A mixture of 0.5 g. of the chloride, 1 cc. of 10% aqueous potassium hydroxide and 10 cc. of alcohol was refluxed for ten minutes, poured into water, and the precipitated solid filtered and recrys-

tallized. The yield was practically quantitative. Its properties showed that it was the bimolecular product.

To prove the presence of a carbonyl group, the 2,4-dinitrophenylhydrazone was prepared. One gram of 2,4-dinitrophenylhydrazine was dissolved in 1 cc. of concentrated sulfuric acid and carefully diluted with 10 cc. of alcohol; this mixture was at once added to a solution of 1 g. of the chloride in 30 cc. of alcohol, and the whole warmed for five minutes. On cooling, a fine reddish solid separated and was filtered; it was purified by recrystallization from acetic acid, and formed red needles, m. p. 217°; yield, 0.9 g. or 54%. It is insoluble in all the common organic solvents

Anal. Calcd. for $C_{23}H_{17}N_4Cl$: N, 12.5. Found: N, 12.4.

(c) The Bromide (V) (Br for Cl).—Ten grams of anhydracetonebenzil was suspended in 25 cc. of chloroform, previously saturated with hydrogen bromide. After twenty-four hours the solvent was evaporated and the deeply colored residue taken up in alcohol and repeatedly crystallized. It yielded 6 g. (50%) of white, diamond-shaped prisms, m. p. 113°.

Anal. Calcd. for $C_{17}H_{13}OBr$: Br, 25.6. Found: Br, 25.6.

Like the chloride, this bromide was not affected by the metal acetates, but with alcoholic potash gave the bimolecular product.

(d) The Methyl Ether (X).—In methyl alcohol in the presence of lead or silver acetates, the chloride (III) formed the corresponding methyl ether. The latter was also formed in small amounts when very dilute methyl alcoholic potassium acetate or hydroxide was used, but the principal product was the bimolecular compound; only the latter was obtained with more concentrated solutions.

A suspension of 10 g. of the chloride, 10 g. of lead acetate, and 60 cc. of methyl alcohol was refluxed for a half hour; the solid soon went into solution, and then lead chloride precipitated. The latter was removed by filtration and from the filtrate white hexagonal prisms separated in a yield of 7 g. (69%). These were recrystallized from methyl alcohol; m. p. 126°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.7; H, 6.1; OCH_3, 11.7. Found: C, 81.2, 81.4; H, 6.2, 5.9; OCH_3, 12.0.

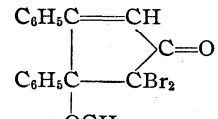
The methyl ether is insoluble in petroleum ether, sparingly soluble in ethyl ether, and readily soluble in the other usual organic solvents.

The oxime was prepared in the usual way and formed rods, m. p. 173°, after recrystallization from methyl alcohol.

Anal. Calcd. for $C_{18}H_{17}O_2N$: N, 5.0. Found: N, 5.0.

On reduction with red phosphorus and iodine[4] it formed the cyclopentenone (IX). It was not necessary to vacuum distil, as the solid separated on partial evaporation of the ether. It had a melting point of 110° which showed no depression when mixed with a sample prepared from anhydracetonebenzil. On reduction with tin and hydrochloric acid, it formed the same bimolecular reduction product, $C_{34}H_{34}O_2$, m. p. 187–8°, as anhydracetonebenzil.[1b]

The methyl ether is not attacked by potassium permanganate; in acetic acid hot chromic acid oxidizes it to benzil and benzoic acid. Sodium hypobromite oxidizes anhydracetonebenzil to desylacetic acid[1e] but attacks the methyl ether only very slowly and then introduces two atoms of bromine. The same dibromide was also formed by direct bromination. Since both the bromine atoms are removed by alcoholic potash it is unlikely that either is on the double bond, and the most probable formula is XXIII. Unfortunately, it was



XXIII

[4] Ref. 1e, p. 131.

not possible to isolate any bromine-free hydrolysis products, complete decomposition having taken place.

A mixture of 5 g. of finely powdered methyl ether was mechanically stirred for two hours with a solution of 10 g. of bromine in an excess of 15% sodium hydroxide; no action was apparent. However, on close inspection the filtered solid seemed to be composed of two kinds of crystals; it was separated by means of methyl alcohol, 4 g. of the ether crystallizing first. On longer standing, 0.6 g. of needles formed—these melted at 175° and a mixture with the dibromo ether below also melted at 175°.

A chloroform solution containing an excess of bromine was added to a solution of 1 g. of the methyl ether in 10 cc. of chloroform and the mixture allowed to stand for two days at room temperature; hydrogen bromide was slowly evolved. The solvent and unused bromine were removed and the product crystallized from alcohol. It formed fine needles, m. p. 175°.

Anal. Calcd. for $C_{18}H_{14}O_2Br_2$: Br, 37.9; OCH_3, 7.4. Found: Br, 37.7; OCH_3, 7.4.

The Benzal Derivatives (XIX).—A solution of 30 cc. of absolute alcohol, 5 g. of the methyl ether, an equal weight of benzaldehyde, and the sodium ethylate from 0.5 g. of sodium and 10 cc. of alcohol was refluxed for ten minutes; the solid that separated was filtered and crystallized from alcohol; yield, 4.5 g. It formed rods, m. p. 160°. The reddish filtrate was poured into water to precipitate the isomeric form, which after several recrystallizations from alcohol or dilute acetone melted at 124°.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.2; H, 5.7; OCH_3, 8.8. Found: (160°) C, 85.5; H, 5.5; OCH_3, 8.8; (124°) C, 84.7; H, 5.6.

Both of these benzal derivatives on treatment with acetic anhydride and concd. sulfuric acid formed the known acetate (XVII), m. p. 175°, identical with the one prepared in the same manner from anhydracetonebenzil.[2]

Hydrogen chloride converted the methyl ether into a mixture of Japp's chloride (V), and the bimolecular compound, $C_{34}H_{24}O_2$; probably chloride (III) was a primary product, and then was altered as already described.

A solution of 1 g. of the ether in 20 cc. of alcohol was saturated with hydrogen chloride; the reddish solution was left at room temperature overnight and then poured into 150 cc. of water. The amorphous precipitate was filtered and taken up in alcohol; from the latter solution, 0.4 g. of the bimolecular compound separated first, and on spontaneous evaporation a few milligrams of Japp's chloride was isolated and identified by a mixed melting point.

(e) **Action of Sulfuryl Chloride; Preparation of Chlorides (XIII) and (XIV).**—From a mixture of 10 g. of anhydracetonebenzil, 30 cc. of benzene and 5 cc. of sulfuryl chloride that had stood overnight, 9 g. of a white solid separated; it crystallized from alcohol in fine white needles, m. p. 194°; the halogen could be removed quantitatively by alcoholic potash. On pouring the filtrate into water, an oil was precipitated—it soon became crystalline and after recrystallization from alcohol weighed 1.5 g. It formed flat rods, m. p. 129°.

Anal. Calcd. for $C_{17}H_{12}O_2Cl$ (194°): Cl, 12.5: for $C_{34}H_{20}O_3Cl_6$ (129°): Cl, 30.9; mol. wt., 688. Found: (194°) Cl, 12.6, 12.7 (129°) Cl, 30.8, 30.8; mol. wt., 546 (Rast's method).

(f) **Bromination.**—Anhydracetonebenzil was treated with bromine, following Japp's directions[1a] as exactly as possible. Our product, obtained in a yield of 6 g., also formed fine white needles from alcohol, but the melting point was 198° instead of the 172° he recorded.

Anal. Calcd. for $C_{17}H_{13}O_2Br$: Br, 24.3. Found: Br, 24.4.

The bromo compound gave an oil on treatment with alcoholic potash. With

acetic anhydride and concd. sulfuric acid a mixture of an acetate and a bimolecular product containing two atoms of bromine was formed.

A suspension of 5 g. of the bromine compound (XV) in 15 cc. of acetic anhydride cleared up and became warm when a trace of sulfuric acid was introduced. On cooling, 1.5 g. of a solid separated and was filtered, and the filtrate decomposed by ice. An oily mixture resulted, from which 1.5 g. of an acetate and a small amount of the first solid separated. The acetate was purified by recrystallizing several times from alcohol, and formed needles, m. p. 148°.

Anal. Calcd. for $C_{19}H_{15}O_3Br$: Br, 21.6. Found: Br, 21.4.

The high melting solid was recrystallized from *n*-butyl ether; it formed prisms, m. p. 212°, with gas evolution.

Anal. Calcd. for $C_{34}H_{22}O_2Br_2$: Br, 25.7. Found: Br, 26.0.

It is practically insoluble in petroleum ether, ethyl ether, the alcohols, benzene, acetone, and glacial acetic acid, but moderately soluble in chloroform.

The chloride (XIII) on similar treatment with acetic anhydride and a trace of sulfuric acid also formed an acetate and a bimolecular product. The acetate separated as needles from alcohol, m. p. 159°, and the bimolecular product crystallized in very fine prisms from *n*-butyl ether, m. p. 217° with gas evolution.

Anal. Calcd. for $C_{19}H_{15}O_3Cl$ (159°): Cl, 10.9; for $C_{34}H_{22}O_2Cl_2$ (217°): Cl, 13.3. Found: (159°) Cl, 10.6, 10.8; (217°) Cl, 13.3.

The bimolecular chloride was the only product if acetic acid was substituted for the anhydride. It was also formed in all attempts to hydrolyze the acetate, even when using ammonia at room temperature.

The bimolecular chloride and bromide exhibit the same peculiar properties as Japp's bimolecular compound, $C_{34}H_{24}O_2$; their structures will be considered in a later paper.

(g) Reactions with β,β-Dimethylanhydracetonebenzil (XX).—This was prepared by a method essentially like Japp's.[1f] The requisite methyl *i*-propyl ketone and *i*-butyraldehyde were obtained by oxidation of methyl-*i*-propylcarbinol and *i*-butyl alcohol, respectively; the carbinol was made by the action of methylmagnesium iodide on *i*-butyraldehyde. The latter was prepared by the general directions for propionaldehyde,[5] keeping the water in the reflux condenser at 65°; the yield was 50%.

The methyl-*i*-propylcarbinol was made through the Grignard reaction as follows. In the usual type of apparatus were placed 150 cc. of dry ether and 53 g. of magnesium turnings, and a mixture of 355 g. of methyl iodide and 150 cc. of dry ether added, with stirring, at such a rate as to keep the solution refluxing vigorously, followed by thirty minutes' heating on the water-bath. The mixture was then chilled to −5°, and, with stirring, 159 g. of *i*-butyraldehyde in 150 cc. of dry ether slowly admitted; the whole was then heated on the water-bath for two hours. The contents of the flask were decomposed by pouring upon 1 kg. of cracked ice and the basic magnesium salt was dissolved by the addition of 500 cc. of 15% sulfuric acid. The upper layer was separated, the aqueous solution extracted with three 150-cc. portions of ether, the combined ethereal solutions washed with sodium carbonate and water, and dried over anhydrous sodium sulfate. The solvent was removed and the residue fractionated; 94 g. (60%) of carbinol, b. p. 109–111°, was obtained.

The methyl *i*-propyl ketone was then prepared by oxidation of this carbinol as follows. In a 1-liter three-necked flask, fitted with a good fractionating column, stirrer and dropping funnel, was placed 73 g. of the above carbinol, the flask was immersed in a water-bath, the temperature of which was 60°, and, while stirring vigorously, a mixture of 82 g. of potassium dichromate, 60 cc. of concd. sulfuric acid and 500 cc. of water was

[5] "Organic Syntheses," Vol. XII.

slowly admitted through the dropping funnel. When addition had been completed, the contents of the flask were distilled as long as oily drops appeared in the condenser. The distillate, composed of two layers, was saturated with solid potassium carbonate, the ketone separated and dried with potassium carbonate. On fractionating, 39 g. (55%) of a product was secured, b. p. 90–94°. Potassium permanganate was unsatisfactory as an oxidizing agent. Diethyl ketone was similarly prepared from the commercial diethylcarbinol, at 65°, and methyl *n*-propyl ketone from methyl-*n*-propylcarbinol at 60° in yields of 73 and 70%, respectively.

Neither dimethylanhydracetonebenzil (XX) nor its isomer (XVIII) was affected by dissolving in concd. sulfuric acid; they were precipitated unchanged when the colored solutions were poured upon ice. The former gave deep green solutions with mineral acids, but we were unable to isolate a perchlorate. The latter was not affected by thionyl chloride.

The Chloride (IV).—A mixture of 3 g. of dimethylanhydracetonebenzil and 10 cc. of thionyl chloride was refluxed for a half hour, poured into water and filtered. The solid was then dissolved in ether, the solution dried with calcium chloride and decanted, and a small amount of petroleum ether added; on spontaneous evaporation a solid separated. The latter formed fine needles when recrystallized from *n*-butyl ether, m. p. 133°. It is very soluble in the usual solvents except petroleum ether, and the only one suitable for crystallizing was the one used.

Anal. Calcd. for $C_{19}H_{17}OCl$: C, 76.4; H, 5.7. Found: C, 76.9; H, 5.7.

Hydrolysis.—On refluxing 0.1 g. with a very dilute solution of potassium hydroxide in alcohol for ten minutes, a white solid separated; this was filtered and found to be the hydroxyl compound by mixed melting point and solubilities. Potassium and silver acetates in alcohol led to the same result.

The Acetate (XXII).—A mixture of 0.2 g. of the chloride and 0.3 g. of silver acetate in 10 cc. of glacial acetic acid was refluxed for ten minutes, cooled and filtered into 100 cc. of water. The precipitated acetate was removed and crystallized from alcohol; it melted at 137° and a mixture with a sample of the acetate prepared by Gray's method likewise melted at 137°. On hydrolysis as described by Gray, it formed the hydroxy ketone (XVIII).

The Ether (XXI).—A mixture of 1 g. of the chloride and an equal weight of silver acetate in 15 cc. of absolute methyl alcohol was refluxed a quarter hour, filtered hot and water added slowly to precipitate the ether. It crystallized from dilute methyl alcohol in clusters of prisms, m. p. 144°; the yield was 0.6 g. It was very soluble in alcohol, acetic acid, benzene and acetone, but separated from the first two on dilution with water.

Anal. Calcd. for $C_{20}H_{20}O_2$: OCH_3, 10.6. Found: OCH_3, 10.7.

This work has been assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. By the action of thionyl, acetyl, phosphoryl, and anhydrous aluminum chlorides on anhydracetonebenzil, a tertiary chloride that resembled triphenylchloromethane in several respects was prepared. This reaction furnished direct proof of the presence of a tertiary hydroxyl group in anhydracetonebenzil.

2. The structure of an isomeric chloride formerly prepared by Japp has been established, and a mechanism proposed to account for its formation.

3. Sulfuryl chloride acted principally as a chlorinating agent.
4. Some new relations were determined in the dimethyl series.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

CONDENSATIONS AND RING CLOSURES IN THE NAPHTHALENE SERIES. III.[1] *PERI*-SUCCINOYLACENAPHTHENE

BY LOUIS F. FIESER AND (IN PART) MARY A. PETERS

RECEIVED JUNE 16, 1932 PUBLISHED NOVEMBER 5, 1932

Having found that the condensation of β-naphthol with phthalic anhydride leads to the production of a compound of an unusual structural type,[1a] it has become a matter of interest to study the reaction of various other naphthalene derivatives with this and other anhydrides. It has been our immediate concern to investigate more fully certain condensations which fall within the field specified, but which have been described only in the patent literature. These condensations are between succinic or maleic anhydride and various substitution products of naphthalene. In a series of patents originating with the I. G. Farbenindustrie,[2] it is claimed that cyclic compounds of novel structure may be obtained either by heating the components in molten sodium aluminum chloride or by applying this method of condensation to the intermediate products resulting from the Friedel and Crafts reaction of the anhydride with the hydrocarbon.

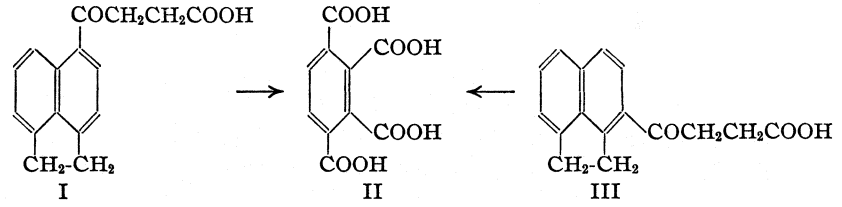
After some trial of these reactions it was decided that the case most favorable for detailed study was that of the condensation of succinic anhydride with acenaphthene. As specified in the patents, these components interact smoothly at 0° in nitrobenzene solution in the presence of aluminum chloride.[3] The keto acid melting at 208° is not, however, the sole reaction product, but is accompanied by an isomer melting at 181°. The separation of the isomers is easily accomplished and it was further found that the relative proportions of the two acids is somewhat dependent upon the reaction temperature. Thus the yields at 0° were 78 and 15% for the higher and the lower melting isomers, respectively, while at −15° the yields were 87 and 5%. The structures were established by oxidation. The higher melting acid is β-(3-acenaphthoyl)-propionic acid, I, for it yields 1,4,5-naphthalenetricarboxylic acid on controlled permanganate oxidation. No acid of the naphthalene series could be obtained from the

[1] (a) First paper, Fieser, THIS JOURNAL, **53**, 3546 (1931); (b) second paper, Fieser and Peters, THIS JOURNAL, **54**, 3742 (1932).

[2] (a) I. G. Farbenindustrie, French Patent 636,065 (1928); (b) Swiss Patent 131,-959 (1929); (c) H. Gruene, U. S. Patent 1,759,111 (1930).

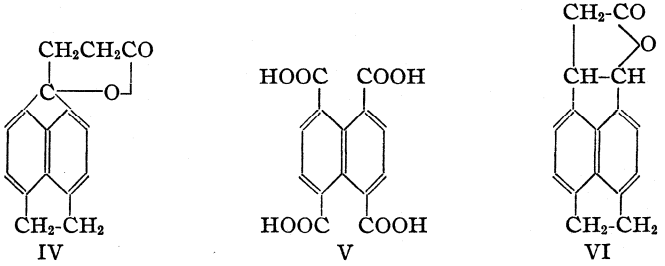
[3] The reaction is also described by F. Mayer, German Patent 376,635 (1923).

isomer melting at 181°, but on complete oxidation it was converted into a substance having the properties of mellophanic acid, II.[4]



Since, however, this acid melts at practically the same temperature as the other possible oxidation product, prehnitic acid (1,2,3,5), it was necessary to obtain an authentic sample of mellophanic acid for comparison. This was conveniently prepared by oxidizing the higher melting keto acid, I, and the two products were found to be identical. The acid melting at 181° is thus β-(1-acenaphthoyl)-propionic acid, III.

When the 3-acenaphthoylpropionic acid is heated in molten sodium aluminum chloride at 150°, it is converted, with loss of the elements of water, into an alkali-insoluble, yellow compound. A condensation of the type described in our first paper[1a] would give a substance of the structure of IV, but this formula for the yellow compound is ruled out by the observation recorded in the patent literature,[5] which we have confirmed, that the yellow substance is converted smoothly into 1,4,5,8-naphthalenetetracarboxylic acid, V, on oxidation.



Presumedly on the basis of this reaction, the authors of the series of patents have suggested formula VI as the structure of the condensation product. This would represent not only a novel reaction but a type of ring structure which has not yet been obtained. It would be a derivative of the unknown "aceacenaphthene" which Mayer and Kaufmann sought to prepare by closing a second five-membered ring across the remaining *peri*-positions of acenaphthene.[6] No more successful was an attempt

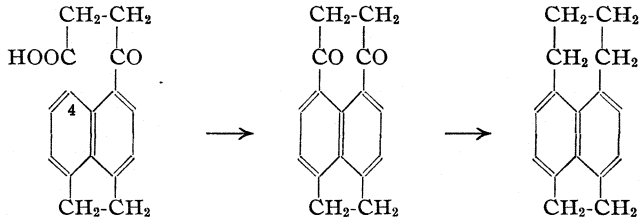
[4] Bamford and Simonsen, *J. Chem. Soc.*, **97**, 1908 (1910), proved that this is the structure of mellophanic acid, rather than of prehnitic acid, as stated in most of the current works of reference.

[5] I. G. Farbenindustrie, Swiss Patent 134,084 (1929).

[6] Mayer and Kaufmann, *Ber.*, **53**, 289 (1920).

made in the course of the present work to effect an intramolecular Friedel and Crafts reaction with β-bromo-β-(3-acenaphthoyl)-propionic acid, a reaction which might have opened the way for a synthesis of VI. Much more significant than the failure of these attempted ring closures is the observation of Scholl that 1,4-anthrahydroquinonedicarboxylic acid forms a mono- but not a di-lactone, whereas the 1,5-acid forms a dilactone.[7] This is a good indication of the resistance to the closing of five-membered rings across both *peri*-positions of the naphthalene nucleus.

Further study of the yellow condensation product soon showed that the properties of the compound are not consistent with the lactone formula, VI. The solubility of the compound in alcohol is indeed increased by the addition of alkali, but no salt or free acid could be obtained. It has, on the other hand, the properties of a diketone, for it yields a dioxime, and it may be reduced smoothly by the Wolff–Kishner method. These facts, together with the result of oxidation, establish the structure, indicated in formula VII, of *peri*-succinoylacenaphthene. The reduction product must have the structure of VIII. The condensation involves the splitting



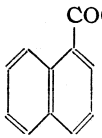
out of water between the carboxyl group of the keto acid, I, and the hydrogen atom in position 4. The surprising feature of the reaction is that it leads to the closure of a seven-membered ring. The aromatic keto acids condense readily enough under the influence of aluminum chloride, but they yield 6-ring products.[1b]

It is of interest to inquire into the factors favoring the unusual condensation here noted. The difficulty of formation of a 7-ring, particularly where the closure of a 6- or 5-ring is also possible, is clearly indicated by the investigations of von Braun.[8] In the case of acenaphthoylpropionic acid, the closure of a 6-ring is also possible, but it would involve substitution at a position *ortho* to an unsaturated group, and it is perhaps this factor which impedes the reaction. It is reasonable to suppose that, on the other hand, the closing of a 7-ring through a *peri* condensation is facilitated by the presence of the acenaphthene dimethylene bridge, which must activate the 4-position. This idea is to a certain extent substantiated

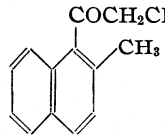
[7] Scholl and Böttger, *Ber.*, **63**, 2128 (1930).

[8] Von Braun and collaborators, *Ann.*, **468**, 259, 277 (1929); *Ber.*, **50**, 56 (1917); **59**, 1922 (1926); **60**, 1182 (1927); **61**, 956 (1928); **62**, 145 (1929).

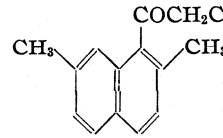
by the observation that β-(1-naphthoyl)-propionic acid (IX), in which such activation is lacking, does not undergo condensation but is converted into the 2-isomer in the sodium aluminum chloride melt. Attempts to pursue the question further through a study of the methylated acids X



IX



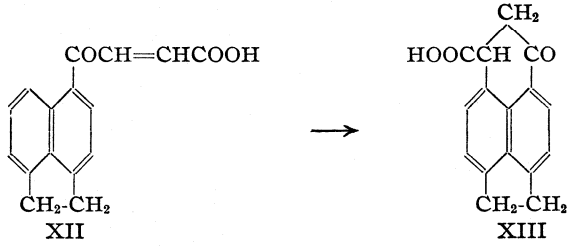
X



XI

and XI were without conclusive result, for we were unable to isolate any reaction products from the resins resulting from the action of aluminum chloride on these substances. No better results were obtained with the keto acid prepared from β-naphthol and succinic anhydride.

In short, in so far as our observations extend, the formation of *peri*-succinoylacenaphthene represents a wholly unique reaction. In no other case investigated do all of the features of structure so combine to favor the closing of a 7-ring as they do in the case of β-(3-acenaphthoyl)-propionic acid. That even the corresponding acenaphthylbutyric acid reacts in a different manner will be shown in a forthcoming paper. The claim set forth in the patents that the formation of cyclic compounds of this type is a general one is thus to be discounted. It should be stated, however, that not all of the condensations claimed in the patents in question are of exactly the above type, for some of them involve the use of an unsaturated keto acid. We have made no study of this type of reaction beyond preparing and analyzing the condensation product from the unsaturated acid XII.



XII XIII

The substance is acidic and isomeric with the starting material, so that the reaction is evidently quite different from the one described above. It appears probable that the reaction consists in intramolecular addition to the conjugated system, and that the condensation product has the structure of XIII.

Experimental Part

1. Preparation of the Acenaphthoyl Propionic Acids.—The essential features of the general procedure given in the patent literature[2,3] for the condensation of succinic anhydride with naphthalene and its derivatives are: the use of nitrobenzene as the

solvent, a low reaction temperature, a 10% excess of the anhydride and of aluminum chloride. In the course of our work we took occasion to change the solvent, the temperature and the molecular ratio, but the best results were always obtained by adhering to the conditions specified.

A solution of 100 g. of pure acenaphthene and 72 g. of succinic anhydride in 600 cc. of nitrobenzene was prepared in a 3-liter long-necked flask equipped with a mechanical stirrer working through a 3-way addition tube, and cooled in a large ice-bath. In the course of one hour 195 g. of aluminum chloride was added in small portions. Stirring was continued at 0° for four hours more and the deep red solution was allowed to stand for twelve hours and come to room temperature. After the cautious addition, with cooling, of 200 g. of ice and 100 cc. each of water and concentrated hydrochloric acid, the solvent was removed with a rapid stream of steam and using an efficient condensing system. After about one and one-half hours the product separated as a pasty lump which disintegrated after four to five hours of further steaming to a grayish-white powder. This material was collected, dissolved in a solution of 115 g. of sodium carbonate decahydrate in 1 liter of water, and the last traces of nitrobenzene were removed by steam distillation. One hundred grams of sodium chloride was dissolved in the hot, filtered, brown solution, which was then allowed to cool without disturbance. The sodium salt of β-(3-acenaphthoyl)-propionic acid separated as colorless, fibrous needles, while the 1-acid largely remained in solution. The solid was washed free of the dark mother liquor (A) with half-saturated sodium chloride solution and crystallized a second time from a hot, clarified solution containing 50 g. of sodium chloride. The mother liquor (B) was again saved. On acidifying a solution of the purified sodium salt the 3-acenaphthoylpropionic acid was obtained as a white powder and in very pure condition; m. p. 208°; yield, 120 g. (73%).

On acidifying the first mother liquor (A) there was obtained a product which was dark and tarry but which soon solidified on being stirred. After boiling a soda solution of the material with animal charcoal and reprecipitating it from a cold solution, a light tan product was obtained (35 g.). It was combined with the solid (8 g.) precipitated from the mother liquor (B) and esterified with methyl alcohol (300 cc.) and sulfuric acid (15 cc.). On boiling for a short time the material all went into solution and on cooling there was obtained a mass of dark crystals consisting largely of the ester of β-(1-acenaphthoyl)-propionic acid. This is considerably less soluble than the 3-ester, and it was easily obtained in pure condition by crystallization from alcohol; m. p. 126°; yield, 26.4 g. (15%). The recovery of the 3-acid from the alcoholic mother liquors is hardly profitable, but it is easily accomplished by concentrating the solutions, hydrolyzing with alkali, and purifying the 3-acid through the sodium salt, the yield being 8 g. (5%).

The total yields at 0° were thus 78% of the 3-acid and 15% of the 1-acid. At −15° these substances were obtained in yields of 87 and 5%, respectively. At room temperature there was some increase in the proportion of the 1-acid but the product was very dark and difficult to work up and the total yield was lower.

β-(3-Acenaphthoyl)-propionic acid (I) is only moderately soluble in glacial acetic acid, alcohol or xylene, but it crystallizes well from these solvents as stout needles melting at 208° with some decomposition. It decomposes somewhat on distillation at diminished pressure. The solution in concentrated sulfuric acid is red and the material is either sulfonated by this treatment or recovered unchanged. Only dark tars were obtained on attempting to prepare an acid chloride.

Anal.[9] Calcd. for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.55; H, 5.65.

[9] The analyses here reported were ably carried out by Mr. C. L. Bickel.

The methyl ester was prepared by heating a suspension of 100 g. of the acid in 500 cc. of methyl alcohol with 25 cc. of concentrated sulfuric acid. The material soon dissolved and the ester was deposited on cooling in good yield and in nearly pure condition. The substance is very soluble in methyl alcohol and forms plates melting at 89°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.01. Found: C, 76.35; H, 6.22.

The methyl ester oxime forms colorless needles, m. p. 146°, from benzene–ligroin.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.06; H, 6.05. Found: C, 72.29; H, 6.02.

β-(1-Acenaphthoyl)-propionic acid (III), obtained by hydrolyzing the ester with alcoholic alkali, crystallized from dilute alcohol as small needles melting at 181°. It is considerably more soluble than the isomer and this is also true of the sodium salt. The sulfuric acid solution is red-orange in color.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.56; H, 5.55. Found: C, 75.79; H, 5.77.

The methyl ester gives long needles from alcohol or dilute acetic acid, m. p. 126°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.09; H, 6.01. Found: C, 76.16; H, 5.98.

2. Oxidation of the Keto Acids.—Attempts to convert β-(3-acenaphthoyl)-propionic acid into an acenaphthenecarboxylic acid were without success. The first oxidation product isolated, using 12.7 g. of the acid and 48 g. of potassium permanganate in alkaline solution, was a yellow acid melting at 259° which has not been identified.

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.85; H, 3.97. Found: C, 71.05; H, 3.76.

Oxidation of the same quantity of acid with 64 g. of potassium permanganate gave *1,4,5-naphthalenetricarboxylic acid.* At the end of the reaction the mixture was treated with sulfur dioxide, which dissolved the brown precipitate and gave a clear solution. On adding hydrochloric acid and heating, the oxidation product precipitated in the form of the anhydride (5 g.). Crystallized from dilute alcohol it melted at 274°.

Anal. Calcd. for $C_{13}H_6O_5$: C, 64.46; H, 2.50. Found: C, 64.62; H, 2.64.

It was found that the *monomethyl ester of the anhydride* is a convenient derivative with which to characterize the compound. It is easily prepared by esterification of the anhydride with methyl alcohol and sulfuric acid. Being sparingly soluble in the medium, it separates at once from the hot solution. It crystallizes well from glacial acetic acid as colorless needles melting at 222°.

Anal. Calcd. for $C_{14}H_8O_5$: C, 65.62; H, 3.15. Found: C, 65.34; H, 3.34.

The 1,4,5-naphthalenetricarboxylic acid anhydride was identified by comparison with a sample, m. p. 274°, prepared according to Graebe.[10]

Mellophanic acid was obtained by gradually adding 105 g. of potassium permanganate to a hot solution of 12.7 g. of the keto acid in 500 cc. of water containing 3 g. of potassium hydroxide, and heating the mixture for one hour on the steam-bath. The solution was decolorized by the addition of a little alcohol, filtered, and the precipitated manganese dioxide was extracted thoroughly with hot water. The filtrate and washings were acidified, boiled down to a volume of 500 cc. and treated with 32 g. of hydrated barium hydroxide. The precipitated barium salt was digested at the boiling point, collected, and boiled with 200 cc. of water containing 3 cc. of concentrated sulfuric acid. The solution, filtered from barium sulfate, was evaporated to a sirup, cooled and treated with 50 cc. of concentrated hydrochloric acid. This precipitated the mellophanic acid in a colorless, crystalline condition; m. p. 236°, with loss of water; yield, 3.2 g. (25%). The tetramethyl ester, conveniently prepared with diazomethane, melted at 129–130°, which corresponds with the observations recorded in the literature.

[10] Graebe, *Ann.*, **327**, 77 (1903).

This method of preparing mellophanic acid has some advantages over the many methods previously recorded, for the starting material is easily prepared and the usual sealed-tube reaction is avoided.

Oxidized in exactly the same manner, β-(1-acenaphthoyl)-propionic acid likewise gave mellophanic acid, m. p. 233°, ester 129–130°.

3. *Peri*-succinoylacenaphthene.—The best results were obtained by condensing the ester rather than the free keto acid. The condensation product was also obtained directly from acenaphthene and succinic anhydride, as specified in the patent literature, but the yields were very poor.

A melt was prepared by fusing together 50 g. of sodium chloride and 250 g. of aluminum chloride. When it had cooled to the point of incipient crystallization (100°), 40 g. of β-(3-acenaphthoyl)-propionic acid methyl ester was stirred in in the course of five minutes. The bright red melt was stirred well, brought to 150° in fifteen minutes, and kept at that temperature for one-half hour, when it had become dark brown. It was stirred into ice and water, which precipitated a dull yellow, slightly tarry product (25 g.). This was boiled with glacial acetic acid and the solution was filtered from a black residue, boiled down and treated with water. The product which precipitated was dried well and distilled *in vacuo*. A considerable residue was left, but the distillate was a good yellow solid from which the pure diketone was easily obtained by crystallization; yield, 15.2 g. (43%).

***Peri*-succinoylacenaphthene** is readily soluble in benzene or glacial acetic acid, moderately soluble in alcohol, and it crystallizes well from any of these solvents, forming long, flat, yellow needles melting at 180°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.25; H, 5.19.

In concentrated sulfuric acid it forms a yellow solution with a faint green fluorescence. Working in the absence of air, it was observed that a suspension of the diketone in alcohol could be brought into solution by the addition of alkali. No stable sodium salt is formed, however, for the diketone precipitated when a relatively small amount of water was added. The solution in alcoholic alkali turns green and then brown on exposure to the air and a black substance is formed. The diketone is not affected by boiling with acetic anhydride and sodium acetate; it is converted into a black tar by concentrated hydrochloric acid at 200°. When heated with methylmagnesium iodide at 100°, 0.2 mol. equiv. of gas was given off and the total consumption of reagent was 2.0 mol. equivalents.

The dioxime was prepared by warming a mixture of 4 g. of the diketone, 6 g. of hydroxylamine hydrochloride, and 30 cc. each of water, alcohol and 6 *N* sodium hydroxide solution until all of the solid had dissolved. The dioxime (4.4 g.) precipitated when the solution was acidified. It crystallized from glacial acetic acid as small, pale yellow needles which decompose on heating. It dissolves easily in concentrated hydrochloric acid and is easily hydrolyzed by this reagent, the diketone crystallizing from the warmed solution.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.15; H, 5.30. Found: C, 72.27; H, 5.25.

The dioxime diacetate crystallizes well from acetic anhydride as tan needles.

Anal. Calcd. for $C_{20}H_{18}O_4N_2$: C, 68.55; H, 5.18. Found: C, 68.87; H, 5.23.

Oxidation of the diketone (2.5 g.) in glacial acetic acid (50 cc.) was carried out, as specified in the patent to which reference has been made,[5] by the addition in portions of 25 g. of sodium dichromate at 80–90°. After boiling the solution for three hours it was poured into 150 cc. of dilute sulfuric acid. The oxidation product was heated in alkaline solution with 0.5 g. of potassium permanganate and reprecipitated from the decolorized and filtered solution. It formed colorless, glistening crystals (1.6 g.).

While 1,4,5,8-naphthalenetetracarboxylic acid has no characteristic melting point, it responds to certain highly specific tests (dissolution of the dianhydride in ammonia solution, precipitation of the diimide, formation and decomposition of the yellow sodium salt of the diimide).[11] Our product corresponded precisely with the description given.

Peri-tetramethyleneacenaphthene (VIII).—We had no success in attempting to reduce the diketone by the Clemmensen method, but the Wolff–Kishner reaction proved satisfactory. A mixture of 1.2 g. of the material, 0.5 cc. of hydrazine hydrate and a solution of 0.9 g. of sodium in 12.5 cc. of absolute alcohol was heated at 160° for eight hours. The reaction product was rather dark colored, but it was easily purified by distillation and crystallization from ligroin. The hydrocarbon gives clusters of well-formed, colorless needles melting at 138°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 92.27; H, 7.72.

4. Other Keto Acids.—As stated in the theoretical part some attempts were made to obtain ring compounds similar to that resulting from the action of aluminum chloride on β-(3-acenaphthoyl)-propionic acid by subjecting similarly constituted acids to the same treatment. Since these attempts were in every case unsuccessful, it will be sufficient here to record very briefly a description of the new compounds investigated. Their properties and analyses are recorded in the table. The condensations of succinic anhydride with β-methylnaphthalene, 2,7-dimethylnaphthalene or β-methoxynaphthalene were carried out in the manner described in the first section, but the products were not as easily purified, for their sodium salts could not be crystallized, and the yields were poorer (60–75%). The reaction of glutaric anhydride and acenaphthene gave a particularly poor result.

KETO ACIDS AND DERIVATIVES

	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	M. p., °C.
β-(2-Methyl-1-naphthoyl)-propionic acid[12]	74.36	74.24	5.83	6.00	168
Methyl ester	74.97	74.89	6.30	6.51	85
β-Bromo deriv. of methyl ester	57.32	56.99	4.51	4.54	81
β-(2,7-Dimethyl-1-naphthoyl)-propionic acid	74.97	74.97	6.30	6.33	130
β-(2-Hydroxy-1-naphthoyl)-propionic acid	68.83	68.38	4.96	5.10	232
β-(2-Methoxy-1-naphthoyl)-propionic acid	69.75	69.68	5.47	5.55	152
γ-(3-Acenaphthoyl)-butyric acid	76.09	76.09	6.01	6.13	201
Methyl ester	76.56	76.46	6.43	6.39	120

The condensation of succinic anhydride with naphthalene using nitrobenzene as the solvent has been described recently by Haworth,[13] and we can confirm his statements as to the general superiority of this method over the earlier procedures. Instead of a 50% excess of the hydrocarbon, as specified by Haworth, we used a 10% excess of the anhydride and obtained somewhat better yields: β-(1-naphthoyl)-propionic acid (172°), 36%; β-(2-naphthoyl)-propionic acid (129°), 47%. The latter acid was purified through the methyl ester, which distilled without decomposition *in vacuo* and which melted at 14–15°. We have found no advantage in changing the order of addition of the reagents.

[11] Bamberger and Philip, *Ann.*, **240**, 147 (1887); Freund and Fleischer, *ibid.*, **399**, 182 (1913).

[12] This acid without doubt is identical with the substance described as β-(6-methyl-2-naphthoyl)-propionic acid by Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932), in a paper published after completion of the present paper.

[13] Haworth, *J. Chem. Soc.*, 1125 (1932).

In the patents of the I. G. Farbenindustrie[2] the statements regarding the "condensation product" obtained by heating β-(1-naphthoyl)-propionic acid with sodium aluminum chloride are somewhat confused, but the claim appears to be to the effect that a carboxylic acid derivative of a cyclic compound is produced, and the melting point is given as either 150 or 165°. The only product which we obtained from this reaction melted, after careful purification, at 172° and was identified as β-(2-naphthoyl)-propionic acid.

5. The Condensation of an Unsaturated Keto Acid.—According to the patent literature maleic anhydride condenses just as well with naphthalene as does succinic anhydride, but we cannot confirm this statement. No product was isolated in the reaction with naphthalene, while with acenaphthene the yield of keto acid was very poor (32%) and the working up of the material was a very tedious process. The unsaturated acid is more easily prepared from the corresponding saturated compound through the bromo derivative.

The Methyl Ester of β-Bromo-β-(3-acenaphthoyl)-propionic acid was prepared by adding a solution of 16 g. of bromine in chloroform to an ice-cold solution of 26.8 g. of methyl β-(3-acenaphthoyl)-propionate in 50 cc. of chloroform in the course of one-half hour. The solvent was taken off at the water pump and the oil left as a residue was taken up in ether. The product soon separated from the solution in the form of an amorphous paste which was then crystallized from benzene–ligroin; yield, 25 g. (77%). The bromo ester forms a crust of thick, yellow prisms melting at 113°.

Anal. Calcd. for $C_{16}H_{15}O_3Br$: C, 58.79; H, 4.36. Found: C, 58.72; H, 4.67.

Attempts to effect an intramolecular ring closure with this bromo ester were unsuccessful. Heated in carbon bisulfide solution with aluminum chloride, the substance formed a deep red addition product but was recovered unchanged. It was completely decomposed by molten sodium aluminum chloride or by heat.

β-(3-Acenaphthoyl)-acrylic Acid (XII).—A solution of 10 g. of the bromo ester and 3 g. of fused sodium acetate in 30 cc. of glacial acetic acid was heated for one hour on the steam-bath and poured into water. This precipitated a yellow oil which soon solidified and which was then crystallized from methyl alcohol. The methyl ester thus obtained (7 g.) formed yellow plates melting at 113° when completely pure.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.42; H, 5.33.

The free acid itself was obtained in poor yield by condensing acenaphthene with maleic anhydride, and the ester was compared with the above products and found to be the same. The acid forms small, yellow crystals melting at 165°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.05; H, 4.97.

Condensation Product (XIII?).—The unsaturated ester was heated in a sodium aluminum chloride melt at 140° for one-half hour and the dark brown solution was poured into water. The dark, somewhat tarry product was dissolved in soda solution and precipitated, then crystallized from alcohol. It forms canary-yellow needles melting at 214° with vigorous effervescence. The solution in concentrated sulfuric acid is yellow, with a beautiful green fluorescence.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.02; H, 4.75.

The yield of condensation product was only about 5% of the theoretical amount. The crude product is difficult to purify, and in several experiments the material was completely destroyed.

6. Anthracene and Succinic Anhydride.—In the hope of trying to effect a ring closure with a suitable keto acid of the anthracene series, the reaction between this hydrocarbon and succinic anhydride in nitrobenzene solution was investigated. Mayer

states in a patent[3] that the sole product is an acid melting at 160°, but we obtained a complicated mixture of substances from which only one acid, m. p. 228°, was isolated. It is easily separated as the sparingly soluble sodium salt, but the yield is only 10% of the theoretical amount. The acid group was found to be in the β-position, for the substance on oxidation yielded first an anthraquinone keto acid and then β-anthraquinonecarboxylic acid, which was identified as the methyl ester, m. p. 168°, by comparison with an authentic sample. The acid is thus of no interest in connection with the present study of *peri* condensations. The properties of the acid and its derivatives may be recorded briefly.

β-(2-Anthroyl)-propionic acid: long, yellow needles, m. p. 228°. *Anal.* Calcd. for $C_{18}H_{14}O_3$: C, 77.67; H, 5.07. Found: C, 77.29; H, 4.88.

The methyl ester formed pale yellow blades, m. p. 148°. *Anal.* Calcd. for $C_{19}H_{16}O_3$: C, 78.05; H, 5.52. Found: C, 77.90; H, 5.51.

β-(2-Anthraquinonyl)-propionic acid: yellow needles, m. p. 207°. *Anal.* Calcd. for $C_{18}H_{12}O_5$: C, 70.11; H, 3.92. Found: C, 69.58; H, 3.95.

γ-(2-Anthryl)-butyric acid: greenish-yellow plates, m. p. 197°. *Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.11. Found: C, 81.56; H, 6.08.

Summary

When β-(3-acenaphthoyl)-propionic acid (I) is heated in molten sodium aluminum chloride, a rather remarkable intramolecular condensation takes place. A seven-membered ring is closed across the *peri* positions of acenaphthene with the formation of *peri*-succinoylacenaphthene (VII). The reaction is far from being a general one, for none of the other keto acids investigated gave similar results.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WYOMING]

SOME NEW ESTERS OF ALPHA-HEXABROMOSTEARIC ACID[1]

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Introduction.—The solid α-hexabromostearic acid, $C_{17}H_{29}Br_6COOH$, (often called α-linolenic acid hexabromide), in contrast to its parent acid, the unsaturated linolenic acid, $C_{17}H_{29}COOH$, which forms only liquid esters, has the property of forming solid salts and esters.[2] As pure linolenic acid is obtained by the debromination of the solid α-hexabromostearic acid, it seems possible that the solid esters of the latter acid might also be debrominated to yield linolenic acid or its esters. As a related phase of this prob-

[1] Based upon a thesis by Kenneth E. Stanfield submitted to the Department of Chemistry, and the Committee on Graduate Work of the University of Wyoming, in partial fulfilment of the requirement for the Degree of Master of Arts (1931).

[2] (a) Erdmann and Bedford, *Ber.*, **42**, 1330 (1909); (b) Samuel Coffey, *J. Chem. Soc.*, **119**, 1412 (1921); (c) Imperial and West, *Philippine J. Sci.*, **31**, 441 (1926); (d) Almoradie and West, *ibid.*, **33**, 257 (1927); (e) Vincente and West, *ibid.*, **36**, 73 (1928).

lem thirteen new esters of α-hexabromostearic acid have been prepared and their melting points determined.

Experimental

The solid α-hexabromostearic acid used in this investigation was prepared by brominating the free acids of linseed oil according to the method of Erdmann and Bedford,[2a] with the modifications suggested by Eibner and Muggenthaler.[3] The slightly yellow hexabromide so obtained was recrystallized two or three times from boiling benzene and dried in a vacuum desiccator over concentrated sulfuric acid. The melting point of the flour-like product was 179.5–180.5°. This hexabromide, often known as the alpha form to distinguish it from the liquid beta form,[2a,b] was then esterified with various alcohols in the presence of sulfuric acid (0.5 cc./50 cc. of alcohol) according to a procedure suggested by Vincente and West.[2e] The alcohols were commercial products of the highest purity obtainable and were used without further purification. The yield of the ester obtained compared to the theoretical yield based upon the weight of the α-hexabromostearic acid used was from 30 to 84%.

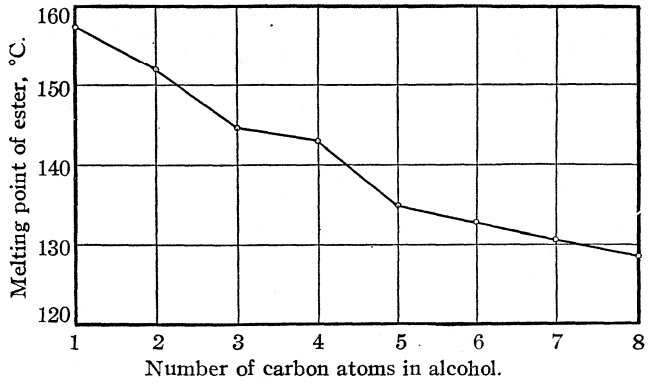

Fig. 1.—Graph of the melting points of the α-hexabromostearic acid esters against the number of carbon atoms in the primary alcohol.

The esters were further purified to give constant melting points by successive recrystallizations. Ethyl alcohol was found to be the most satisfactory solvent although glacial acetic acid and ethyl acetate were also used. After the esters had been dried in a vacuum desiccator over concentrated sulfuric acid for twenty-four hours the melting points were determined.

The constant melting products obtained in two different preparations of the same ester were proved to be identical by showing that a mixed sample of the two products had the same melting point as each of the individual samples. These melting points were found to remain constant when the esters had been allowed to stand in a desiccator for a period of three months.

The esters were confirmed by comparing their actual bromine content with the calculated value. These values were expressed as the number of moles of bromine and the per cent. of bromine in the esters. According to a modified method of Fisher[4] a mixture

[3] Eibner and Muggenthaler, *Farben.-Ztg.*, **131**, 641 (1912).

[4] Fisher, "Laboratory Manual of Organic Chemistry," 2d ed., John Wiley and Sons, Inc., New York, 1924, p. 317.

of a known weight of the ester and powdered sodium peroxide, potassium nitrate and sugar ($C_{12}H_{22}O_{11}$) was fused in a Parr sulfur bomb. The cold melt was then disintegrated in hot water, acidified with nitric acid, and the bromine precipitated as insoluble silver bromide by the addition of an excess of standard silver nitrate solution. The excess silver nitrate was determined by back titration with a standard solution of potassium thiocyanate according to the Volhard method. An analysis for the bromine in α-hexabromostearic acid gave the following results.

	No. moles bromine	Bromine, %
Determined	3.01	63.49
Calculated	3.00	63.28

With the exception of the esters of the tertiary alcohols these esters were generally soluble in the following hot solvents: acetone, glacial acetic acid, benzene, toluene, chloroform, carbon tetrachloride, carbon disulfide, methyl alcohol, methyl acetate, ethyl ether, ethyl alcohol, ethyl acetate, propyl alcohol, butyl alcohol, amyl alcohol and amyl acetate. The esters of the tertiary alcohols were soluble in hot glacial acetic acid and the acetone but only slightly soluble in the other solvents. All of the esters were insoluble in petroleum ether and water.

When the melting points of the esters are graphed against the number of carbon atoms in the alcohol, a general decrease in the melting point is noted with the increase in the number of carbon atoms. This is especially evident when the esters are classified according to whether they are derived from primary, secondary, or tertiary alcohols.

TABLE I

ESTERS OF HEXABROMOSTEARIC ACID

The temperatures were not corrected because but 1.2 cm. of the mercury thread of the thermometer extended above the surface of the liquid in the Thiele tube. The liquid was circulated by a current of air.

Ester of	Type of alc.	Cc./g. of hexabromide	Yield, %	No. of crystns.	Bromine: Moles detd.	Bromine: % detd.	Bromine: % calcd.	Melting point, °C.
MeOH[a]	prim.							157–158
EtOH[a]	prim.							151.5–152.5
n-PrOH[b]	prim.	120.0	76					144–146
Iso-PrOH[b]	sec.	120.0	66					141–143
n-BuOH	prim.	39.0	54	8	2.98	58.58	58.92	143.0–143.1
Iso-BuOH[b]	prim.	120.0	56			58.79	58.92	136–138
Tert.-BuOH	tert.	62.5	49	5	3.02	59.24	58.92	162.0–162.5
n-AmOH[c]	prim.	35.7	52	4	3.03	58.67	57.92	135.0-135.2
Et_2CHOH	sec.	6.7	59	4	2.97	57.37	57.92	135.8–135.9
Iso-$BuCH_2OH$	prim.	7.1	45	4	2.97	57.41	57.92	135.0–135.1
MePrCHOH	sec.	7.1	64	4	3.02	58.32	57.92	135.7–135.9
Me_2EtCOH	tert.	6.3	85	6	3.03	58.54	57.92	159.0–159.5
Sec.-$BuCH_2OH$	sec.	10.0	73	4	2.99	57.58	57.92	133.4–133.8
Hexanol	prim.	7.0	30	6	3.04	57.80	56.96	132.6–132.8
Heptanol	prim.	15.5	38	6	3.01	56.05	56.03	130.6–130.8
Heptanol-4	sec.	6.3	49	4	3.03	56.72	56.03	135.1–135.2
Octanol	prim.	5.0	41	4	3.05	56.06	55.12	128–129
Octanol-2	sec.	6.3	57	4	3.03	55.80	55.12	129.1–129.2
Benzyl alc.	prim.	17.3	81	4	3.00	56.53	56.56	140.4–140.5

[a] First prepared by Erdmann and Bedford. [b] First prepared by Vincente and West. [c] First prepared by Vincente and West, but the data given are those obtained by the authors.

In the case of the series of esters of the primary alcohols a zig-zag graph is obtained when adjacent points are joined by straight lines. The esters of the alcohols containing an even number of carbon atoms have melting points which lie above a smooth curve approximating the points, whereas those esters of alcohols containing an odd number of carbons lie below this curve. This type of graph is not unusual, for similar step-like arrangements are observed when the melting points are graphed against the number of carbons in various series of hydrocarbons, acids, aldehydes, amines and esters of monobasic and dibasic acids.

Several unsuccessful attempts were made to prepare the α-hexabromostearic acid esters of the following alcohols: dimethylpropylcarbinol, diphenylcarbinol, triphenylcarbinol and myricyl alcohol. The crude products obtained in these cases resembled the above esters; however, due to difficulty in extracting them, they could not be obtained in the pure state.

Summary

Thirteen new esters of α-hexabromostearic acid were prepared and their melting points determined. These white, wax-like solids have definite melting points and are generally soluble in hot organic solvents. The esters of the tertiary alcohols seem to deviate considerably from those of the primary and secondary alcohols in that they have abnormally high melting points and are much less soluble in hot organic solvents. The melting points of the esters decrease with the increase in the number of carbons in the alcohol. A graph of the melting points against the number of carbons in the alcohol indicates a step-like arrangement in which the esters of the alcohols having an even number of carbons lie above a smooth curve approximating the points.

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[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS WELLCOME AND COMPANY]

MIXED BENZOINS. IX. MESO CHLORO DERIVATIVES

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The original purpose of this work was to seek a route for the conversion of a mixed benzoin into its isomer. Four benzoins were investigated—benzoin (as check), 4′-methoxybenzoin[1] (benzanisoin), 2-chloro-4′-methoxybenzoin (*o*-chlorobenzanisoin) and 2-chloro-3′,4′-dimethoxybenzoin (*o*-chlorobenzveratroin). The first steps were the conversion of the benzoin into the corresponding benzil, and this in turn into the phenyl α,α-dichlorobenzyl ketone. On the basis of data in the literature, it was believed that the chlorine atoms might be sufficiently firmly attached to withstand catalytic reduction, while the CO group was reduced to CHOH. The chlorine atoms could then be removed. Assuming that the chlorine atoms attached themselves to the carbon atom which originally carried

[1] Nomenclature of Buck and Ide, THIS JOURNAL, **54**, 3302 (1932).

the OH group in the benzoin (as would seem probable from the fact that the original benzoin and not its isomer is formed on catalytically reducing the benzil), then the isomeric benzoin would be produced according to the scheme

$$RCHOHCOR' \longrightarrow RCOCOR' \longrightarrow RCCl_2COR' \longrightarrow (RCCl_2CHOHR') \longrightarrow RCOCHOHR'$$

Unfortunately the reaction did not take this course, the phenyl α,α-dichlorobenzyl ketone being reduced first to the phenyl α-chlorobenzyl ketone (desyl chloride) and then to the desoxy compound. The phenyl α-chlorobenzyl ketone, if treated with sodium ethylate, rapidly regenerated the original benzoin, a result in line with the work of Ward.[2] The series of reactions

$$RCCl_2COR' \longrightarrow RCHClCOR' \begin{cases} \longrightarrow RCHOHCOR' \\ \longrightarrow RCH_2COR' \end{cases}$$

fixes the position of the chlorine atoms in the dichloro and monochloro compounds since the positions of the CHOH and CH_2 groups are known.[3,4]

An attempt was next made to convert the dichloro compound into the diethyl acetal, with the object of reducing this. The compound, however, immediately broke up into a mixture of the corresponding benzoic ester and the benzal chloride, according to the equation

$$RCCl_2COR' + EtOH = RCHCl_2 + R'COOEt$$

Smaller amounts of a benzaldehyde diethylacetal are also produced as follows

$$RCCl_2COR' + EtOH + 2NaOEt = RCH(OEt)_2 + R'COOEt + 2NaCl$$

These reactions independently establish the position of the chlorine atoms in the dichloro compounds, and, incidentally, offer a new method for determining the structures of benzoins, since benzoins are derived, in a direct manner, from the dichloro compounds.

Zinin[5] has noted the production of benzaldehyde and potassium benzoate by the action of alcoholic potassium hydroxide on "chlorobenzil" (phenyl α,α-dichlorobenzyl ketone), the reaction taking place slowly in the cold, and quickly on heating. The fission by the action of sodium ethylate, on the contrary, takes place almost immediately at room temperature.

Redsko[6] reported the production of phenyl α,α-dichlorobenzyl ketone[5] by the action of phosphorus pentachloride on benzoin. Evidently its production is a side reaction and not the main reaction. The present authors confirm the production of this compound under modified condi-

[2] Ward, *J. Chem. Soc.*, 1541 (1929).

[3] Buck and Ide, THIS JOURNAL, **53**, 1536 (1931).

[4] Buck and Ide, *ibid.*, **53**, 1912 (1931).

[5] Zinin, *Ann.*, **119**, 177 (1861).

[6] Redsko, *J. Russ. Phys.-Chem. Soc.*, **21**, [1] 421 (1889); *Ber.*, Ref. **22**, 760 (1889).

tions. The reaction appears to be general, as the corresponding dichloro compounds are produced from the mixed benzoins examined, although only in poor yield. Benzoin itself and the mixed benzoins examined were found to give, in benzene solution and at room temperature, relatively large amounts of the corresponding benzil, when treated with phosphorus pentachloride. The phenyl α-chlorobenzyl ketones (desyl chlorides), which might have been expected, were not found. Under suitable conditions the yield of the benzil is surprisingly large. Once the benzil is formed, the production of the dichloro compound would follow naturally, on raising the temperature. Since the benzil is an intermediate, this method of formation of the dichloro compound is valueless as an indication of the position of the chlorine atoms.

Zinin did not observe the formation of tolane tetrachloride in the reaction between benzil and phosphorus pentachloride, although later Eiloart[7] obtained it by using excess of pentachloride on benzil. The present authors always found tolane tetrachloride, to the extent of about 10%, to be formed. Smaller amounts of *p*-methoxytolane tetrachloride are formed from 4-methoxybenzil. With the other mixed benzoins examined, the corresponding tolane tetrachlorides are produced in very small amounts and are inseparable by fractional crystallization. They remain as small residues when the phenyl α,α-dichlorobenzyl ketones are removed in a reaction (*e. g.*, catalytic reduction).

The three unsymmetrical benzils were reduced catalytically. Up to the present only the original benzoins and none of the isomeric benzoins have been obtained. This fact, together with the formation in each case of only one phenyl α,α-dichlorobenzyl ketone, brings out the marked difference of reactivity between the two carbonyl groups of the benzils. In the cases of the *o*-chlorobenzils examined, it was thought that the ortho chlorine atom might have some steric effect, tending to cause the carbonyl groups remote from it to react with the phosphorus pentachloride. As a matter of fact, the contrary effect was observed, the phenyl α,α-dichlorobenzyl ketone being formed with greater ease in the cases of the *o*-chlorobenzils, the group attacked being the carbonyl adjacent to the ortho chlorine atom.

The high degree of reactivity of the meso chlorine atoms (toward sodium ethylate and catalytic reduction) is noteworthy, particularly in view of the alleged stability of α,α-dichlorobenzyl ketone toward silver salts, etc.[5]

A point of interest is that if the phenyl α-chlorobenzyl ketone from 4′-methoxybenzoin is reduced catalytically, there is obtained benzyl 4-methoxyphenyl ketone, and not 4-methoxybenzyl phenyl ketone, which is produced on the reduction of 4′-methoxybenzoin by tin and

[7] Eiloart, *Am. Chem. J.*, **12**, 231 (1890).

hydrochloric acid.[3] The other chloro compounds give the usual desoxy compounds on catalytic reduction, as would be expected.

The experimental work presents some unusual difficulties. Most of the compounds show marked supercooling effects, so that it is very difficult, in the absence of seeding crystals, to obtain crystalline products. The separation of the tolane tetrachlorides from the phenyl α,α-dichlorobenzyl ketones by fractional crystallization is difficult, and, indeed, in some cases impossible. The uncontrollable nature of catalytic reduction, when applied to mixed benzoin work, is also brought out. Thus (adding hydrogen in the proportion of two atoms for each molecule of ketone), an unsymmetrical benzil gives the benzoin, together with the unchanged benzil and the hydro compound. Similarly, with the dichloro compounds, unchanged material and the desoxy compounds are usually present in the reduction mixtures.

Experimental

The mixed benzoins used were prepared as described elsewhere.[8,9]

Phenyl α,α-Dichlorobenzyl Ketone (*ms-ms*-Dichlorodesoxybenzoin, Chlorobenzil).—The method of Zinin[5] was used. It is very difficult to separate completely the product from the tolane tetrachloride simultaneously formed.

Substituted Phenyl α,α-Dichlorobenzyl Ketones.—The method of Zinin was found to be unsuitable for substituted benzils. The general method used consisted of dissolving the substituted benzil (0.03 mole) in benzene (100 cc.), adding the phosphorus pentachloride (0.09 mole), and refluxing the solution. The benzene was evaporated under reduced pressure (stopping the operation as soon as phosphorus pentachloride is seen to sublime), the flask cooled, and the contents rapidly and cautiously treated with cold water (about 25 times the weight of the benzil used, the water added in one lot). When the resulting reaction is over, the milky emulsion is extracted with ether (if solid is present this is removed before extraction), the extract washed with water, the ether evaporated, and the resulting oil, together with any solid material removed, dissolved in warm alcohol. On seeding and standing, the product crystallized out. From the dichloro compound from 4-methoxybenzil, a little *p*-methoxytolane tetrachloride can be separated by fractional crystallization, but in the other cases the amount of the tolane tetrachloride formed is insignificant. The results are given in Table I. The time of refluxing is rather critical. Yields are given for a good grade of product, not necessarily analytically pure. Alcohol is the best solvent for recrystallization. The compounds are very soluble in ether and benzene, moderately soluble in alcohol, and sparingly soluble in petroleum ether.

TABLE I

PHENYL α,α-DICHLOROBENZYL KETONES

	Compound -chlorobenzyl ketone	Hours re- fluxed	Yield, %	M. p., °C.	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
1	4-Methoxyphenyl α,α-di-	4.5	67	81	$C_{15}H_{12}O_2Cl_2$	61.01	4.10	60.89	4.41
2	4-Methoxyphenyl α,α-2-tri-	2.2	97	109	$C_{15}H_{11}O_2Cl_3$	54.63	3.37	54.93	3.59
3	3,4-Dimethoxyphenyl α,α-2-tri-	1.8	82	120	$C_{16}H_{13}O_3Cl_3$	53.41	3.63	53.73	3.77

[8] Buck and Ide, THIS JOURNAL, **52,** 4107 (1930).

[9] Kinney, *ibid.*, **51,** 1592 (1929) (omitting the steam distillation).

p-**Methoxytolane tetrachloride,** recrystallized from alcohol in which it is sparingly soluble, forms bundles of slender, tiny needles, melting at 153°.

Analysis. Calcd. for $C_{15}H_{12}OCl_4$: C, 51.44; H, 3.46. Found: C, 51.65; H, 3.72.

Phenyl α-Chlorobenzyl Ketones.—The general method used was to dissolve 0.02 mole of the phenyl α,α-dichlorobenzyl ketone in 50 cc. of absolute alcohol, and to reduce this catalytically, as slowly as possible, using slow shaking and very little (10–20 mg.) platinum oxide. Hydrogen was added in the proportion of two atoms for each molecule of ketone. The solution was filtered and concentrated on the steam-bath. On seeding and standing the product crystallized out. Results are given in Table II.

The corresponding desoxy compounds were isolated, as side products, in three of the four cases, none being found in the reduction of 4-methoxyphenyl α,α-2-trichlorobenzyl ketone.

The compounds are rather soluble in alcohol, very soluble in ether and benzene and moderately or sparingly soluble in petroleum ether.

TABLE II

PHENYL α-CHLOROBENZYL KETONES

Compound, -chlorobenzyl ketone	Yield, %	M. p., °C.	Formula	Analyses Calcd. C	Calcd. H	Found C	Found H
Phenyl α-	65	68	$C_{14}H_{11}OCl$	72.87	4.81	72.78	4.86
4-Methoxyphenyl α-2-di-	81	75	$C_{15}H_{12}O_2Cl_2$	61.22	4.12	61.53	4.55
3,4-Dimethoxyphenyl α-2-di-	70	99	$C_{16}H_{14}O_3Cl_2$	59.07	4.34	59.05	4.37

4-Methoxyphenyl α-chlorobenzyl ketone was only obtained as a thick oil, doubtless owing to the presence of unchanged material and the desoxy compound. By pouring an alcoholic solution into water and extracting with petroleum ether, benzyl 4-methoxyphenyl ketone was obtained in about 10% yield on concentrating the extract. It was identified by comparison and by mixed melting point determinations with an authentic specimen, prepared by the Friedel–Crafts method.[6] After extraction with petroleum ether, the emulsion was extracted with ether. The oil obtained on evaporating the ether gave 4′-methoxybenzoin in good yield on treatment with sodium ethylate (see later), proving that the oil was mainly the 4-methoxyphenyl α-chlorobenzyl ketone.

Conversion of Phenyl α-Chlorobenzyl Ketones into Benzoins.—The method used was to dissolve about 5 g. of the phenyl α-chlorobenzyl ketone in absolute alcohol (*ca.* 50 cc.), cool the solution, and add to it a cold solution of three molecules of sodium ethylate in the minimum amount of absolute alcohol. The mixture was kept at about 40° for fifteen minutes, during which time sodium chloride separated out. The whole was then poured into cold water (500 cc.) containing 20 cc. of concd. hydrochloric acid. The oil which separated soon solidified on standing in a cold place and the solid was then filtered off and recrystallized from alcohol. The benzoin was identified by analysis and by comparison and mixed melting point determinations with authentic specimens. The yield of the pure benzoin is very good and the structure of the product agrees in each case with the assumption that the chlorine atom is directly replaced by the hydroxyl group.

Reduction of Phenyl α-Chlorobenzyl Ketones to Phenyl Benzyl Ketones (Desoxy Compounds).—0.01 mole of the phenyl α-chlorobenzyl ketone, dissolved in 50 cc. of alcohol, was reduced with platinum oxide, two atoms of hydrogen being added per molecule of ketone. After filtration and concentration on the steam-bath, the solution deposited crystals on standing. The product was identified by comparison and by mixed melting point determinations with authentic specimens. The yields are very

good, averaging about 80% of the theoretical for the pure product. In each case the structure of the desoxy compound formed is that which would be expected if the chlorine atom were directly replaced by a hydrogen atom.

Benzils from Benzoins by the Action of Phosphorus Pentachloride.—The benzoin (about 10 g.) was dissolved in 100 cc. of benzene, the solution cooled if necessary, and one mole of phosphorus pentachloride added cautiously, in one lot. Hydrogen chloride was evolved briskly, but there was only a slight heat effect. The reaction was soon completed, and the solution was then allowed to stand at room temperature. After standing it was poured into ice water (700 cc.), the benzene layer separated and the liquors extracted with ether. The total extracts were evaporated under reduced pressure and the residue dissolved in alcohol. On standing the benzil crystallized out and was identified by comparison and mixed melting point determinations with an authentic specimen.

Similar experiments were carried out using three times the amount of phosphorus pentachloride (3 moles), adding the chloride rapidly in small portions, and so regulating the addition that violent frothing did not occur. The best results, excepting in the case of 4'-methoxybenzoin, are obtained by using 3 moles of phosphorus pentachloride and allowing the solution to stand for only ten minutes. Under these conditions the yields were, for benzil, 72%; for 2-chloro-4'-methoxybenzil, 90% and for 2-chloro-3'-4'-dimethoxybenzil, 50%. From 4'-methoxybenzoin, after standing for four hours with 3 moles of phosphorus pentachloride, a yield of 42% was isolated while under other conditions only oils were obtained.

If the solutions (3 moles of phosphorus pentachloride) be refluxed for four hours and then worked up as above, it is possible to isolate the corresponding phenyl α,α-dichlorobenzyl ketones, but only after laborious fractional crystallization. The yield is best in the case of benzoin itself (about 30%) but in the other cases it was no more than 10%.

Fission of Phenyl α,α-Dichlorobenzyl Ketones.—About 10 g. of the phenyl α,α-dichlorobenzyl ketone was dissolved in the minimum amount of absolute alcohol (50 to 100 cc.) and the solution cooled. To this solution was added a cold solution of two molecular proportions of sodium ethylate. A slight rise in temperature took place and some sodium chloride usually separated out. After standing at room temperature for twenty minutes, the mixture was poured into 700 cc. of water and extracted three times with ether. The ether was evaporated and the residual oil distilled under reduced pressure, separating it into two fractions as far as possible. The fractions were then further distilled at ordinary pressure, until approximately pure. The higher fraction was identified by its boiling point and by its saponification (alcoholic potash) to the acid. The lower fraction was hydrolyzed by heating with hydrochloric acid (four hours at 150° with 10% hydrochloric acid for the benzaldehyde fraction, seven hours at 175° with 35% hydrochloric acid for the *o*-chlorobenzaldehyde fraction. There was considerable destruction of material in the latter case). The benzaldehyde formed was identified as the phenylhydrazone, and the *o*-chlorobenzaldehyde as 2-chloro-benz-anti-aldoxime. Mixed melting point determinations were carried out in each case with authentic specimens. Allowing for fractionation losses, the yields approached the theoretical. Usually a small residue (5 to 10%) remained after the first distillation. The absence of free aldehydes in the lower-boiling fractions was verified by means of sodium bisulfite, etc.

Analytical results not given here (C, H, Cl) indicate clearly that the lower-boiling fractions consist chiefly, to the extent of about 90%, of the benzal chloride. From the separation of sodium chloride in the reaction it is assumed that the contaminant is the diethylacetal. With the amounts of material available, it was not possible to separate the components by fractional distillation.

Ethyl anisate and benzal chloride were obtained from 4-methoxyphenyl α,α-dichlorobenzyl ketone; ethyl anisate and *o*-chlorobenzal chloride from 4-methoxyphenyl α,α-2-trichlorobenzyl ketone and ethyl veratrate, and *o*-chlorobenzal chloride from 3,4-dimethoxyphenyl α,α-2-trichlorobenzyl ketone. The reaction mixture from phenyl α,α-dichlorobenzyl ketone proved to be inseparable by fractional distillation; it was therefore heated for four hours at 150° with hydrochloric acid (1:2) and the product separated into benzaldehyde and benzoic acid.

Summary

1. The phenyl α,α-dichlorobenzyl ketones from three representative mixed benzoins have been prepared and examined. They have been reduced catalytically to the phenyl α-chlorobenzyl ketones, and these in turn to the desoxy compounds. The conversion of the phenyl α-chlorobenzyl ketones to the parent benzoins was also carried out.

2. It has been found that phosphorus pentachloride in the cold behaves chiefly as an oxidizing agent toward benzoins, good yields of the benzils being obtained.

3. The phenyl α,α-dichlorobenzyl ketones, when treated with alcoholic sodium ethylate in the cold, rapidly break up into a mixture of the corresponding benzoic ester and the benzal chloride. Small amounts of the diethylacetal are also formed.

4. Parallel experiments on benzoin were carried out as a check.

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THE SYNTHESIS OF BETA-ETHOXYAMINES[1]

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The method of preparation of β-ethoxyamines described in this paper was evolved with the idea that it might be possible to synthesize numerous substituted derivatives, in the manner that Boord[2] and his co-workers have used in the preparation of isomeric olefins. It was further felt that these ethoxyamines might be more easily resolved than the corresponding alcohols and the active ethers might then be split to yield various optically active β-hydroxyamines which should be of interest from a pharmaceutical point of view. A second point of interest concerning these ethoxyamines was their possible use as basic resolving agents. In this respect they form a continuation of a study by Brode and Littman[3] on the synthesis and resolution of a quite different type of asymmetric amine. The method of

[1] Presented at the Mid-West regional meeting of the American Chemical Society, St. Louis, Mo., April 5, 1932.

[2] Boord and co-workers, THIS JOURNAL, **52**, 651, 3396 (1930); **53**, 1505 (1931); **54**, 751 (1932).

[3] Brode and Littman, *ibid.*, **52**, 1655, 5056 (1930); **53**, 1531 (1931).

synthesis of the amines described in this paper is a combination of methods of Bookman,[4] Houben and Führer[5] and de Montmollin,[6] with certain improvements and modifications as applied to β-bromoethyl ethyl ethers as prepared by the methods of Boord.[2]

The method of preparation of these amines can best be indicated by equations as follows

$$R{-}CH_2{-}CHO + EtOH + HCl = R{-}CH_2{-}CHCl{-}OEt + H_2O \quad (I)$$

$$R{-}CH_2{-}CHCl{-}OEt + Br_2 = R{-}CHBr{-}CHBr{-}OEt + HCl \quad (II)$$

$$R{-}CHBr{-}CHBr{-}OEt + R'{-}MgBr = R{-}CHBr{-}CHR'{-}OEt + MgBr_2 \quad (III)$$

$R{-}CHBr{-}CHR'{-}OEt + NH_3 = R{-}CH(NH_2){-}CHR'{-}OEt.HBr$ and the corresponding secondary amine

$$\begin{array}{l} R{-}CH{-}CHR'{-}OEt \\ | \\ NH \qquad \cdot HBr \\ | \\ R{-}CH{-}CHR'{-}OEt \end{array} \quad (IV)$$

In (IV) amines such as RNH_2 or R_2NH may be used to yield mixed secondary or tertiary amines. Although reactions have been carried out indicating the practicality of the use of various aldehydes in (I), the work described in this paper was confined to the derivatives obtained from acetaldehyde, since this aldehyde yields an amine in equation (IV) of the type $NH_2{-}CH_2{-}CHR'{-}OEt$ which contains only one asymmetric carbon, and hence should be more easily resolved.

By the use of a method[7,8] for the conversion of α-alkyl or aryl substituted β-bromo ethers of the type obtained in equation (III) into unsaturated ethers by the removal of hydrogen bromide, and by subsequent bromination, one obtains an α-alkyl or aryl-substituted α,β-dibromoethyl ethyl ether. Treatment of this ether with the same or a different Grignard reagent as in equation (III) yields an amine ether (a) which can be split to yield the corresponding alcohol.

$$\begin{array}{l} \qquad\quad R' \\ \qquad\quad | \\ R{-}CH{-}C{-}OEt \\ \quad | \quad | \\ \quad NH_2 \; R'' \\ \quad (a) \end{array} + HBr = \begin{array}{l} \qquad\quad R' \\ \qquad\quad | \\ R{-}CH{-}C{-}OH \\ \quad | \quad | \\ \quad NH_2 \; R'' \end{array} + EtBr \quad (V)$$

Two methods were tried in the conversion of the β-bromo ethers into the corresponding amines. The first was to dissolve the bromo ether in methyl alcohol saturated with ammonia, and continue the introduction of ammonia gas into this solution over a period of several weeks. This method, while yielding the desired amines, was not satisfactory from the standpoint of convenience or yields obtained. The second and more satisfactory method was to dissolve the bromo ether in a solution of methyl

[4] Bookman, *Ber.*, **28**, 3111 (1895).

[5] Houben and Führer, *ibid.*, **40**, 4993 (1907).

[6] De Montmollin and co-workers, *Helv. Chim. Acta*, **12**, 610, 873 (1929).

[7] Lauer and Spielman, THIS JOURNAL, **53**, 1533 (1931).

[8] Schmitt and Boord, *ibid.*, **54**, 751 (1932).

alcohol which had been saturated at 0° with ammonia. This solution, usually about 1500 cc. in volume, was then placed in a steel bomb with a capacity of about 2 liters. The bomb was sealed by a threaded steel plug and immersed in a water-bath which was kept at a temperature slightly below 100°. As will be noticed in Table I, an appreciable quantity of the secondary amine was formed in both methods, but better yields were in general obtained from the bomb method, a larger portion of which was the primary amine. In the case of the phenyl derivative no secondary amine was obtained, although a tarry residue indicated that some might have been formed. In no case were tertiary amines isolated, although they may have been formed and were part of the residues obtained in the isolation and distillation of the amines.

Both the primary and secondary amines are markedly stable, and while their boiling points are in general recorded at reduced pressures, many of them were subsequently distilled at atmospheric pressure without any noticeable decomposition or coloring. These amines are apparently unaffected by oxidation and can be kept for a long time without deterioration.

Experimental

Preparation of the 1-Bromo-2-ethoxy-2-(aryl or alkyl)-ethanes CH_2Br-CHR-OEt.—Previously described methods were used in the preparation of these compounds.[2] The average yield obtained in the preparation of the α-chloroethyl ethyl ether (equation I) was 89.1%. For the dibromo ether (equation II) an average yield of 92.6% was obtained and for the α-alkyl or aryl substituted β-bromo ethers an average yield of 72%.[9]

Preparation of the β-Ethoxyamines, (NH_2–CH_2–CHR–OEt, **and the Corresponding Secondary Amines (Equation IV).**—Two methods were used in the preparation of these

TABLE I

PREPARATION OF β-ETHOXYAMINES (C_2H_5–O–CHR–CH_2–NH_2 AND (C_2H_5–O–CHR–CH_2)$_2$NH)

R	Bromo ether, g.	Liters of methyl alcohol	Time of reaction in weeks	Yield of primary amine g.	%	Yield of secondary amine g.	%	Total yield of amine %
A. Room temperature								
C_2H_5-	230	1.5	7	62.8	42.2	27.0	19.4	61.6
C_2H_5-	420	3	5	81.5	30.0	40.5	16.1	46.1
n-C_3H_7-	309.5	2	15	92	44.2	56.5	29.0	73.2
n-C_4H_9-	387	2	15	93	34.6	45.5	18.0	52.6
sec.-C_4H_9-	316.5	2	12	90	40.9	40	19.3	60.2
C_6H_5-	250	1.5	21	58	32.1	..	..	32.1
B. At 90–100° (Bomb method)								
n-C_4H_9-	600	3	36 hrs.	252	60.4	61.5	15.5	76.1
sec.-C_4H_9-	701	3.5	36 hrs.	289.5	59.4	96	20.9	80.3
C_6H_5-	500	2	48 hrs.	222	61.6	..	..	61.6

[9] This value does not include the yields obtained from the secondary butyl Grignard reagent and the α,β-dibromoethyl ethyl ether which were between 30 and 35% on several runs. Poor yields on this same reaction have been noted previously by other observers[2] and are probably due to the secondary character of the Grignard reagent.

TABLE II

PHYSICAL CONSTANTS AND ANALYSES OF β-ETHOXYAMINES

Compound	B. p., °C. (mm.)	d_4^{20}	n_D^{20}	Mol. ref. Calcd.	Mol. ref. Obs.	Analysis, % N Calcd.	Analysis, % N Found
β-Ethoxy-β-phenylethylamine	107–9(12)	0.9867	1.5102	49.84	50.04	Previously described[5]	
N-β-Ethoxybutylamine	153.5(21)	.9636	1.5174	60.44	60.68	15.44 (Cl)	15.30, 15.40 (Cl)
β-Ethoxybutylamine	138.5–140.5	.8449	1.4190	34.97	35.01	11.95 (N)	11.88, 11.75 (N)[4,6]
β,β′-Diethoxydibutylamine	132–135(31)	.8657	1.4260	64.50	64.29	Previously described[4,6]	
β-Ethoxyamylamine	56.0–56.5(15)	.8427	1.4220	39.59	39 55	10.68	10 57, 10.48
β,β′-Diethoxydiamylamine	133.5–134.5(14)	.8627	1.4318	73.74	73.71	5.71	5.62, 5.81
β-Ethoxy-γ-methylamylamine	64–65(13)	.8507	1.4290	44.21	43.99	9.65	9.38, 9.37
β,β′-Diethoxy-γ,γ′-dimethyldiamylamine	144–147(14)	.8705	1.4380	82.97	82.42	5.13	5.00, 4.95
β-Ethoxyhexylamine	68–69(13)	.8429	1.4271	44.21	44.22	9.65	9.41, 9.54
β,β′-Diethoxydihexylamine	151–154(12)	.8618	1.4368	82.97	83.05	5.13	5.00, 4.98

amines, one at room temperature and atmospheric pressure, and the other at 100° and under pressure.

In the first procedure, the β-bromo ether was dissolved in a large amount of commercial methyl alcohol. Although the proportions varied, as shown in Table I, approximately 500 cc. of methyl alcohol was used per 100 g. of the bromo ether. This solution was saturated with ammonia gas at a temperature lower than 15°, thus ensuring complete saturation at room temperature (approximately 25°). This alcoholic solution was allowed to stand for several weeks, during which time additional ammonia was passed into the mixture at intervals of about one week.

The second procedure used in the synthesis of these amines was similar to the first, except that the methyl alcohol–β-bromo ether solution was saturated with ammonia at about 0°, the solution then poured into a steel bomb, sealed with a threaded steel plug and heated at a temperature of 90–100° for the periods of time indicated in Table I.

The same procedure was employed for the separation of the amines from the solutions obtained by either of the above two methods. As much of the methyl alcohol as possible was distilled from the solution, until severe bumping started, due to the separation of the amine hydrobromide. Five hundred to 1000 cc. of water was added and the oily material which separated was removed. If necessary the solution was extracted with ether to complete the removal of the oil. This oil, usually small in amount, included any unreacted β-bromo ether and certain decomposition products. Extraction of this oily material with dilute hydrochloric acid indicated the absence of any amines in this material.

The water was then removed by allowing the solution to boil slowly under reduced pressure. The distillation was stopped upon precipitation of the amine hydrobromide from the aqueous solution. By this time all of the excess ammonia and methyl alcohol had been removed. The solution was made strongly alkaline with concentrated sodium hydroxide and the amine layer which formed was removed with a separatory funnel. The solution was extracted three times with ether, the ethereal extract added to the amine and the whole dried over solid sodium hydroxide. Distillation first removed the ether and then gave in general two fractions of markedly different boiling points (the primary and secondary amines). These fractions were redistilled to obtain the pure amines. The percentage yields of the redistilled material are given in Table I.

In Table II are given the physical constants determined for these amines. The N-β-ethoxy-*n*-butylaniline was prepared by refluxing a methyl alcohol solution of aniline and the β-bromo ether at atmospheric pressure.

Summary

A method has been described for the synthesis of β-ethoxyamines. The following amines were prepared by this method: β-ethoxy-β-phenylethylamine, N-β-ethoxy-*n*-butylaniline, β,β′-diethoxydi-*n*-butylamine, β-ethoxy-*n*-amylamine, β,β′-diethoxydi-*n*-amylamine, β-ethoxy-γ-methyl-*n*-amylamine, β,β′-diethoxy-γ,γ′-dimethyldi-*n*-amylamine, β-ethoxy-*n*-hexylamine, and β,β′-diethoxydi-*n*-hexylamine. Of these amines only the β-ethoxy-β-phenylethylamine, the β′,β′-diethoxydi-*n*-butylamine and the β-ethoxy-*n*-butylamine have been previously described.[5,6] Physical constants of the prepared amines have been observed and recorded.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDUSTRIAL SCIENCE DIVISION, WEST VIRGINIA UNIVERSITY]

SOME AROMATIC ESTERS OF THE MONOALKYL ETHERS OF ETHYLENE GLYCOL AND DIETHYLENE GLYCOL[1]

BY R. C. CONN, A. R. COLLETT AND C. L. LAZZELL

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Although a few aromatic esters of the monoalkyl ethers of ethylene glycol ($HOCH_2CH_2OR$) and diethylene glycol ($HOCH_2CH_2OCH_2CH_2OR$) are recorded in the literature, no systematic preparation of such a series of compounds has ever been made. Palomaa[2] has reported the preparation of the benzoates of the monomethyl, monoethyl, monopropyl and monoallyl ethers of ethylene glycol but gives no data for any but the monomethyl compound. Since several of these glycol ethers have recently become commercially available, it has been considered worth while to prepare a series of their benzoates and *p*-nitrobenzoates. These esters are generally liquids of high boiling point. They are insoluble in water but soluble in all common organic solvents. The benzoates are all colorless liquids, the β-methoxy and β-ethoxy compounds possessing characteristic pleasant odors which lessen and almost vanish with the lengthening of the aliphatic side chain.

Benzoylation of the glycol ethers was carried out in pyridine solution according to the following type reactions

$$C_6H_5COCl + HOCH_2CH_2OR = C_6H_5COOCH_2CH_2OR + HCl$$
$$C_6H_5COCl + HOCH_2CH_2OCH_2CH_2OR = C_6H_5COOCH_2CH_2OCH_2CH_2OR + HCl$$

The method was the same as that previously used by Palomaa.[2]

A known quantity of the glycol ether and an excess of dry pyridine were placed together in a flask and an equivalent amount of the acid chloride slowly added from a dropping funnel with continual stirring or shaking. The solid *p*-nitrobenzoyl chloride was first dissolved in a quantity of anhydrous ether. The flask was cooled by ice throughout the course of this addition and the reaction mixture allowed to stand for at least two hours at room temperature. Dilute sulfuric acid (6 *N*) was then added with cooling until the precipitated hydrochloride had dissolved. A separation into two layers was observed. The lower layer was removed in a separatory funnel and the upper, containing the ester, was washed successively with water, dilute sulfuric acid, dilute sodium carbonate solution and then again three times with water. In the case of the *p*-nitro esters, it was necessary to wash the ethereal solution repeatedly with dilute sodium carbonate solution until, upon acidification of the washing solution, no further precipitate of *p*-nitrobenzoic acid was obtained. After drying over anhydrous sodium sulfate the ester was distilled under either atmospheric or diminished pressure.

Experimental

β-Methoxy Ethyl Benzoate.—In order to investigate the reaction of glycol ethers and benzoyl chloride in a medium other than pyridine, 15 g. (0.197 mole) of the mono-

[1] From a thesis presented by R. C. Conn to the Graduate School of West Virginia University in partial fulfilment of the requirements for the degree of Master of Science, June, 1932.

[2] Palomaa, *Ber.*, **42**, 3873 (1909).

methyl ether of ethylene glycol was dissolved in 40 g. of dry benzene contained in a 500-cc. round-bottomed flask and 28 g. (0.2 mole) of benzoyl chloride added. The flask was fitted with a reflux condenser and heated upon a steam-bath for three hours. The benzene was then removed and the remaining material distilled. After the removal of the unchanged benzoyl chloride, the main portion of the liquid distilled at 252–253° and 744 mm. pressure. The yield was 65%.[3]

The same quantities of glycol ether and benzoyl chloride reacting in 70 g. of pyridine gave a yield of 95%. It was concluded from this that it was better to use pyridine as a medium for such esterifications.

p-**Nitro β-Methoxy Ethyl Benzoate.**—26.5 g. (0.16 mole) of *p*-nitrobenzoyl chloride was dissolved in 15 cc. of pyridine. The ester was obtained as a yellowish solid which crystallized into almost transparent, rectangular plates and clusters of needles.

p-**Nitro β-Ethoxy Diethylene Glycol Benzoate.**—Thirty-five grams (0.2 mole) of *p*-nitrobenzoyl chloride was dissolved in 200 cc. of absolute ether and added to 25.3 g. (0.19 mole) of the monoethyl ether of diethylene glycol. The ester was obtained as a yellow amorphous oily solid which could not be crystallized. Analysis showed it to be impure and further purification will be made.

Table I lists the analyses of the compounds prepared. All nitrogen determinations were made by titration with titanous chloride solution.

TABLE I

ANALYSIS OF COMPOUNDS

Compound Benzoates	Calcd. for	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Yield, %
β-Ethoxy ethyl[a]	$C_{11}H_{14}O_3$							90.0
β-Butoxy ethyl	$C_{13}H_{18}O_3$	70.27	70.54	8.10	7.91			86.0
β-Ethoxy diethylene glycol	$C_{13}H_{18}O_4$	65.56	66.29	7.57	7.80			93.0
β-Butoxy diethylene glycol	$C_{15}H_{22}O_4$	67.55	66.72	8.27	8.05			88.0
p-Nitrobenzoates								
β-Methoxy ethyl	$C_{10}H_{11}O_5N$					6.22	6.24 6.19	95.0
β-Ethoxy ethyl	$C_{11}H_{13}O_5N$					5.86	5.96 5.93	87.5
β-Butoxy ethyl	$C_{13}H_{17}O_5N$					5.24	5.28 5.29	67.4
β-Ethoxy diethylene glycol[b]	$C_{13}H_{17}O_6N$							
β-Butoxy diethylene glycol	$C_{15}H_{21}O_6N$					4.50	4.57 4.52	57.9

[a] Palomaa states that he has prepared this compound but gives no analysis for it nor any of its physical constants. *Mol. wt.* (freezing point in benzene): theoretical, 194; found, 190.4, 190.5. [b] Analysis showed a nitrogen content of 5.4% as compared with a theoretical value of 4.98%. It was concluded that the material was impure.

Table II gives the physical constants determined for all the liquid esters prepared. All boiling points were determined with thermometers certified by the United States Bureau of Standards. Corrections for stem emergence have been made. Refractive indices were determined by means of an Abbé refractometer at 25°. Surface tensions were determined by means

[3] All yields recorded are given for the ester before distillation and are based upon the quantities of the glycol ether used.

of a du Noüy tensiometer at 26° and Harkins corrections for the ring method applied.

TABLE II

PHYSICAL CONSTANTS OF THE LIQUID ESTERS PREPARED

Compound Benzoates	B. p., °C.	*P*, mm.	D_{25}^{25}	n_D^{25}	γ^{26}
β-Methoxy ethyl	251.6–252.6[a]	738.5	1.0891[b]	1.5040	45.00
β-Ethoxy ethyl	260.0–261.0	738.5	1.0585	1.4969	40.67
β-Butoxy ethyl	156.5–157.0	14.5	1.0277	1.4925	39.86
	131.6–132.6	3.0			
β-Ethoxy diethylene glycol	160.0–161.0	14.5	1.1049	1.5080	43.79
	141.0–143.0	2.0			
β-Butoxy diethylene glycol	179.3–181.3	4.0	1.0407	1.4927	40.35
p-Nitrobenzoates					
β-Methoxy ethyl[c]	158.3–160.3	4.0			
β-Ethoxy ethyl	163.5–164.5	4.0	1.2086	1.5220	44.49
β-Butoxy ethyl	179.0–180.0	3.5	1.1518	1.5125	41.97
β-Ethoxy diethylene glycol[d]	207.0–209.0	4.0			
β-Butoxy diethylene glycol	230.0–232.0	4.0	1.1516	1.5078	41.02

[a] Palomaa gives 254–256° at 760 mm. [b] Palomaa gives 1.1067 at 15°. [c] Solid; crystallized in flat plates and needles; melting point 49.5°. Recrystallized from alcohol and water in white, glistening plates and needles, melting point 50.5°. These melting points were determined by means of a Gerhardt short stem thermometer with the stem completely immersed in the melting point tube. [d] The viscous liquid distillate sets to form an oily, amorphous solid.

Acknowledgment.—The authors wish to acknowledge their indebtedness to the Carbide and Carbon Chemical Company of Charleston, West Virginia, for their kind supply of the glycol ethers used in this investigation.

Summary

1. The following new compounds have been prepared and analyzed: β-butoxy ethyl benzoate, β-ethoxy diethylene glycol benzoate, β-butoxy diethylene glycol benzoate, *p*-nitro-β-methoxy ethyl benzoate, *p*-nitro β-ethoxy ethyl benzoate, *p*-nitro β-butoxy ethyl benzoate, *p*-nitro β-butoxy diethylene glycol benzoate.

2. β-Methoxy ethyl benzoate and β-ethoxy ethyl benzoate, compounds previously reported, have been prepared and additional data concerning them obtained.

3. Some of the physical constants of these compounds have been determined.

MORGANTOWN, WEST VIRGINIA

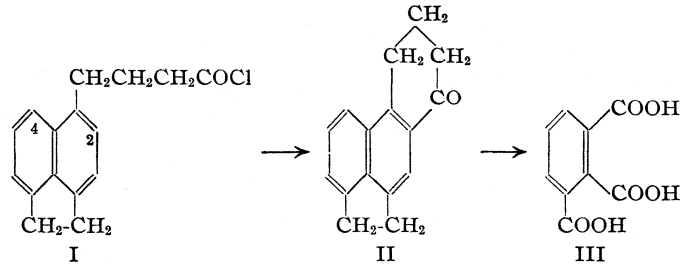
[Contribution from the Chemical Laboratory of Harvard University]

CONDENSATIONS AND RING CLOSURES IN THE NAPHTHALENE SERIES. IV. A SYNTHESIS OF ACEPHENANTHRENE

By Louis F. Fieser and Mary A. Peters

Received June 21, 1932 Published November 5, 1932

The striking behavior of β-(3-acenaphthoyl)-propionic acid on dehydration, when a seven-membered ring is closed across the *peri*-positions of acenaphthene,[1] suggested a study of the reduction product of this keto acid, namely, γ-(3-acenaphthyl)-butyric acid. If the acid chloride, I, were to react in a similar manner, condensation would take place at the activated position, 4; whereas condensation normally would be expected to occur at position 2.



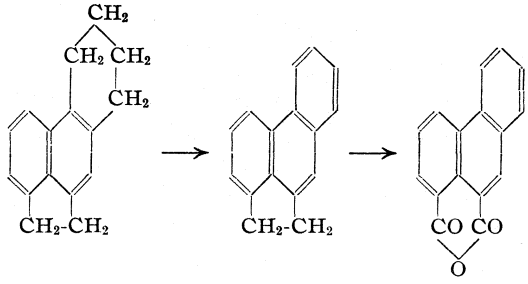
The reduction of the keto acid by the Clemmensen method presented some difficulties, arising from the high melting point (208°) and the slight solubility of the starting material; but it was found that the low-melting methyl ester survives hydrolysis long enough to permit reduction to take place. A second reaction in which a modification of the usual procedure had to be developed was the reaction of the reduced acid with thionyl chloride. Our method consisted in the use of ether as a diluent and pyridine as an active and, with highly purified reactants, an essential, catalyst. The acid chloride (I) condensed smoothly in cold nitrobenzene solution in the presence of aluminum chloride to give a cyclic ketone which was found to have the structure of II. The evidence is that the compound on oxidation yields hemimellitic acid, III, whereas the product of a condensation at position 4 could give only mellophanic acid. Further evidence is that on reduction by either the Clemmensen or the Wolff–Kishner method the ketone is converted into a hydrocarbon which is isomeric with peri-tetramethylene-acenaphthene[1] and which thus must have the only other possible formula, namely, that of IV.

That the condensation of the acenaphthylbutyric acid follows the normal course and thus differs from the reaction of the corresponding keto acid is not odd. The hindrance to condensation at position 2 exerted

[1] Fieser and Peters, This Journal, **54**, 4347 (1932).

by the keto group in the ortho position disappears on the reduction of this unsaturated group.

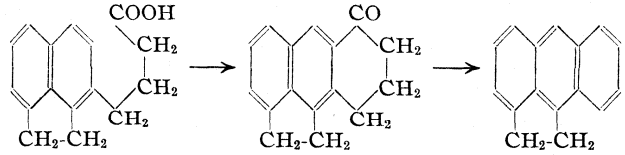
Since the cyclic ketone, II, obviously contains the phenanthrene skeleton, it opens the way to a synthesis of the interesting aromatic hydrocarbon, V, for which we propose the name acephenanthrene (or 8,9-acephenanthrene).



IV V VI

This hydrocarbon was obtained by the dehydrogenation of the tetrahydro derivative, IV, but the preparation of the latter compound by either of the two methods which we have so far investigated is far from satisfactory. It was found, however, that the ketone (II) on distillation with zinc dust is converted into a mixture of the desired product, V, and the tetrahydro derivative, IV. By heating the crude distillate with sulfur and distilling the product, pure acephenanthrene is easily obtained, and the yield from the ketone amounts to 26% of the theoretical. By substituting catalytic methods of reduction throughout the synthesis, we hope in the future to improve the method of producing the new hydrocarbon and to study its substitution reactions. The only observation which can be recorded now is that the substance is easily converted by oxidation into phenanthrene-8,9-dicarboxylic acid anhydride, VI, a compound which has been synthesized by Pschorr.[2]

The isomeric hydrocarbon, aceanthrene, has been prepared by Liebermann and Zsuffa,[3] but the substance evidently was not obtained in a pure condition for their product melted at 115–140°. It thus seemed worth while to prepare a sample by the synthesis: VII ⟶ VIII ⟶ IX,



VII VIII IX

for which β-(1-acenaphthoyl)-propionic acid[1] served as the starting material. There was no difficulty in obtaining a pure hydrocarbon.

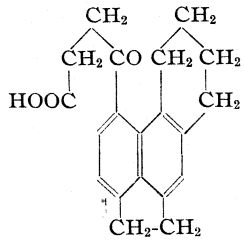
[2] Pschorr, *Ber.*, **39**, 3115 (1906).

[3] Liebermann and Zsuffa, *ibid.*, **44**, 852 (1911).

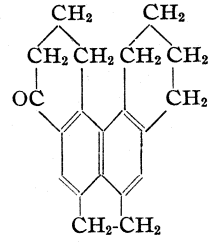
The series is thus complete and the compounds may be compared as follows

Acenaphthene, m. p. 95°; picrate, m. p. 161°
Acephenanthrene, m. p. 106°; picrate, m. p. 145°
Aceanthrene, m. p. 113°; picrate, m. p. 120°

The possibility of preparing a still higher benzolog of acenaphthene by repeating the series of reactions used in the above syntheses was examined briefly. Condensed with succinic anhydride in nitrobenzene solution, tetrahydroacephenanthrene gave in good yield a keto acid which probably has the structure of X. This is inferred from the fact that sub-



X



XI

stituents enter the 4-position of 3-alkylacenaphthenes.[4] The keto acid was easily reduced and the product converted through the acid chloride into the cyclic ketone, XI. The conversion of this, however, into a completely aromatic hydrocarbon did not proceed well, at least on the small scale of operation made necessary by the difficulty in preparing the starting material, IV.

Experimental Part

γ-(3-Acenaphthyl)-butyric Acid.—β-(3-Acenaphthoyl)-propionic acid itself is not affected by prolonged boiling with amalgamated zinc and hydrochloric acid. The methyl ester is reduced easily by this method when a small quantity of material (5 g.) is used, but we experienced difficulties in working with larger amounts, for in this case the ester became hydrolyzed to the high melting keto acid before enough of it had been reduced to keep the mixture in a liquid condition. The following procedure, though far from ideal, gave the most satisfactory and reliable results.

Fifty grams of β-(3-acenaphthoyl)-propionic acid was esterified with 250 cc. of methyl alcohol and 12.5 cc. of concentrated sulfuric acid. The hot solution of the ester was poured into a 3-liter flask containing 500 cc. each of water and concentrated hydrochloric acid and 150 g. of granulated zinc, which had been amalgamated with a solution of 30 g. of mercuric chloride. On boiling the mixture under the reflux condenser, the oily layer assumed a frothy consistency in about five hours, and the froth subsided after about ten hours of further heating. The water was then run out of the condenser and the alcohol was distilled off by gently boiling the mixture for about ten hours. Fresh acid and zinc were added during this period. Boiling was continued under the reflux condenser for about fifteen hours more, when the reduced acid formed a solid or semi-solid crust on top of the solution and the reaction was complete.

The crude material was extracted from the zinc with alkali and reprecipitated as a pasty solid. This was taken up in soda solution and the filtered solution was treated

[4] Dziewonski and Rychlik, *Ber.*, **58**, 2239 (1925).

with enough solid sodium chloride to force out the sodium salt. The salt is quite soluble and it is not greatly improved by further crystallization at this stage. It was converted into the free acid, which again came down in a somewhat oily condition. It was dried on the steam-bath and distilled *in vacuo*. A considerable residue was always left, but the acid was now easily obtained in a completely pure condition by crystallization from benzene. The yield of pure acid amounted to 17–22 g. (36–47%). When the keto ester was reduced by the ordinary Clemmensen method the yields occasionally mounted as high as 65% of the theoretical, but they sometimes fell to about 10%, and no reliable method of procedure was found.

The acenaphthylbutyric acid is very soluble in alcohol, readily soluble in benzene and sparingly so in ligroin. It forms stout, colorless needles melting at 148°.

Anal.[5] Calcd. for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 79.88; H, 6.82.

γ-(3-Acenaphthyl)-butyric Acid Chloride, I.—It was found essential to use for the reaction highly purified acid as well as thionyl chloride, for the acid chloride is very sensitive to traces of foreign materials in the reaction mixture and is easily converted into a dark resin. The thionyl chloride was thus distilled over quinoline and over linseed oil. The reaction was apparently too vigorous when the acid was warmed gently with an excess of thionyl chloride, for a dark, intractable tar was usually formed. We thus used ether as a medium in which to carry out the reaction but, owing to the slight solubility of the acid in this solvent, it was necessary to prepare the material in a finely divided condition. Even then little reaction between the very pure substances took place until a catalyst was added. Pyridine was found to be a good catalyst.

The acid used had been distilled and crystallized from benzene. It was then precipitated from an alkaline solution, digested at the boiling point, collected and thoroughly dried. Fifty grams of this colorless, powdery material was suspended in 250 cc. of anhydrous ether and 45 cc. of pure thionyl chloride was added. The mixture was brought into gentle reaction by adding five drops of pyridine and warming gently on the steam-bath. In about one-half hour, during which time some of the ether was allowed to boil off, the acid all went into solution. The solvent was then evaporated at the water pump, the flask being heated to 60–70°. The residue soon set to a hard, dark brown solid. It was dissolved in anhydrous ether and the solution was filtered from a small amount of dark residue and again evaporated to dryness. The acid chloride, which formed a hard gray solid, was warmed under a good vacuum in order to remove traces of thionyl chloride. In this form it is suitable for use in the condensation reaction described below, and the yield is practically theoretical.

The acid chloride dissolves readily in ether and crystallizes well as tufts of large, colorless needles. The dark impurities are washed out by cold ether. The pure substance melts at 83°.

Anal. Calcd. for $C_{16}H_{15}OCl$: C, 74.26; H, 5.85. Found: C, 74.22; H, 5.91.

1-Keto-1,2,3,4-tetrahydro-8,9-acephenanthrene, II.—Eight grams of aluminum chloride was added to a solution of 10 g. of the acid chloride in 50 cc. of nitrobenzene at 0°, the mixture was stirred until dissolution was complete and then allowed to stand for several hours in an ice-bath. The clear, orange-red solution was treated with water and the solvent removed by steam distillation. The condensation product separated as light brown, solid lumps. Nearly pure material was obtained by one distillation *in vacuo*. Using pure acid chloride the yield was 7.4 g. (87%); with the uncrystallized material the average yield was 6.3 g. (74%). The ketone was also prepared directly from the acid by using the method recently described by Haworth[6] for the ring closure

[5] For the analyses reported in this paper we are indebted to Mr. C. L. Bickel.

[6] Haworth, *J. Chem. Soc.*, 1125 (1932).

of the naphthylbutyric acids. In the present case, however, sulfuric acid of strength sufficient to produce the desired dehydration invariably sulfonated a considerable amount of material and the yields were in the order of 20%.

The ketone is moderately soluble in alcohol, more soluble in glacial acetic acid or in benzene. It crystallizes well from these solvents in the form of needles melting at 147°. As ordinarily prepared it is pale yellow, but the pure material is colorless. The solution in concentrated sulfuric acid is orange-yellow.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.22; H, 6.45.

The melting points of a few derivatives of the ketone are as follows: *oxime*, 225°; *phenylhydrazone*, 206°; *semicarbazone*, 302°.

Two oxidation products were obtained from the ketone. The first of these was prepared by heating 0.6 g. of the material with 2.5 cc. of concentrated nitric acid and 1.2 cc. of water for five hours at 160°. The clear solution resulting from this treatment left a colorless solid on evaporation to dryness *in vacuo*. This crystallized from an aqueous solution to which an equal volume of concentrated hydrochloric acid had been added as glistening plates melting at 225° (uncorr.) with vigorous gassing. The substance corresponds with the descriptions given in the literature[7] for phenylglyoxyldicarboxylic acid, for which a melting point of 238° (corr.) is recorded, and it was identical with the acid, m. p. 225°, obtained by a similar nitric acid oxidation of naphthalic anhydride. The keto acid was oxidized further with potassium permanganate and the final reaction product, purified through the potassium salt, crystallized as needles melting at 192°. It was identified as hemimellitic acid by comparison with a sample, m. p. 192°, prepared according to Graebe and Bossel.[7]

Reaction of the Ketone, II, with Grignard Reagents.—From the reaction of the ketone with an excess of phenylmagnesium bromide, there was obtained a hydrocarbon having the composition of *1-phenyl-3,4-dihydro-8,9-acephenanthrene*. It crystallized from alcohol or glacial acetic acid as colorless leaflets melting at 144°.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.53; H, 6.39.

In one experiment with methylmagnesium iodide the addition compound was decomposed with hydrochloric acid and an attempt was made to distil the reaction product. There was considerable decomposition or polymerization, but a small amount of a pure substance was isolated. This formed long blades, m. p. 159°, from alcohol. From the analysis it appears that the substance is the dehydrogenation product of the expected unsaturated hydrocarbon, namely, **1-methyl-8,9-acephenanthrene.**

Anal. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.40; H, 6.53.

In a second experiment the ketone was boiled in a solution containing a large excess of methylmagnesium iodide, ammonium chloride was used for the decomposition, and the distillation was omitted. This time there was obtained in good yield a hydrogenated hydrocarbon which separated very slowly from a ligroin solution as colorless prisms melting at 133° with swelling and frothing of the melt. It appears to be **1-methyl-1,2,3,4-tetrahydro-8,9-acephenanthrene.**

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.45; H, 8.25.

1,2,3,4-Tetrahydro-8,9-acephenanthrene, IV.—The Wolff–Kishner and the Clemmensen methods were both used for the reduction of the cyclic ketone, but neither reaction gave satisfactory results. The reaction with hydrazine always gave a considerable amount of the azil as a by-product, while with zinc and acid the desired hydrocarbon was accompanied by a product of bimolecular reduction. Though the yields were thus poor, the hydrocarbon is easily separated from the sparingly soluble by-products. It

[7] Graebe and Bossel, *Ann.*, **290**, 206 (1896).

distils well and crystallizes from alcohol as colorless plates melting at 92.5°. The picrate forms red needles melting at 112°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 92.10; H, 7.70.

Acephenanthrene, V.—Four grams of keto-tetrahydro-acephenanthrene was dissolved in benzene in a small distilling flask, 30 g. of zinc dust was added and the solvent was boiled off and completely removed by evacuation. The hard cake so formed was covered with 70 g. of zinc dust and the flask was sealed off at the top. The mixture was heated to a full red glow until no more material distilled. The distillate from three such reactions was combined, distilled once *in vacuo*, and treated with 0.8 g. of sulfur. Hydrogen sulfide was evolved copiously on gentle boiling, and after ten minutes the hydrocarbon was distilled at atmospheric pressure. The light yellow distillate formed a pasty solid, which was crystallized from alcohol. This gave 2.8 g. (26%) of material melting at 103–104°. A completely pure sample is best prepared by a distillation *in vacuo* followed by crystallization from alcohol. The hydrocarbon dissolves readily in this solvent and separates as faintly greenish-yellow plates melting at 106°. The picrate forms orange needles from alcohol, m. p. 145°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.93. Found: C, 93.70; H, 6.20.

8,9-Phenanthrenedicarboxylic Acid Anhydride, VI.—Four grams of powdered sodium dichromate was added in one portion to a warm solution of 0.8 g. of acephenanthrene in 10 cc. of glacial acetic acid. The mixture was stirred and warmed gently until the first, vigorous reaction was over, and then heated on the steam-bath for one-half hour. By this time considerable of the oxidation product had separated from the hot solution. The material was all precipitated by the addition of water and it was crystallized from glacial acetic acid. The anhydride (0.4 g.) formed small yellow needles melting at 266° (uncorr.). It corresponded in properties with the description given by Pschorr,[2] who reports a melting point of 283–284° (corr.).

Anal. Calcd. for $C_{16}H_8O_3$: C, 77.41; H, 3.25. Found: C, 77.49; H, 3.52.

The dimethyl ester of the free acid, prepared with the use of dimethyl sulfate in alkaline solution, was found to melt at 111°.

γ-(1-Acenaphthyl)-butyric Acid, VII.—β-(1-acenaphthoyl)-propionic acid, in the form of its methyl ester, was reduced easily by the usual method of Clemmensen, though the yield of pure product was only about 60% of the theoretical amount. The crude acid was purified by distillation and crystallization from benzene–ligroin. The compound forms small plates melting at 155°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 80.12; H, 6.81.

1-Keto-1,2,3,4-tetrahydro-5,10-aceanthrene, VIII.—The acid chloride for this ring closure was prepared by the ether–pyridine method already described and the unpurified material melted at 43°. The addition compound formed by reacting this acid chloride with aluminum chloride in nitrobenzene solution separated out in the form of a red paste. The pure cyclic ketone was obtained in 73% yield. It forms slender pale yellow needles melting at 145°. It is moderately soluble in alcohol and distils unchanged.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.20; H, 6.16.

Aceanthrene, IX.—This hydrocarbon resulted from the zinc dust distillation of the above ketone. It formed pale yellow, glistening plates melting at 113° from alcohol. The solutions are fluorescent. It yielded an anthraquinone on oxidation (vat test). The picrate formed long, dark red needles melting at 120°.

Anal. Calcd. for $C_{16}H_{12}$: C, 94.07; H, 5.93. Found: C, 93.95; H, 6.06.

β-(Tetrahydroacephenanthroyl)-propionic Acid, X.—Tetrahydroacephenanthrene (2.5 g.), IV, was condensed with succinic anhydride in nitrobenzene solution in the presence of aluminum chloride and the reaction product was extracted with soda solution after removal of the solvent. The material which separated on acidification was oily, but it was converted into a clear solid, m. p. 212–215°, by digestion with alcohol. The acid was purified in the form of the ester, obtained by boiling with methyl alcohol and sulfuric acid and crystallizing the product, which is only sparingly soluble in this medium, from glacial acetic acid; yield, 3.2 g.; m. p. 145°. The *methyl ester* forms slender needles, m. p. 146°, from glacial acetic acid or ligroin.

Anal. Calcd. for $C_{21}H_{22}O_3$: C, 78.22; H, 6.88. Found: C, 78.04, 77.70; H, 6.49, 6.97.

The free acid obtained from the purified ester formed silvery white plates, m. p. 218°, from glacial acetic acid.

γ-(Tetrahydroacephenanthryl)-butyric Acid.—The methyl ester of the keto acid (3.2 g.) was boiled with 300 cc. of 20% hydrochloric acid and 30 g. of amalgamated zinc for about fifteen hours. The material changed from a solid to a semi-solid condition and then again became solid at the end of the reaction. It was extracted from the zinc with soda solution and crystallized from benzene–ligroin until pure, the yield being 1.2 g. The acid forms colorless plates melting at 158°.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.54. Found: C, 81.46; H, 7.52.

5,6-Tetramethylene-1-keto-1,2,3,4-tetrahydro-8,9-acephenanthrene, VIII.—Ring closure of the above acid was accomplished by the general procedure already described, except that the acid in question, being fairly soluble in ether, could be used in the crystalline rather than the precipitated condition. The aluminum chloride compound of the ketone formed a bright red solution in nitrobenzene. The reaction product was purified by distillation, and crystallization from alcohol; yield, 0.7 g. The ketone formed slender, straw-yellow needles melting at 172°.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.91; H, 7.30. Found: C, 87.07; H, 7.64.

Summary

Acephenanthrene, a new hydrocarbon of an interesting type, and aceanthrene have been synthesized from the two keto acids resulting from the Friedel and Crafts reaction between acenaphthene and succinic anhydride.

Converse Memorial Laboratory
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

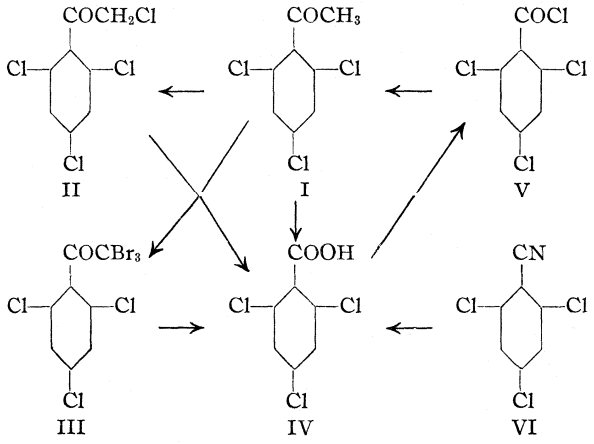
THE HALOFORM REACTION. VII. THE EFFECT OF ORTHO CHLORINE ATOMS

BY REYNOLD C. FUSON, JOHN W. BERTETTI AND WM. E. ROSS

RECEIVED JUNE 23, 1932 PUBLISHED NOVEMBER 5, 1932

It has been shown that the cleavage of methyl ketones by the action of hypohalite solutions involves the intermediate formation of corresponding trihalomethyl ketones. These intermediates have been found to be stable to cold solutions of alkali in those cases in which the positions ortho to the carbonyl group are occupied. The stabilizing effect of methyl groups[1] and of bromine atoms[2] in the ortho positions has been found to be very great. Cleavage of the trihalomethyl ketones in these cases has been effected only by long treatment with hot, concentrated solutions of alkali. The effect of methoxy groups[3] has, however, proved to be less pronounced. The di-*o*-methoxy trihalomethyl ketones, while sufficiently stable toward cold solutions of alkali, have been found to be cleaved readily by hot alkaline solutions.

The present paper is a report of a similar study of the effect of ortho chlorine atoms For this purpose 2,4,6-trichloroacetophenone (I) was used.



In the synthesis of this ketone, 2,4,6-trichloroaniline was used as the starting material. It was converted into 2,4,6-trichlorobenzonitrile (VI) by means of the Sandmeyer reaction.[4] The hydrolysis of the nitrile to 2,4,6-trichlorobenzoic acid (IV) was effected by heating it with a mixture of

[1] Fuson and Walker, THIS JOURNAL, **52**, 3269 (1930); Gray, Walker and Fuson, *ibid.*, **53**, 3494 (1931).

[2] Fuson, Lewis and DuPuis, *ibid.*, **54**, 1114 (1932).

[3] Fuson, Farlow and Stehman, *ibid.*, **53**, 4097 (1931).

[4] Compare Sudborough, Jackson and Lloyd, *J. Chem. Soc.*, **71**, 231 (1897).

concentrated sulfuric acid and glacial acetic acid. The yield in this step was about 50% of the theoretical. A good yield of 2,4,6-trichlorobenzoyl chloride (V) was obtained from the acid by treatment with phosphorus pentachloride.

The ketone was prepared from the acid chloride by treatment of the latter with a solution of methylmagnesium chloride. The rate of this reaction is remarkably slow. Four hours of heating of the reaction mixture left the acid chloride largely unchanged, and it was necessary to heat for twenty-four hours in order to obtain the ketone. This treatment gave 2,4,6-trichloroacetophenone in yields of about 50% of the theoretical.[5]

By treatment with a solution of sodium hypobromite, the ketone was converted into α,α,α-tribromo-2,4,6-trichloroacetophenone (III). The yield was very good, showing that the tribromomethyl ketone is not affected by protracted treatment with cold solutions of alkali. When heated with a 50% solution of sodium hydroxide, however, the ketone was almost quantitatively converted into the corresponding acid, 2,4,6-trichlorobenzoic acid (IV).

Attempts to prepare the α,α,α,2,4,6-hexachloroacetophenone led to unexpected results. Treatment of 2,4,6-trichloroacetophenone with solutions of hypochlorite failed to yield the hexachloro compound but gave instead α,2,4,6-tetrachloroacetophenone. This result was surprising because it is the first case of the formation of a monochloromethyl ketone by treatment of a methyl ketone with a hypochlorite solution. Moreover, attempts to convert the tetrachloro compound into the hexachloro derivative by further treatment with hypochlorite solutions were likewise unavailing. In these attempts the tetrachloro compound was either recovered unchanged or was converted into the corresponding acid, 2,4,6-trichlorobenzoic acid. It was found possible also to obtain this acid by prolonged treatment of the methyl ketone with hypochlorite solutions. Although in both of these cases the hexachloro compound must have been formed as an intermediate, direct evidence of its existence was not obtained.

Experimental

2,4,6-Trichlorobenzonitrile.—The method of Sudborough, Jackson and Lloyd[4] was used. The average yield of nitrile obtained was about 35% of the theoretical.

2,4,6-Trichlorobenzoic Acid.—Forty-five grams of 2,4,6-trichlorobenzonitrile was placed in a 2-liter flask fitted with a reflux condenser and containing 500 cc. of a mixture of two parts concentrated sulfuric acid, one part water, and one part glacial acetic acid—all by volume. The mixture was refluxed for three hours. It was cooled to

[5] This reaction between 2,4,6-trichlorobenzoyl chloride and methylmagnesium chloride is interesting because it shows the effect of steric hindrance on a reaction which may be either additive or metathetical. In view of the fact that reactions of the former type are generally much more greatly affected by steric factors than are those known to be of the latter type, the results here reported suggest that the primary reaction between RMgX and an acid chloride is one of addition.

10° and the calculated amount of sodium nitrite, dissolved in as little water as possible, was run in slowly, vigorous stirring being maintained all the while and the sodium nitrite solution being run beneath the surface of the liquid. The mixture was then heated on the steam cone until all of the gas was expelled. The acid was filtered, dissolved in sodium hydroxide solution and reprecipitated with hydrochloric acid. An average yield of 34% of the theoretical was obtained from three runs. The acid precipitated as nearly colorless platelets which melted at 162°.

2,4,6-Trichlorobenzoyl Chloride.—Sixteen grams of 2,4,6-trichlorobenzoic acid was mixed with 15 g. of phosphorus pentachloride in a small beaker. The mixture liquefied at once. After the mixture was allowed to stand for half an hour, the phosphorus oxychloride was distilled under slightly diminished pressure and the acid chloride was collected from 107–107.5° under 6 mm. pressure. An average yield of 73% of the theoretical was obtained.

2,4,6-Trichloroacetophenone.—Twenty-five cubic centimeters of two-molal methylmagnesium chloride was placed in a 200-cc. flask fitted with a condenser. Twelve and three-tenths grams of the acid chloride was dissolved in 50 cc. of dry ether and added at one time to the Grignard reagent. The mixture was refluxed for twenty-four hours. At the end of this time the reaction mixture was decomposed with dilute hydrochloric acid and the ketone extracted with ether. It was recrystallized from alcohol, from which it precipitated in the form of fine, almost colorless needles. The product melted from 156–157°. A yield of 50% of the theoretical was obtained.

Anal. Calcd. for $C_8H_5OCl_3$: Cl, 47.6. Found: Cl, 47.8.

α,α,α-Tribromo-2,4,6-trichloroacetophenone.—Five grams of 2,4,6-trichloroacetophenone was placed in a 500-cc. three-necked flask, fitted with a mercury-sealed stirrer and a thermometer and containing 500 cc. of sodium hypobromite solution. The sodium hypobromite solution was prepared by dissolving 50 g. of bromine in 500 cc. of 10% sodium hydroxide solution at 0°. The mixture was stirred for eighty hours. The temperature was kept around 50° for the first thirty hours and then raised to 70°. The product was filtered, washed several times with water and recrystallized from alcohol. Eight grams of the tribromo compound, melting at 126–127°, was obtained. The compound crystallizes in fine, almost colorless granules. A yield of 80% of the theoretical was obtained.

Anal. Equivalents of halogen per gram of substance: Calcd. for $C_8H_2OCl_3Br_3$: X, 0.0130. Found: X, 0.01284.

Action of Alkali on α,α,α-Tribromo-2,4,6-trichloroacetophenone.—Three grams of α,α,α-tribromo-2,4,6-trichloroacetophenone was heated for four hours on a steam cone at 90° with 200 cc. of 50% sodium hydroxide solution. Nothing appeared to happen to the ketone, but on diluting the solution, all of the suspended material went into solution. The solution was made acid with hydrochloric acid and the 2,4,6-trichlorobenzoic acid precipitated. One and three-tenths grams of the acid was obtained, which corresponds to a nearly quantitative cleavage of the halogenated ketone. The acid melted at 161–162° after one precipitation.

α,2,4,6-Tetrachloroacetophenone.—Two grams of 2,4,6-trichloroacetophenone was shaken with 200 cc. of sodium hypochlorite solution for fifty hours at room temperature. The sodium hypochlorite solution was prepared by bubbling chlorine into 200 cc. of 10% sodium hydroxide solution, cooled to 0°, until the solution was acidic. Another 200 cc. of 10% sodium hydroxide solution was then added to this. Two and one-half grams of material was obtained. After three recrystallizations from alcohol, the compound melted at 106.5–107.5°.

The tetrachloro compound was also obtained by heating 2,4,6-trichloroacetophenone with sodium hypochlorite solution for eight hours at 90°.

Anal. Calcd. for $C_8H_4OCl_4$: Cl, 55.0. Found: Cl, 55.1.

2,4,6-Trichlorobenzoic Acid from 2,4,6-Trichloroacetophenone.—Five-tenths gram of 2,4,6-trichloroacetophenone was shaken with a mixture of 100 cc. of 10% sodium hypochlorite solution and 20 cc. of pyridine for seventy-two hours at room temperature. The solution was acidified with hydrochloric acid and extracted with ether. The material obtained on evaporation of the ether was dissolved in dilute sodium hydroxide solution and reprecipitated with hydrochloric acid. It melted from 159–162°. The conversion of the ketone to the acid was practically quantitative.

2,4,6-Trichlorobenzoic Acid from α,2,4,6-Tetrachloroacetophenone.—Five-tenths gram of α,2,4,6-tetrachloroacetophenone was stirred with 100 cc. of 10% sodium hypochlorite solution and 10 cc. of pyridine at 90° for twenty-four hours. The solution obtained on evaporation of the ether was dissolved in dilute sodium hydroxide solution and reprecipitated with hydrochloric acid. It melted at 160°. The yield of the acid was 97% of the theoretical.

Summary

2,4,6-Trichloroacetophenone has been prepared and its reaction with solutions of sodium hypohalites has been studied. When hypobromite solutions were used, α,α,α-tribromo-2,4,6-trichloroacetophenone was obtained. Treatment with hot, concentrated solutions of sodium hydroxide converted this ketone into 2,4,6-trichlorobenzoic acid.

With sodium hypochlorite solutions 2,4,6-trichloroacetophenone gave α,2,4,6-tetrachloroacetophenone. Prolonged treatment with the hypochlorite solutions converted both the trichloro and the tetrachloro compounds into 2,4,6-trichlorobenzoic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HOLY CROSS COLLEGE]

PHENACYL AND *p*-BROMOPHENACYL ESTERS OF MONOSUBSTITUTED BENZOIC ACIDS[1]

BY T. LEONARD KELLY AND HARTLEY W. HOWARD

RECEIVED JUNE 24, 1932 PUBLISHED NOVEMBER 5, 1932

The use of phenacyl and *p*-bromophenacyl esters was introduced by Reid and co-workers[2] as a means of identifying acids. Since easily prepared and easily purified esters of organic acids are highly desirable the present investigation was undertaken.

Experimental

The procedure for the preparation of the esters was essentially the same as that of Reid. In the case of the amino acids, however, a modified procedure was used. By using the method of Reid on the amino acids very low yields were obtained. It was then considered possible that one mole

[1] This paper is constructed from a thesis submitted by Hartley W. Howard to the Faculty of Holy Cross College in partial fulfilment of the requirements for the degree of Master of Science.

[2] Reid and co-workers, THIS JOURNAL, **41**, 75 (1919); *ibid.*, **42**, 1043 (1920).

of the reagent might substitute in place of an amino hydrogen, thereby forming a N-phenacyl derivative of the acid as well as the ester of this derivative. A search revealed that Scholtz[3] had prepared the N-phenacyl acids of *o*-, *m*- and *p*-aminobenzoic acids. He also prepared and analyzed the phenacyl esters of the N-phenacyl *o*- and *p*-amino acids. The procedure we used was to take 0.005 equivalent of the acid, which was not quite neutralized with sodium carbonate in 5 cc. of water, and 2 g. of the reagent dissolved in alcohol and reflux for ninety minutes. After cooling, the precipitate was filtered and washed. It was then stirred into 100 cc. of 1% sodium hydroxide to dissolve the N-substituted acid. The ester, insoluble in alkali, was filtered and washed. The N-substituted acid was recovered by acidifying the alkaline filtrate with hydrochloric acid. The ester was then recrystallized to constant melting point.

Results

The results are expressed in tabular form, the first column giving the melting point of the acid used, the second the melting point of the ester and the third the percentage yield.

TABLE I

PHENACYL AND *p*-BROMOPHENACYL ESTERS

Acid	M. p., °C.	Phenacyl esters Ester m. p., °C.	Yield, %	*p*-Bromophenacyl esters Ester m. p., °C.	Yield, %
o-Bromobenzoic	147	83.2	99	101.6	86
m-Bromobenzoic	154	113.4	88	126.4	85
p-Bromobenzoic	252	...	..	133.8	84
o-Chlorobenzoic	138	83	97	106	80
m-Chlorobenzoic	153	116.4	98	117.2	82
p-Chlorobenzoic	235	87.6	98	126	80
o-Iodobenzoic	162	71	96	110.2	91
m-Iodobenzoic	185	115.6	78	127.6	81
p-Iodobenzoic	268	101 dec.	84	146.4	61
o-Nitrobenzoic	144	124.5	83	100.6	88
m-Nitrobenzoic	139	104.5	86	133.6	85
p-Nitrobenzoic	237	...	..	134	89
m-Hydroxybenzoic	196	146.5	79	168	79
p-Hydroxybenzoic	211	178	91	184	79
o-Nitrocinnamic	243	126	91	141.5	92
m-Nitrocinnamic	197	145.5	89	177.5	91
p-Nitrocinnamic	285	146.2		190.5	89

TABLE II

p-BROMOPHENACYL ESTERS OF N-*p*-BROMOPHENACYL AMINOBENZOIC ACIDS

Acid	M. p., °C.	Ester m. p., °C.	Yield, %
o-Aminobenzoic	144	172	52
m-Aminobenzoic	169	190	36
p-Aminobenzoic	187	200	62

[3] Scholtz, *Ber.*, **51**, 1645 (1918).

These three esters were analyzed for bromine and checked with the calculated percentages. Acetone was used as solvent for recrystallizations. No precipitate was obtained upon acidifying the alkaline filtrate from the ortho acid. From the meta acid a precipitate, presumably N-*p*-bromophenacyl-*m*-aminobenzoic acid, was obtained. It melted at 198°. From the para acid a precipitate, presumably N-*p*-bromophenacyl-*p*-aminobenzoic acid, was obtained which melted at 208°.

Summary

1. The esters formed by phenacyl bromide and *p*-bromophenacyl bromide with the aminobenzoic acids are shown to be substituted in the amine group as well as the carboxyl group.

2. A number of substituted benzoic acids have been converted to the phenacyl and *p*-bromophenacyl esters and their melting points recorded.

WORCESTER, MASSACHUSETTS

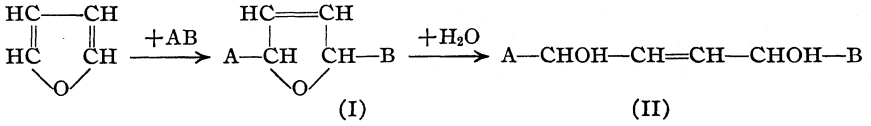
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

REARRANGEMENT OF UNSATURATED 1,4-GLYCOLS. 2-METHYL-2-BUTENE-1,4-DIOL

BY A. F. SHEPARD[1] AND JOHN R. JOHNSON

RECEIVED JUNE 27, 1932 PUBLISHED NOVEMBER 5, 1932

It has been suggested that the mechanism of a number of reactions of furan and its simple derivatives involves a preliminary 1,4-addition to the furan ring. Such reactions include the processes of halogenation[2] and nitration,[3] as well as the rearrangement of the α-furfuryl group in metathesis[4] and in ring opening reactions.[5,6] The postulation of 1,4-addition leads to the formulation of an intermediate 2,5-dihydrofuran derivative (I), which is merely the cyclic ether of a substituted 2-butene-1,4-diol (II).



(I) (II)

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[1] This article is an abstract of a portion of a thesis submitted by A. F. Shepard to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1929.

[2] Gilman and Wright, THIS JOURNAL, **52**, 3349 (1930).

[3] Freure and Johnson, *ibid.*, **53**, 1142 (1931).

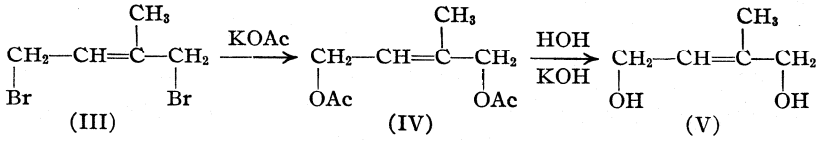
[4] (a) Reichstein, *Ber.*, **63**, 749 (1930); (b) Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930).

[5] Pummerer and Gump, *Ber.*, **56**, 999 (1923).

[6] In dealing with furan derivatives such as C_4H_3O—CH=CH—CO—R, in which the conjugated system extends into the side chain, it has been suggested that 1,6- or 1,8-addition may occur.[2]

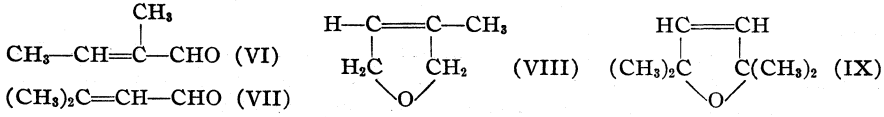
The present investigation deals with a study of the preparation and reactions of a simple aliphatic compound containing this system.

For the synthesis of a typical glycol of the desired structure, isoprene was used as the starting material.[7] This was treated with bromine to give 1,4-dibromo-2-methylbutene-2 (III), the structure of which has been established.[8] The dibromide was converted to the corresponding diacetate, 1,4-diacetoxy-2-methylbutene-2 (IV); the structure of this ester was established by catalytic hydrogenation, which gave the diacetate of 2-methylbutane-1,4-diol. The unsaturated ester, upon hydrolysis with alkalies, gave the expected glycol, 2-methyl-2-butene-1,4-diol (V). That no change of structure had occurred during hydrolysis was shown by the fact that the product upon catalytic hydrogenation gave 2-methylbutane-1,4-diol. The latter was identified through its bis-diphenylurethan and by conversion into 3-methyltetrahydrofuran.



(III) (IV) (V)

The unsaturated glycol was found to undergo dehydration very easily upon warming with halogen acids, and a liquid having the composition C_5H_8O and boiling at 116.5–117.5° was produced in yields up to 65%. The same product was also obtained by warming the glycol with zinc chloride, or by subjecting its diacetate (IV) to the action of alcoholic hydrogen chloride. The liquid product, C_5H_8O, took up two atoms of bromine and it was thought at first to be 3-methyl-2,5-dihydrofuran (VIII). Further examination disclosed that the substance gave the reactions of an aldehyde and proved it to be tiglic aldehyde (VI). This was established by means of physical and chemical properties and by comparison of its semicarbazone with that of authentic tiglic aldehyde. A careful examination indicated that neither 3-methyl-2,5-dihydrofuran nor 3-methyl-2-butenal (VII) was present in appreciable quantity.



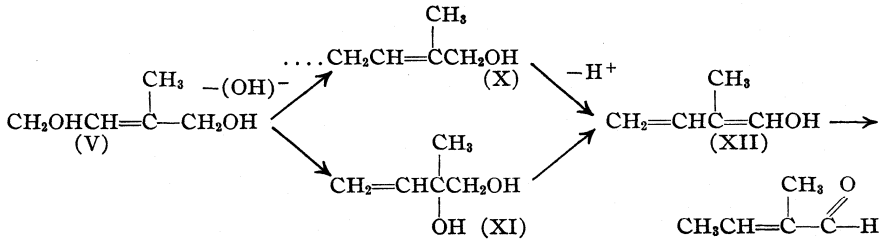
In view of the observation that an analogous unsaturated 1,4-glycol containing tertiary alcohol groups (2,4-dimethyl-3-hexene-1,4-diol) is readily

[7] We wish to express our appreciation to Mr. Thomas Midgley, Jr., for his generous gift of the isoprene used in this work, and to Dr. Albert L. Henne for valuable suggestions in the course of the experimental work.

[8] (a) Bergmann, *J. Russ. Phys.-Chem. Soc.*, **52**, 24 (1920), [*Chem. Abstracts*, **17**, 1420 (1923)]; (b) Staudinger, Muntwyler and Kupfer, *Helv. Chim. Acta*, **5**, 756 (1922).

dehydrated to the corresponding dihydrofuran (IX),[9] and the ease with which saturated 1,4-glycols undergo ring closure to form derivatives of tetrahydrofuran, the observed rearrangement was quite unexpected. It is of interest to note that Prévost[10] has reported the formation of small amounts of crotonic aldehyde and of γ-methylcrotonic aldehyde, respectively, as by-products in the hydrolysis of 1,4-dibromo-2-butene and 1,4-dibromo-2-pentene by aqueous sodium carbonate. He has suggested a mechanism for the rearrangement and considers the reaction to be quite general for unsaturated 1,4-dihalides of this type, provided at least one primary halogen ($—CH_2X$) is present.

The observed rearrangement of an unsaturated 1,4-glycol is like that of a number of saturated glycols (hydrobenzoin rearrangements). It appears that the presence of the double bond in the 1,4-glycol (and in similar 1,4-dihalides) allows a 1,4-shift to occur in this unsaturated system as readily as a 1,2-shift occurs in a saturated structure. In considering a mechanism for this rearrangement it seems inadvisable to assume the formation of 3-methyl-2,5-dihydrofuran (VIII) as an intermediate stage, since this compound would hardly be expected to undergo ring opening under the various conditions used to bring about the rearrangement (particularly, heating with zinc chloride).



It is more likely that an unstable open-chain enol (XII) is formed as an intermediate stage and the enol undergoes a 1,4-tautomeric shift to produce tiglic aldehyde. This 1,4-tautomeric shift is strictly analogous to the 1,4-enolization of crotonic aldehyde suggested by Prévost[10] and by Kuhn and Ishikawa.[11] The formation of the intermediate enol may occur by a direct non-simultaneous elimination of hydroxyl and hydrogen from the 4- and 1-positions, respectively, through the unstable structure (X) or by a preliminary α,γ-allylic shift of the 4-hydroxyl group to produce an unsaturated 1,2-glycol (XI), followed by 1,2-dehydration. On the whole, it seems quite unnecessary to assume the α,γ-allylic shift suggested as the second alternative. The latter would imply a detachment of the hydroxyl from the 4-position and removal to the 2-position, only to become detached

[9] Salkind, *Ber.*, **56**, 189 (1923).

[10] Prévost, *Bull. soc. chim.*, [4] **43**, 1005 (1928).

[11] Kuhn and Ishikawa, *Ber.*, **64**, 2348 (1931).

a second time and finally converted to water by combination with a hydrogen from the 1-position.

It is evident from the behavior of the particular 2-butene-1,4-diol under examination that a further study of these structures is necessary before the results can be used with assurance in dealing with the reactions of substituted 2,5-dihydrofuran structures.

Experimental Part

Isoprene.—The isoprene used in these experiments was obtained from Mr. Thomas Midgley, and had been prepared from crepe rubber by the process described by Midgley and Henne.[12] The material boiled at 34–36°, and contained small amounts of the isomeric 2-methylbutenes as impurities.

1,4-Dibromo-2-methylbutene-2 (Isoprene Dibromide).—To a well-stirred solution of 68 g. (1 mole) of isoprene in 100 cc. of chloroform, maintained below −25° with a slush of ether and carbon dioxide snow, was added dropwise an ice-cold solution of 160 g. (1 mole) of bromine in 250 cc. of chloroform. A fairly sharp end-point of the reaction could be noted when practically all the bromine had been added. The slight excess of bromine was removed by shaking with sodium bisulfite, and the chloroform was removed by heating on a water-bath. The purification of the dibromide was tedious and involved loss of material through decomposition during the repeated distillations.

The product from 145 g. of isoprene after three fractionations under reduced pressure gave 165 g. of a fraction boiling at 90–96° under 12 mm. This fraction corresponds with that used by Staudinger[8b] in his proof of the 1,4 structure of the dibromide. The lachrymatory product was only slightly colored when freshly distilled, but darkened rapidly on standing.

Anal. Calcd. for $C_5H_8Br_2$: Br, 70.14. Found: Br, 71.12, 70.97.

Diacetate of 2-Methyl-2-butene-1,4-diol.—A mixture of 147 g. of the above dibromide, 149 g. of freshly fused, finely powdered potassium acetate and 100 cc. of glacial acetic acid was heated for eighteen hours on a boiling water-bath. The reaction mixture was poured into a liter of water, and the brown oily layer was separated. The water solution was extracted several times with ether, and after removal of the ether this extract was combined with the oily layer and vacuum distilled. The main fraction (120 g.) distilled from 110–132° at 14 mm., and still contained about 7% of combined bromine.

To complete the removal of bromine the product was refluxed for eight hours with 30 cc. of glacial acetic acid and 40 g. of potassium acetate. The product was isolated as before, and upon careful fractionation gave 70 g. of a fraction boiling at 120.5–122.5° under 10 mm. Analysis of this material showed that it contained only a trace of bromine (0.27%). Physical constants were determined on a specimen of this purity: d_4^{20} 1.0703, n_D^{20} 1.4494, MR_D, calcd. 46.60, obs. 46.67.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.03; H, 7.58. Found: C, 57.90, 58.08; H, 7.64, 7.59; (Br, 0.27).

The diacetate is a colorless and practically odorless liquid; it is miscible with alcohol and ether but is sparingly soluble in water. It adds bromine readily; a solution of 0.05 mole of the diacetate in carbon tetrachloride at −25° took up 0.05 mole of bromine. The structure of the diacetate was established by catalytic hydrogenation, which gave the diacetate of 2-methylbutane-1,4-diol.

[12] Midgley and Henne, THIS JOURNAL, **51**, 1215 (1929).

In preparing large quantities of the diacetate of 2-methyl-2-butene-1,4-diol, it was found advantageous to convert the crude isoprene dibromide directly to the diacetate, by the method described above, without subjecting the dibromide to repeated fractionations. In this way there was obtained from 204 g. (3 moles) of isoprene, 200–230 g. of the purified diacetate (32–40% of the theoretical yield). As by-products of the reaction a mixture of lower boiling unsaturated bromides (b. p. 140–160°) and a quantity of complex decomposition products are formed.

Diacetate of 2-Methylbutane-1,4-diol.—A solution of 27 g. (0.14) of the unsaturated diacetate (b. p. 111.5–113.5° at 8 mm.) in 20 cc. of alcohol was reduced catalytically using 0.1 g. of platinum oxide.[13] Five grams of pure calcium carbonate was added to neutralize any hydrobromic acid produced from traces of bromide in the diacetate. The calcium carbonate appeared to diminish the rate of reduction but it was found that in the absence of a neutralizing agent, more than one mole of hydrogen was taken up.

The theoretical quantity (0.14 mole) of hydrogen was taken up in about two hours and no more was absorbed thereafter. The entire product distilled at 110–122° under 17 mm.; the principal fraction was collected at 115.5–116.5° (17 mm.) and had the following constants: d_4^{20} 1.0476, n_D^{20} 1.43301; MR_D (calcd.) 47.07, (obs.) 46.67. This diacetate has been described by Harries and Nerescheimer,[14] who prepared it from the glycol obtained by reducing ethyl methylsuccinate with metallic sodium and alcohol. They reported the following constants: b. p. 116–117 at 17 mm., d_4^{20} 1.0415, n_D^{20} 1.42717, MR_D (obs.), 46.3.

2-Methylbutane-1,4-diol.—For further identification the saturated diacetate was hydrolyzed with barium hydroxide and the saturated glycol was isolated: b. p. 127.5–128.5° at 13 mm., n_D^{18} 1.4515 (previously reported: b. p. 124–125° at 13 mm., n_D^{18} 1.4517). The bis-diphenylurethan of this glycol melted at 99.5–100.5° (corr.) after one crystallization from ligroin (b. p. 70–80°). Harries and Nerescheimer reported the melting point of 102° for the bis-diphenylurethan of 2-methylbutane-1,4-diol.

3-Methyltetrahydrofuran.—A sample of the saturated glycol was converted into 3-methyltetrahydrofuran by warming with 25% sulfuric acid and distilling off the volatile product during the course of the heating. In this way 15 g. of the glycol gave 5 g. of 3-methyltetrahydrofuran: b. p. 84–88°, n_D^{20} 1.4090 (previously reported:[14] b. p. 86–87°, n_D^{20} 1.4112).

Several attempts to dehydrogenate 3-methyltetrahydrofuran were unsuccessful. It was unaffected by passage through a 40-cm. tube of platinized asbestos at 300–450°. When passed over a nickel catalyst at 400°, about one-half of the material was lost. The condensed product had the same characteristic ethereal odor and the same refractive index as the original preparation and did not give the furan test (green coloration) with concd. hydrochloric acid.

2-Methyl-2-butene-1,4-diol.—Twenty-three grams of the diacetate of 2-methylbutenediol was refluxed for two hours with 15 g. of potassium hydroxide in 100 cc. of methyl alcohol. After distilling off the solvent, the glycol was removed from the residual semi-solid mass by distillation under reduced pressure. There was obtained 8 g. of the crude glycol, which distilled at 130–135° under 12 mm., and on redistillation 4 g. of a pure product: b. p. 127.5–128° at 7 mm., d_4^{20} 1.0434, n_D^{20} 1.4815, MR_D (calcd.) 27.87, (obs.) 27.87.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.79; H, 9.87. Found: C, 58.93, 59.02; H, 9.74, 9.97.

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[13] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, pp. 10, 92.

[14] Harries and Nerescheimer, *Ann.*, **383**, 168 (1911).

The glycol had a very faint yellow color even when freshly distilled, and a slightly sweet burnt taste. It is miscible with alcohol and water, but is practically insoluble in ether, benzene and carbon tetrachloride. It decolorized a solution of bromine in carbon tetrachloride.

The glycol was much more conveniently obtained by refluxing the diacetate with ten parts of ethyl alcohol and twice the theoretical amount of powdered barium hydroxide for five hours. The dissolved barium salts separated out nearly completely on cooling and were filtered off and washed with alcohol. The small amount of dissolved barium salts was then completely removed by passing in carbon dioxide. After filtration, 80–85% of the theoretical amount of pure glycol could be recovered from the alcoholic solution by vacuum distillation.

Five grams of the unsaturated glycol was dissolved in 50 cc. of alcohol, to which 0.1 g. of platinum oxide and 1.0 g. of sodium bicarbonate were added, and reduced with hydrogen. The reduction was complete in about twenty minutes. After filtering the solution and removing the solvent, the product boiled entirely from 127–135° at 15 mm. and no other fraction was obtained. The saturated glycol obtained thus was identical with the specimen of 2-methylbutane-1,4-diol described above. The bis-diphenylurethan melted at 99–100° and a mixture of this urethan and the one previously prepared melted at 99.5–100.5°. This glycol was also converted to 3-methyltetrahydrofuran by heating with 25% sulfuric acid.

Tiglic Aldehyde (2-Methyl-2-butenal).—2-Methyl-2-butene-1,4-diol was converted into tiglic aldehyde in several ways. On warming 4.0 g. of the glycol with 0.3 g. of anhydrous zinc chloride, in a 10-cc. distilling flask provided with a condenser attached directly to the side arm, a vigorous reaction occurred and a liquid distilled at 110–120°. This distillate consisted of 0.7 g. of water and 2.7 g. of crude tiglic aldehyde. This aldehyde was also obtained merely by heating the glycol at atmospheric pressure, by warming the glycol in the presence of a trace of hydrogen chloride and by warming the diacetate with a solution of hydrogen chloride in methyl alcohol. The procedure described below was found to be a convenient method for use with quantities of 40–50 g. of the glycol.

To 41 g. (0.4 mole) of 2-methyl-2-butene-1,4-diol, maintained at 0°, was added slowly 37.6 g. (0.4 mole) of 11 *N* aqueous hydrochloric acid. After shaking thoroughly the solution was allowed to stand at 0° for two hours, when 31.6 g. (0.4 mole) of pyridine was added. On warming gently the solution separated into two layers, and the tiglic aldehyde was removed by distilling the aqueous mixture. The product was freed from pyridine by steam distillation from slightly acid solution, and dried over anhydrous sodium sulfate. On fractionation there was obtained 22 g. (65% yield) of tiglic aldehyde, b. p. 115–119°. All preparations of the aldehyde contained small amounts of high-boiling material which was easily removed by distillation. No low-boiling fraction (in which 3-methyl-2,5-dihydrofuran would have appeared) was found in any of the preparations. For analysis and determination of physical constants a redistilled specimen was used: b. p. 116.5–117.5° (corr.) at 738 mm., d_4^{20} 0.8710, n_D^{20} 1.4475, MR_D (calcd.) 24.83, (obs.) 25.81.

Anal. Calcd. for C_5H_8O: C, 71.38; H, 9.59. Found: C, 71.10, 71.00; H, 9.57, 9.45.

The physical constants are in reasonably good agreement with those reported for tiglic aldehyde by previous investigators:[15,16] b. p. 115.8° at 739 mm.; b. p. 116°, d_4^{18} 0.870, n_D 1.44956. The isomer, 3-methyl-2-butenal, has the following properties:[17] b. p. 132–133° at 730 mm., d_4^{20} 0.8722, n_D^{20} 1.4526; semicarbazone, m. p. 221–222°.

[15] Lieben and Zeisel, *Monatsh.*, **7**, 55 (1886).

[16] Grignard and Abelmann, *Bull. soc. chim.*, [4] **7**, 644 (1910).

[17] Fischer, Ertel and Löwenburg, *Ber.*, **64**, 30 (1931).

The aldehyde gave a strong positive test with Schiff's aldehyde reagent and produced a silver mirror on warming with ammoniacal silver oxide. The semicarbazone, after crystallization from alcohol and drying at 110°, melted in a capillary tube at 200–209°, with slight decomposition; on the Maquenne block it melted at 234°. Grignard and Abelmann reported that tiglic aldehyde semicarbazone melts at 225° (uncorr.) but did not state the manner in which this value was determined. To confirm the identity of the semicarbazone in hand, an authentic specimen of tiglic aldehyde was synthesized from acetaldehyde and propionaldehyde by their procedure and its semicarbazone was prepared for comparison: m. p. (capillary tube) 200–208°; (Maquenne block) 232°. A mixture of equal parts of our semicarbazone and the authentic semicarbazone melted in a capillary tube (in the same bath) at 200–208°; on the Maquenne block the mixture melted at 233°.

Dibromides of Tiglic Aldehyde (2,3-Dibromo-2-methylbutanal).—A solution of 14.3 g. of bromine in 15 cc. of chloroform was added slowly to 7.5 g. of tiglic aldehyde in 15 cc. of chloroform, cooled to −10°. The addition of the last 5% of the bromine gave the solution an orange-red coloration which faded slowly on standing. After distilling off the solvent under reduced pressure, there was obtained 15 g. of a colorless, slightly viscous liquid: b. p. 71–73° (corr.) at 3.5 mm., d_4^{20} 1.7747, n_D^{20} 1.5228, MR_D (calcd.) 40.83, (obs.) 41.96.

Anal. Calcd. for $C_5H_8OBr_2$: Br, 65.80. Found: Br, 65.99, 65.82.

On cooling to +18°, crystals separated in the liquid but the mass did not solidify completely even when cooled to 0°. A sample of the liquid was removed for analysis when approximately half of the material had solidified, and it was found that the bromine content of the liquid (65.61%) was the same as that of the original specimen. This result indicates that the product of the addition of bromine is a mixture of the two racemic forms of the dibromide, which arise from the presence of two unlike asymmetric carbon atoms.

Summary

2-Methyl-2-butene-1,4-diol has been synthesized from isoprene, through 1,4-dibromo-2-methylbutene-2 and 1,4-diacetoxy-2-methylbutene-2. The structures of this glycol and the intermediate diacetate were established by catalytic hydrogenation to 2-methylbutane-1,4-diol and its diacetate.

2-Methyl-2-butene-1,4-diol was found to undergo dehydration and rearrangement, under various conditions, to give tiglic aldehyde (2-methyl-2-butenal). The isomeric ring compound, 3-methyl-2,5-dihydrofuran, was not detected as a product of dehydration of this glycol. Tiglic aldehyde was also produced by the action of hydrogen chloride (in methyl alcohol) upon 1,4-diacetoxy-2-methylbutene-2.

It is suggested that the mechanism of this rearrangement involves 1,4-elimination of water and 1,4-tautomeric shift of the resulting enol.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE DEHYDRATION OF 2,3,4-TRIMETHYLPENTANOL-3[1]

BY FRANK C. WHITMORE AND K. C. LAUGHLIN

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The dehydration of this alcohol was prompted by interest in the isomers of diisobutylene[2] and in rearrangements accompanying the dehydration of relatively simple carbinols.[3] In this case no rearrangement was detected. 2,3,4-Trimethylpentanol-3, when dehydrated with a trace of iodine, gave a mixture of the normal dehydration products, 3-methyl-2-isopropylbutene-1 and 2,3,4-trimethylpentene-2 in the ratio 1:2. Their structures were determined by ozonolysis.

Experimental

Diisopropyl ketone was prepared in 85% yield by oxidizing 2,4-dimethylpentanol-3 (Eastman Practical) in 200-g. lots with 235 g. of potassium dichromate and 340 g. of sulfuric acid in 2 liters of water with stirring at 40° for twenty-two hours. The ketone was collected at 122–127° (739 mm.), n_D^{20} 1.3998. The ketone was treated with methylmagnesium chloride according to Stas[4] to give 2,3,4-trimethylpentanol-3 in 76% yield. The product was fractionated through column A (38 × 1.5 cm. total condensation, variable take-off packed column[5]). After the removal of the ether, twelve fractions and a residue of 4 cc. were obtained: Fractions 1–6, 36 cc., b. p. 66° (72 mm.) to 69° (39 mm.), n_D^{20} 1.4029 to 1.4218; fractions 7–12, 189 cc., b. p. 72° (40 mm.) to 66° (25 mm.), n_D^{20} 1.4318 to 1.4342. The main product (fractions 9–12) boiled at 75–77° (40 mm.) and had n_D^{20} 1.4341 to 1.4343.

The carbinol (130 g. from fractions 9–12) was dehydrated by refluxing with a crystal of iodine under a 90 × 2 cm. column provided with a water separator at its top. The product was distilled rapidly through column A to remove any unchanged carbinol, was then dried over 3 g. of sodium and carefully fractionated through a 90-cm. partial condensation column.[6] Twelve fractions and a residue of 10 cc. were obtained: Fractions 1–3, 15 cc., n_D^{20} 1.4083, Cottrell b. p. 101.9° (741 mm.); fractions 11–12, 25 cc., n_D^{20} 1.4263, Cottrell b. p. 114.3° (739 mm.). The intermediate fractions amounted to 34 cc. and had n_D^{20} 1.4105 to 1.4261.

Nine grams of fractions 1–3 was ozonized and decomposed according to the technique of Church.[7] The water layer of the distillate gave a strong test for formaldehyde with resorcinol.[8] The oily layer, amounting to 5 cc., was dried with 1 g. of potassium carbonate. It then had n_D^{20} 1.4007. Its 2,4-dinitrophenylhydrazone prepared by

[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[2] Whitmore and Wrenn, THIS JOURNAL, **53**, 3156 (1931); Whitmore and Church, *ibid.*, **54**, 3710 (1932).

[3] Whitmore, *ibid.*, **54**, 3274 (1932); Whitmore and Laughlin, *ibid.*, **54**, 4011 (1932).

[4] Stas, *Bull. soc. chim. Belg.*, **35**, 379 (1926).

[5] *Cf.* Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

[6] "Johnston Column," Whitmore and Lux, *ibid.*, **54**, 3453 (1932).

[7] Whitmore and Church, *ibid.*, **54**, 3710 (1932).

[8] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., 1st edition, Vol. I, p. 24.

Allen's second method[9] and crystallized twice from absolute alcohol melted at 88°. A known sample prepared from diisopropyl ketone (n_D^{20} 1.3998) melted at 85–86°. A mixture melted at 87°. Thus the lower boiling olefin is 3-methyl-2-isopropylbutene-1.

Nineteen grams of fractions 10–12 was ozonized and decomposed. A small amount of solid ozonide was formed. The water layer gave a slight test for formaldehyde. The water layer was distilled through column A. To the first 5 cc. of distillate was added 0.4 cc. of benzaldehyde (freshly prepared from the bisulfite compound), 2 cc. of alcohol and 0.5 cc. of 10% sodium hydroxide solution. The mixture was boiled and evaporated to dryness on the steam-bath. The product was washed with hot water and the residue was crystallized from alcohol, m. p. 109°. A sample of dibenzylideneacetone prepared from acetone in the usual way[10] melted at 108–109°; mixture, m. p. 108–109°. The oily layer (17 cc.) from the decomposition of the ozonide was fractionated through a 25 × 1 cm. indented partial condensation column at 727 mm. Five fractions were obtained boiling from 48 to 92° and having n_D^{20} 1.3693 to 1.3927. A small residue decomposed violently, apparently due to the presence of unchanged ozonide. Fraction 5 gave a 2,4-dinitrophenylhydrazone, m. p. 119°. The known derivative prepared from methyl isopropyl ketone (n_D^{20} 1.3898) melted at 116–117°; mixture, m. p. 118°. Thus the higher boiling olefin is 2,3,4-trimethylpentene-2.

Summary

1. The dehydration of 2,3,4-trimethylpentanol-3 with iodine gives the normal dehydration products with about twice as much dehydration from the tertiary hydrogen atoms as from those of the methyl group.

2. 3-Methyl-2-isopropylbutene-1 and 2,3,4-trimethylpentene-2 have been obtained and identified by ozonolysis.

[9] Allen, THIS JOURNAL, **52**, 2955 (1930).

[10] Mulliken, Ref. 8, p. 148.

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

THE COMPOSITION AND POSSIBLE CONSTITUTION OF SEVERAL SULFUR DYES[1]

BY W. NORTON JONES, JR., AND E. EMMET REID

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The facts that the majority of the sulfur dyes cannot be obtained in crystal form and that in most cases they form colloidal solutions have made investigation of their constitutions exceedingly difficult. However, the thiazine nature of the black and blue dyes has been established by the collection of a plethora of data from various sources.[2] The full structural formula of only one of the sulfur dyes, *Immedial Reinblau*, which forms a

[1] The material in this article is extracted from a dissertation submitted by W. Norton Jones, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University, June, 1932.

[2] Lange, "Die Schwefelfarbstoffe, ihre Herstellung und Verwendung," Verlag Otto Spamer, Leipzig, 1921, pp. 20.

crystalline complex[3] with sodium bisulfite, has been determined and its fundamental thiazine structure thoroughly established. Since the majority of the sulfur colors are prepared from diphenylamine derivatives, dyes prepared from a few of its simplest derivatives were chosen for this investigation.

The dye known in commerce as Navy Blue RL and the three we shall designate as Bordeaux Y, Bordeaux X and Green Z were prepared by thionation under similar conditions of *p*-hydroxydiphenylamine, *p*-aminotolyl-*p'*-hydroxyphenylamine, *p*-methyl-*p'*-hydroxydiphenylamine and *p*-amino-*p'*-hydroxydiphenylamine, respectively. Investigation showed all four dyes to possess properties characteristic of the class, and efforts to determine their molecular weights by several methods were fruitless.

In preparing the dyes we endeavored to obtain samples of each dye of constant composition, it being a well-known fact that any given sulfur dye may have a widely varying sulfur content according to its conditions of fabrication. With this point in mind, great care was taken to ensure that the period and temperature of sulfuration were the same in the manufacture of each batch. Save in the instance of Green Z, the extent of sulfuration as shown by analysis was fairly constant in each case.

As a rule a sulfur dye derived from an indophenol of the type here considered contains the same nitrogen atom, or atoms, as the intermediate from which it is made; the nitrogen content of the purified product was used as the basis in calculating the empirical formulas from the analyses. The oxygen values run a bit high as is to be expected since the calculations are based on nitrogen determinations which are inclined to run low.

The results of these analyses as tabulated in Table VI show the following formulas to express the composition of the dyes: $C_{12}H_7NOS_3$ for Bordeaux Y, $C_{13}H_9NOS_4$ for Bordeaux X, $C_{13}H_{10}N_2OS_3$ for Navy Blue RL and $C_{12}H_7N_2OS_7$ and $C_{12}H_7N_2OS_9$, respectively, for the two varieties of Green Z.

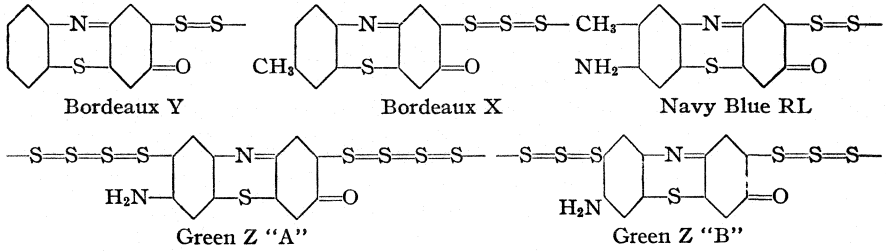
The evolution as hydrogen sulfide of a portion of the sulfur contained in these compounds upon reduction with stannous chloride as shown in Table I was the most enlightening reaction encountered.

TABLE I

Dye	Bordeaux Y	Bordeaux X	N. Blue RL	Green Z "A"	Green Z "B"	(I)	(II)
No. S atoms	3	4	3	9	7	1	2
No. S atoms removed	1	2	1	6	4	0	0
No. S atoms remaining	2	2	2	3	3	1	2

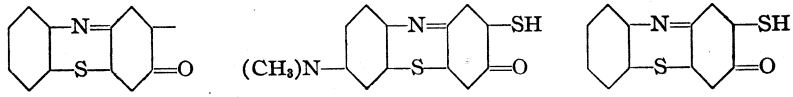
From a consideration of this and certain other facts, the following structures are suggested as the units from which the various dyes investigated assemble themselves

[3] Gnehm and co-workers, *J. prakt. Chem.*, [2] **69**, 169 (1904); *Ber.*, **37**, 2618 (1904).



The compound containing but one atom of sulfur prepared by thionating *p*-hydroxydiphenylamine by refluxing with Na_2S_2 and water and shown to be identical with Bernthsen's[4] oxo-thiodiphenylimide (I) of proved thiazine structure, was unaffected by stannous chloride and acid even when heated strongly. The very similar compound (II) described below, containing two sulfur atoms, one of which must be in the basic thiazine structure, while the other is most likely attached to one of the benzene rings in some sort of a side chain, presumably a sulfhydryl group which may react with a second such group to form a connecting disulfide, is likewise unaffected by such treatment. But the dye, Bordeaux Y, containing three sulfur atoms suffers the loss of one of them by the tin salt reduction. We have taken this to mean that the sulfur atom in the basic thiazine structure and the sulfur of the side chain which is directly attached to a carbon of one of the benzene rings are unattacked by this reducing mixture, but that the sulfur atom of the side chain other than those attached directly to a carbon are removed.

On examination of the mixture left in the reaction flask, it was seen at once that the dye, although having suffered reduction, had not been reduced to the leuco form as with caustic and with hydrosulfite. The material left in the flask showed properties very similar to the oxo-thiodiphenylimides.



The similarity of the two reddish-brown dyes to oxo-thiodiphenylimide (I) is a point in support of this thiazine nature. The blue dyes have long been held to be of a thiazine[5] nature, a point that has been established by the collection of a great amount of data from various sources over a period of years. The behavior of our Navy Blue RL and Green Z supports this contention. The case of *Immedial Reinblau,* whose formula and thiazine nature are established, may be cited and the similarities pointed out.

[4] Bernthsen, *Ann.*, **230**, 182 (1885); *Ber.*, **17**, 2860 (1884).

[5] Bernthsen, *Ann.*, **230**, 73 (1885); *Ber.*, **16**, 1025 and 2896 (1883).

The work of other investigators on the nature of the dye from *p*-tolylamino-*p'*-hydroxyphenylamine may also be pointed out,[6] as well as Vidal's[7] earlier researches on the black and blue sulfur dyes.

Apparently there is but one sulfur atom in the thiazine structures of the various dyes and the sulfur in the side chains may or may not be there as polysulfides; likewise in the case of compounds containing more than enough sulfurs to satisfy the thiazine structure and the various directed positions in its rings, polysulfide chains, which may vary in length, apparently exist as proposed by Möhlaus[8] and substantiated by the work of Schultz and Beyschlag.[9] Whether the limit of S_8 set by Möhlaus is correct, we cannot venture to say. It is thought also that where sulfhydryl groups do exist in a unit they combine with similar groups of other units to form aggregates held together by disulfide bridges and perhaps by other means. This may account, at least in part, for the formation of indefinitely large molecules or colloidal aggregates.

It will be remembered that the two reddish dyes are prepared from compounds containing but one auxochrome group, namely, the hydroxyl group; while the intermediates of the other two colors contain both an hydroxyl and an amino group, each; one recalls also that in the case of the intermediate from which Navy Blue RL is prepared, a methyl group stands ortho to the amino group, thus blocking that position. It is generally conceded that the place of entrance of sulfur-bearing side chains into the nuclei of the dyes is in the positions ortho to auxochrome groups.[10] Now if these dyes be all of a thiazine nature, then the second ortho position of each of the auxochrome groups here involved is also ortho to the carbon bearing the thiazine sulfur. Such a position is rarely ever filled during dye formation except under stress of the strongest sulfuration, although the intermediate may of course bear a substituent there at the outset. Hence, in the instance of the dye from *p*-tolylamino-*p'*-hydroxyphenylamine, one should expect the extrance of but a single sulfur side chain, which indeed is apparently the case. The intermediate of Green Z possesses two auxochrome groups and no other substituents so that the entrance of two sulfur-bearing side chains would be expected during the thionation. This condition apparently obtains since three sulfurs remain after the stannous chloride reduction, whereas only two remain for the other three dyes. The two samples of Green Z also support the varying polysulfide chain idea.

[6] Gnehm, *J. prakt. Chem.*, **69**, 169, 170 (1904).

[7] Vidal, *Mon. sci.*, **17**, 427; **11**, [II] 655 (1897).

[8] Lange, Ref. 2, p. 76; "Eigenbericht Möhlaus auf der Versamml. deutscher Naturf. u. Arzte," Dresden, Sept., 1907.

[9] Schultz and Beyschlag, *Ber.*, **42**, 743 and 753 (1909); *Chem.-Ztg.*, **31**, 937 (1907).

[10] Lange, Ref. 2, p. 71; Friedländer, *Z. angew. Chem.*, **19**, 616 (1906).

Experimental

Preparation and Purification of Intermediates.—*p*-Hydroxydiphenylamine was prepared by the method of Calm.[11] Attempts to employ his methods of purification were unsuccessful, so a modified method was used. The oily portion of the bomb's contents was poured into a three-liter balloon flask and the solid portion dissolved in a quantity of hot water and added to the former. The excess aniline was removed by steam distillation and the residue allowed to solidify. This was filtered off and washed with a little cold water, after which it was added to two liters of hot water containing 40 g. of solid sodium hydroxide and enough sodium hydrosulfite to prevent oxidation. This mixture was boiled until the lumps were entirely disintegrated. This mixture was filtered and the filter washed with 500 cc. of hot water containing 1 g. of sodium hydroxide and a little sodium hydrosulfite. The filtrate and washings were cooled to 20°, when 30% sulfuric acid was added with good stirring until the solution was just acid to brilliant yellow paper. This gave a heavy white precipitate, which was filtered off in an atmosphere of nitrogen in an apparatus described by Hamilton and Major.[12] The filter cake was dried over calcium chloride in a nitrogen-filled desiccator.

p-Methyl-*p'*-hydroxydiphenylamine was prepared in a similar manner from hydroquinone, *p*-toluidine, and calcium chloride after the method of Hatschek and Zega.[13] The reaction mixture was purified according to the foregoing method. The yield was 40%.

p-Amino-*p'*-hydroxydiphenylamine was prepared by heating for three hours at 170–180°, 73.5 g. of *p*-aminophenol, and 27 g. of *p*-phenylenediamine in a stirrer-equipped beaker resting in an oil-bath. The reaction mixture was purified by the method[14] described above; yield, 72%.[15]

The fourth intermediate, *p*-aminotolyl-*p'*-hydroxyphenylamine, was furnished by E. I. du Pont de Nemours & Co.

Preparation and Purification of the Dyes

Bordeaux Y.—Into a half-liter balloon flask, equipped with a short reflux condenser through which operated an electrically driven stirring device, were introduced 25 g. of *p*-hydroxydiphenylamine, 90 g. of hydrated sodium sulfide, 50 g. of flowers of sulfur and 70 cc. of distilled water. This mixture was refluxed on the oil-bath for thirty-four[16] hours at 145–150° with constant stirring. When the flask had sufficiently cooled, its contents were washed into a large beaker with about a liter of distilled water, and a stream of air bubbled through the liquid for from twenty-four to forty-eight hours until the oxidized form of the dye was thrown down as a reddish solid. Care must be taken to allow during the first few hours for the excessive foaming which usually occurs.

The precipitated dye was collected on a suction filter where it was washed at some length with warm distilled water, after which it was dried in the oven at 60–80°. When dry, it was ground into a fine powder and extracted in a Soxhlet apparatus with distilled water for some twenty-four hours to remove any adsorbed sodium salts, after which is was again dried as before. It was then returned to the extractor to be washed for another twenty-four hours with carbon disulfide to remove any mechanically held sulfur. The final drying was continued for two days to ensure complete removal of all solvents employed.

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[11] Calm, *Ber.*, **16**, 2799 (1883).

[12] Hamilton and Major, THIS JOURNAL, **47**, 1131 (1925).

[13] Hatschek and Zega, *J. prakt. Chem.*, [2] **33**, 224 (1886).

[14] Deutsche Vidal-Farbstoff-Aktiengesellschaft in Koblenz, German Patent 116,337.

[15] *Cf.* Ullmann and Jüngel, *Ber.*, **42**, 1077 (1909), and *Ann.*, **392**, 45 (1912).

[16] *Cf.* U. S. Patent 1,096,715, example 4.

A test portion of the final product upon being ignited on a clean platinum foil left in every case only an almost imperceptible trace of white soda ash.

The sulfur contents of the four batches of dye prepared from *p*-hydroxy-diphenylamine are given in the table.

TABLE II

Batch	1	2	3	4
Per cent. S	32.30	30.89	33.76	33.86

Samples of the dyes from the other intermediates were prepared in the apparatus described, under identical conditions, and were purified in the same manner. The quantities of sulfur and sodium sulfide used in each case, save that of the *p*-aminotolyl-*p'*-hydroxyphenylamine, were such that their molecular ratios to the quantity of intermediate employed were identical with the ratios in the first preparation above.

The three samples of the dye Bordeaux X were prepared by refluxing together 27 g. of *p*-methyl-*p'*-hydroxydiphenylamine, 90 g. of hydrated sodium sulfide, 50 g. of sulfur, and 70 cc. of water for thirty-four hours at 120°.[17] The following table gives their sulfur contents after purification. The ash was almost imperceptible.

TABLE III

Batch	1	2	3
Per cent. S	36.64	36.40	38.68

Although the conditions of fabrication of the two batches of Green Z were carefully controlled, the extent of sulfuration was considerably different. In both cases 28 g. of *p*-amino-*p'*-hydroxydiphenylamine, 50 g. of sulfur, 90 g. of hydrated sodium sulfide, and 70 cc. of water were refluxed together for thirty-four hours at 120°.[18]

TABLE IV

Batch	1	2
Per cent. S	63.42	52.78

The preparation of the dye known to the trade as Navy Blue RL was undertaken according to a procedure found in the patents. A mixture of 96 g. of crystalline sodium sulfide,[19] 38 g. of flowers of sulfur, and 22 g. of *p*-aminotolyl-*p'*-hydroxyphenylamine was refluxed at 120° for twenty hours. The thick, blue, alkaline melt was poured into distilled water to be precipitated and purified in the usual manner. In its final form the dye is an insoluble black powder with an almost metallic luster.

TABLE V

Batch	1	2	3	4
Per cent. S	30.44	33.53	33.60	37.58

The sulfur–nitrogen ratio for different batches of the same dye was more nearly constant than the percentage of sulfur.

Determination of Empirical Formulas.—All nitrogen determinations were made by the Gunning modification of the Kjeldahl method.[20] The

[17] U. S. Patent 1,098,259.

[18] Meister Lucius u. Brüning, German Patent 179,884 and *cf.* also Deutsche Vidal-Farbstoff-Aktiengesellschaft in Koblenz, German Patents 116,337, 328,110.

[19] Leopold Cassella u. Co., G. m. b. H. in Frankfurt A./M., 1901, German Patent 199,963, example 1.

[20] Leach, "Food Inspection and Analysis," 4th ed., p. 59.

innumerable sulfur analyses were executed by the Parr bomb method, while the carbon and hydrogen were determined by a modification of the standard combustion method.[21] The oxygen was, as usual, determined by difference.

TABLE VI

ANALYSES OF DYES AND EMPIRICAL FORMULAS

Element	Bordeaux Y—Batch 2 %	Bordeaux Y—Batch 2 No. atoms	Bordeaux Y—Batch 3 %	Bordeaux Y—Batch 3 No. atoms
C	51.79	12.15	50.30	10.90
H	2.52	7.04	2.68	6.90
N	4.97	1.00	5.38	1.00
S	30.89	2.72	33.76	2.74
O	9.83	1.72	8.80	1.42
	$C_{12}H_7NOS_3$			
	Navy Blue RL—Batch 1 %	Navy Blue RL—Batch 1 No. atoms	Bordeaux X—Batch 3 %	Bordeaux X—Batch 3 No. atoms
C	47.86	12.75	45.60	12.6
H	3.22	10.28	2.65	8.7
N	8.72	2.00	4.22	1.0
S	30.44	3.04	38.68	4.0
O	9.76	1.95	8.85	1.8
	$C_{13}H_{10}N_2OS_3$		$C_{13}H_9NOS_4$	
	Green Z—Batch 1 %	Green Z—Batch 1 No. atoms	Green Z—Batch 2 %	Green Z—Batch 2 No. atoms
C	27.00	10.23	30.13	10.73
H	1.50	6.8	1.60	6.80
N	6.03	2.0	6.53	2.0
S	63.42	9.0	52.78	7.0
O	2.05	0.3	8.96	1.2
	$C_{12}H_7N_2OS_9$		$C_{12}H_7N_2OS_7$	

Investigation of the Properties of the Dyes.—All four of the dyes were insoluble in water, ether, acetone, ethyl alcohol, methyl alcohol, toluene, xylene, benzene, naphthalene, concentrated hydrochloric acid, dilute sulfuric acid, concentrated acetic acid and chloroform. Their solubility and the nature of their solutions in other solvents are given in the table.

TABLE VII

Solvent	Character of solution: Bordeaux Y	Bordeaux X	Green Z	Navy Blue RL
H_2SO_4 concd.	Deep blue	Deep purple	Slightly sol.	Blue
Aq. Na_2S	Clear brown	Clear brown	Clear green	Clear purple
Pyridine, hot	Deep cherry-red	Deep cherry-red	Insoluble	Deep blue
Pyridine, cold	Slightly soluble	Slightly soluble	Insoluble	Slightly soluble
Aniline, hot	Deep cherry-red	Deep cherry-red	Insoluble	Very slightly sol.
Aniline, cold	Slightly soluble	Very slightly sol.	Insoluble	Insoluble

For the most part, chemical treatment of the four dyes chosen yielded scarcely any results. As shown by the preceding table, all four dyes

[21] Treadwell and Hall, 1924, Vol. II, pp. 364–370.

were soluble in strong aqueous sodium sulfide solution and likewise in caustic solution containing sodium hydrosulfite. From these solutions the addition of dilute hydrochloric acid precipitated the leuco forms of the dyes which began immediately to reoxidize to the dark insoluble dyes.

Samples of the various dyes were refluxed for long periods of time with acetic anhydride, acetyl chloride, monochloroacetic acid, benzyl chloride, benzoyl chloride and *p*-nitrobenzylbromide, respectively, with little or no results. Treatment of Bordeaux Y and Bordeaux X with benzoyl chloride and benzyl chloride, respectively, yielded small amounts of tarry substances which defied identification, while the other two dyes were unaffected.

Attempts to prepare crystalline bisulfite complexes after the method of Gnehm[22] and his co-workers in the case of *Immedial Reinblau* were fruitless.

Oxidation of the dyes by concentrated nitric acid and fusion with sodium hydroxide produced in every case such a complete disruption of the molecule that little concerning its structure could be deduced from the products thereof.

Alkylation undertaken by treating the reduced caustic solutions of the dyes with redistilled dimethyl sulfate gave precipitates ranging in color, according to the dye involved, from bright yellow to brown, which were immediately oxidized, even in an inert atmosphere, to dark insoluble substances.

Solutions of the dyes in aqueous sodium sulfide upon examination with the ultramicroscope were found to be colloidal in nature, and x-ray diffraction photographs of the dye from *p*-hydroxydiphenylamine showed only a single broad band about one centimeter from the primary beam, a diagram which is characteristic of non-crystalline substances. Solutions of the dyes in pyridine and aniline showed no raising of the boiling point and only a slight depression of the freezing point, so no estimation of the molecular weights could be made. In fact, a slight depression of the boiling point was observed probably due to the presence of traces of moisture.

Other Compounds Prepared by the Sulfuration of *p*-Hydroxydiphenylamine.—Treatment similar to that of *p*-hydroxydiphenylamine in the preparation of Bordeaux Y was accorded another portion of the intermediate with a polysulfide mixture corresponding to Na_2S_2 and the product was purified by the method cited above. Analysis showed the presence of but one sulfur atom, and it was shown to be identical with the oxo-thiodiphenylimide prepared by the method of Bernthsen.[23]

Yet another portion of the *p*-hydroxydiphenylamine was treated in the usual manner with a polysulfide mixture corresponding to Na_2S_3. On purification of the product by the method described above, analysis showed the presence of two sulfur atoms for each nitrogen.

[22] Gnehm and co-workers, *J. prakt. Chem.*, [2] **69**, 169 (1904); *Ber.*, **37**, 2618 (1904).

[23] Bernthsen, *Ann.*, **230**, 182 (1885); *Ber.*, **17**, 2860 (1884).

Both of the foregoing compounds in caustic solution suffered reduction by treatment with sodium hydrosulfite, both dissolved in concentrated sulfuric acid with the deep blue color characteristic of the dye, and both are likewise reprecipitated as the reddish solid by addition of water to the strong acid solution. This latter compound is held to be that represented by formula (II) above, or a compound composed of aggregates of these units, which seems more likely.

Reduction of the Dyes with Stannous Chloride.—Samples of one- or two-tenths of a gram of the respective dyes and sulfur compounds were introduced into a two-necked half-liter balloon flask connected to a reflux condenser fitted with a delivery tube fashioned from a 25-cc. pipet. To this was added a mixture of 47 cc. of glacial acetic acid, 2 cc. of concentrated hydrochloric acid and 1 cc. of sirupy phosphoric acid and 10 g. of stannous chloride after the method of Sampey.[24] The apparatus was made air-tight and the outlet of the delivery tube was placed beneath the surface of a portion of the reagent prepared from 10 g. of zinc sulfate, 450 cc. of concd. ammonia and 500 g. of distilled water. The mixture in the flask was heated with a small flame for some sixteen hours while a stream of nitrogen, purified by passage through a wash bottle containing a caustic solution of pyrogallol and thence through a drying tower, was forced through the apparatus.

As the heating continued, a stream of hydrogen sulfide was evolved to be swept out by the nitrogen and precipitated as zinc sulfide which was collected when the reaction was completed and the sulfur determined by the usual iodimetric method. That there was some loss of hydrogen sulfide due to the makeshift nature of the apparatus there can be no doubt.

The amount and percentage of sulfur evolved from the several dyes are given in the table.

TABLE VIII

Dye	Bordeaux Y		Bordeaux X		Green Z "A"	
Sample	1	2	1	2	1	2
Dye, %	0.1767	0.2069	0.1002	0.1431	0.1234	0.1198
S evolved, %	0.01849	0.02147	0.019397	0.023717	0.050498	0.04985
% S evolved	10.47	10.38	19.36	16.57	40.92	41.61
No. S evolved	0.85	0.84	2.001	1.71	5.8	5.9

Dye	Green Z "B"		Navy Blue RL	
Sample	1	2	1	2
Dye, %	0.0977	0.1381	0.1041	0.1025
S evolved, %	0.02955	0.03832	0.009602	0.009256
% S evolved	30.25	27.75	9.23	9.03
No. S evolved	4.03	3.70	0.925	0.907

Summary

1. Dyes were prepared by the thionation of *p*-hydroxydiphenylamine, *p*-methyl-*p'*-hydroxydiphenylamine, *p*-amino-*p'*-hydroxydiphenylamine,

[24] J. R. Sampey, Jr., "A Development in Project 28," Am. Pet. Inst.

and *p*-aminotolyl-*p'*-hydroxyphenylamine. Certain sulfurated derivatives of *p*-hydroxydiphenylamine were also prepared.

2. These dyes were purified and analyzed, and their properties and reactions were investigated.

3. The evolution of a part of the sulfur of these compounds as hydrogen sulfide upon their being heated with stannous chloride and strong acid was the most enlightening reaction encountered.

4. The respective units of which the aggregates of all four dyes are composed are apparently of a thiazine nature and bear polysulfide chains of varying sulfur content attached to the rings composing the nucleus. The longest polysulfide chain encountered contained four sulfur atoms.

5. Constitutional formulas for the four units involved are suggested.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

THE OPTICAL ROTATION OF *d*-TALONIC AMIDE AND OF CERTAIN SALTS OF *d*-TALONIC ACID

BY ALICE G. RENFREW AND LEONARD H. CRETCHER

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d-Talonic amide has been prepared from γ-talonolactone.[1] Aqueous solutions of the amide were found to be levorotating in agreement with Hudson's amide rule of rotation.[2] This rule states that for the amides of the monobasic sugar acids the direction of rotation is determined by the configuration of carbon 2; when the hydroxyl is on the right of the structure, the amide is dextrorotatory, and conversely. Although talonic amide exhibits the expected levorotation, the numerical value of the molecular rotation, [M] = −25.5° (10),[2] is somewhat lower than the value calculated from the estimated molecular rotations of the individual asymmetric carbon atoms[2] in the amides of the hexonic sugar acids. A closely comparable molecular rotation of −27.1° (10)[2] has been reported for *l*-ribonic amide,[2a] in which the α, β and γ carbon atoms have the same configuration of H and OH groups as in *d*-talonic amide. Freudenberg and Kuhn[3] have directed attention to the rather constant difference between the molecular rotations of sugar acids and the corresponding amides. This difference has an approximate value of 78° for the gluconic type and 48° for the gulonic type. Inasmuch as the configuration of talonic acid does not place it in either of the above groups, it is not surprising that the

[1] Cretcher and Renfrew, THIS JOURNAL, **54**, 1590 (1932).

[2] (a) Hudson and Komatsu, *ibid.*, **41**, 1141 (1919); (b) Hudson, "Reports on Carbohydrates," Tenth Conference of the International Union of Chemistry, p. 59, Liége, 1930.

[3] Freudenberg and Kuhn, *Ber.*, **64**, 703 (1931).

molecular rotations of *d*-talonic acid, [M] = +37.4° (10),[2] and of talonic amide differ by a new value of 63°.

Talonic amide was prepared by the action of dry ammonia gas on *d*-γ-talonolactone[1] dissolved in 30–50 volumes of absolute alcohol. The crude amide was obtained as a finely divided crystalline powder, which softened at 116° and melted at 118–120°. After repeated recrystallization from absolute alcohol, the melting point was 121°.

Anal. Calcd. for $C_6H_{13}O_6N$: N, 7.18. Found:[4] N, 7.15, 7.23. *Optical Rotation.* c = 1.926; l = 4; α = −1.01°; $[\alpha]_D^{25}$ −13.1°; [M] −25.5° (10)[2].

The initial levorotation of aqueous solutions of the amide slowly decreased, and after several days reached a zero or faintly dextro reading. That this mutarotation was probably due to the formation of the ammonium salt is indicated by a consideration of the observed rotation of the ammonium salt, and by the fact that a similar mutarotation was reported by Weerman[5] for gluconic amide.

A second crystalline amide, melting at 100–102°, was obtained when 95% alcohol was used as a crystallizing solvent. This preparation was apparently amide with one mole of water of crystallization and could be converted into the anhydrous amide by recrystallization from absolute alcohol.

Anal. Calcd. for $C_6H_{13}O_6N \cdot H_2O$: N, 6.57. Found: N, 6.53, 6.65. *Optical Rotation.* c = 2.208 g.; l = 1; α = −0.27°; $[\alpha]_D^{25}$ −12.22°; [M] −26.0° (10)[2].

The ammonium salt of talonic acid was obtained when talonic lactone was treated with concentrated aqueous ammonia. The reaction product was an oil which crystallized after standing for several days in contact with alcohol. The ammonium salt melted at 148° and showed a small dextro rotation with no mutarotation within a period of several days.

Anal. Calcd. for $C_6H_{15}O_7N$: N, 6.57. Found: N, 6.53, 6.72. *Optical Rotation.* c = 2.746 g.; l = 1; α = +0.08°; $[\alpha]_D^{25}$ + 2.9°; [M] +6° (10)[2].

That a slight dextrorotation characterizes certain salts of *d*-talonic acid in aqueous solution is further evidenced by the study of sodium *d*-talonate. The sodium salt was prepared by titrating an aqueous solution of the lactone with a slight excess of $N/10$ sodium hydroxide.

Optical Rotation. c = 1.5844 g. lactone which is equivalent to 1.9404 g. Na salt; l = 2; α = +0.10; $[\alpha]_D^{25}$ + 2.5°; [M] +5.5° (10)[2].

Levene and Meyer[6] have determined the optical rotation of a series of sodium salts of simple monocarboxylic sugar acids. In each case the salts were dextrorotatory when the hydroxyl group linked with the α-carbon was on the right of the carbon chain and conversely. Although the sodium and ammonium salts of talonic acid failed to show levorotation, the dextro value was small compared with the dextrorotation of solutions of the free acid. From the data thus far available as cited by Levene[7] and from a consideration of the rotations observed for *d*-talonic salts, it may be said of hexonic monocarboxylic sugar acids that the rotation of the sodium salt is more dextro than the corresponding acid if the hydroxyl is on the right of the α-carbon—and the rotation is more levo if the hydroxyl is on the left.

[4] All nitrogen analyses were micro Dumas determinations by Dr.-Ing. A. Schoeller, Berlin.

[5] Weerman, *Rec. trav. chim.*, **37**, 16 (1917).

[6] Levene and Meyer, *J. Biol. Chem.*, **26**, 355 (1916).

[7] Levene, "Hexosamines and Mucoproteins," Longmans, Green and Co., London, 1925, p. 41; *Chem. Rev.*, **2**, 179 (1925–1926).

Summary

1. *d*-Talonic amide is levorotating as would be predicted from Hudson's amide rule.

2. The sodium and ammonium salts of *d*-talonic acid show a small dextrorotation. The rotation is much less dextro than the rotation of solutions of the free acid.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

PYRIDINE BORON TRIFLUORIDE

BY P. A. VAN DER MEULEN AND HUGH A. HELLER

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Boron trihalides are extremely reactive toward ammonia and amines, and Kraus and Brown[1] have recently studied a number of reactions with boron trifluoride. They showed that true addition compounds are formed with ammonia, ethylamine, diethylamine and triethylamine.

All of these compounds can be shown to be examples of coördinate covalency, in which the boron atom acts as acceptor and the nitrogen atom acts as donor. Since the nitrogen atom in pyridine has one lone pair of electrons it should be possible to prepare a similar compound of boron trifluoride and pyridine. The purpose of this investigation was to prepare and study such a compound. After the work was nearly completed, Bowlus and Nieuwland[2] reported experimental work in which they measured the absorption of boron trifluoride by pyridine, and obtained a solid product which they believe to contain two molecules of boron trifluoride to one of pyridine. While the existence of such a compound in the solid state is not inconsistent with modern valence theory, it is probably not simply a case of coördinate covalency. In the present investigation a compound of boron trifluoride and pyridine was prepared, in which the molecular ratio is 1:1.

Experimental

Preparation of Materials.—Boron trifluoride was prepared by heating a mixture of ammonium fluoborate and boric oxide with concentrated sulfuric acid. The boric oxide was prepared by fusing boric acid in an iron crucible.

The pyridine was twice redistilled through an efficient fractionating column, and a constant boiling fraction was used without further purification.

The benzene was likewise redistilled twice using a column in order to ensure the complete absence of water from the reaction chamber.

Preparation of the Compound.—The all-glass apparatus shown in Fig. 1, made of Pyrex glass, was thoroughly dried in an electric oven before use. Eighteen grams of an-

[1] Kraus and Brown, THIS JOURNAL, **51**, 2690 (1929).

[2] Bowlus and Nieuwland, *ibid.*, **53**, 3835 (1931).

hydrous ammonium fluoborate and 9 g. of pulverized boron trioxide were thoroughly mixed and placed in the generator flask, A. Fifty cubic centimeters of concentrated sulfuric acid (sp. gr. 1.83) was added and the flask was heated. The boron trifluoride passed through two bulbs, one empty, B, and the other, C, filled with coarsely ground boric oxide. The pure dry boron trifluoride then entered the reaction tube, D, which contained a solution of 10 g. of pyridine in 20 cc. of benzene. It was found necessary to cool the reaction tube with a bath of running water, as considerable heat was evolved. The boron trifluoride was rapidly absorbed by the benzene solution of pyridine, and the action was continued until after absorption had apparently ceased. The final bulb, F, containing soda lime and calcium chloride, was used to exclude atmospheric moisture.

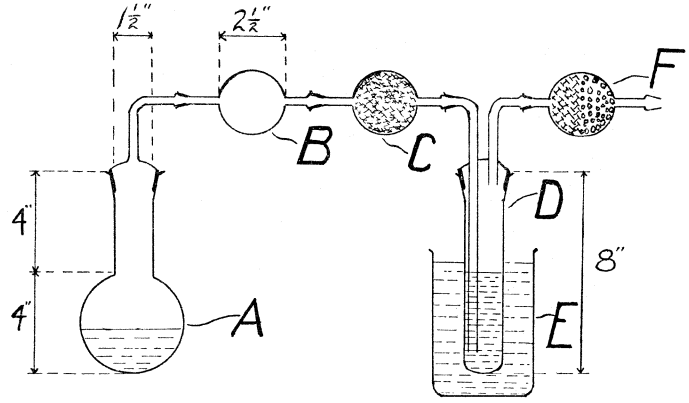

Fig. 1.

Purification of the Compound.—The crude product was crystallized with difficulty from the benzene. The solution had a marked tendency to remain supersaturated, but after prolonged cooling and agitation, crystallization took place. The compound was purified by solution in pure dry benzene, and evaporation of the solvent in a vacuum desiccator over sulfuric acid. Two such treatments yielded a colorless product with a very faint odor of pyridine. The compound was stored in a vacuum desiccator over sulfuric acid.

Analysis of the Compound.—Pyridine was determined by distilling a weighed sample with a solution of sodium hydroxide, collecting the distillate in standard acid and titrating the excess acid, using brom phenol blue as the indicator. Fluorine was determined gravimetrically as calcium fluoride. Boron was determined by the method recommended by Morgan and Tunstall.[3] The molecular weight determined cryoscopically in benzene was 148 (m. w. $C_5H_5NBF_3$ = 146.8). The melting point, determined by heating 4 g. of the solid in a dry test-tube, with the bulb of a thermometer embedded in the melting solid was 45 ± 1°. The boiling point was 300 ± 5°.

Pyridine boron trifluoride was found to be very soluble in benzene and in pyridine, fairly soluble in absolute alcohol, slightly soluble in boiling chloroform and practically insoluble in petroleum ether. Hot 95% alcohol converts it, by hydrolysis, into the pyridine salt of fluoboric acid.

Analysis of the compound gave the following results: pyridine, 53.42% (calcd. 53.81); fluorine, 38.47% (calcd. 38.83); boron, 7.21% (calcd. 7.36).

Dissociation of Gaseous Pyridine Boron Trifluoride.—Measurements of the vapor

[3] Morgan and Tunstall, *J. Chem. Soc.*, **125**, 1963 (1924).

density of pyridine boron trifluoride above its boiling point by the Victor Meyer method were carried out. It was found that the vapor density decreased with rising temperature, showing that the compound is dissociated, and that an equilibrium exists between the gaseous products. The dissociation may be represented by the equation

$$C_5H_5N{\cdot}BF_3 \rightleftharpoons C_5H_5N + BF_3$$

The substances used as heating liquids were boiling mercury, phenanthrene and phenyl benzoate. The actual temperature of the vapor was read from a thermometer hung inside the inner tube of the Victor Meyer apparatus. The degree of dissociation of the vapor was calculated from the apparent molecular weight. The results are given in Table I.

TABLE I

DISSOCIATION OF PYRIDINE BORON TRIFLUORIDE BY HEAT

Temp., °C.	Apparent molecular weight	Degree of dissociation, %
356	89.9	63.3
333	108.2	35.7
313	124.1	18.2

Heat of Dissociation.—The variation in the degree of dissociation of the compound was used to calculate the heat of dissociation.[4] The average value obtained for ΔH is 50,600 cal.

Summary

Pyridine boron trifluoride, $C_5H_5N{\cdot}BF_3$, has been prepared and some of its properties have been studied. It is a white crystalline compound, melting at 45° and boiling at approximately 300° under atmospheric pressure. It is soluble in benzene, pyridine and in hot absolute alcohol. In 95% ethyl alcohol it undergoes hydrolysis. It is dissociated in the vapor state and in the temperature range 313 to 356° its heat of dissociation is 50,600 calories.

NEW BRUNSWICK, NEW JERSEY

[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 298.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE CLEAVAGE OF PHENACYLPYRIDINIUM HALIDES BY ALKALI

BY SIDNEY H. BABCOCK, JR., FRANK I. NAKAMURA AND REYNOLD C. FUSON

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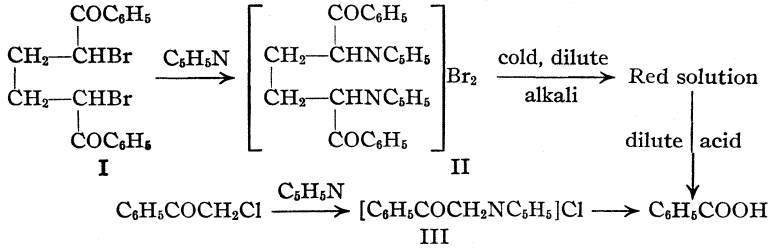
An attempt to eliminate hydrogen bromide from 1,4-dibromo-1,4-dibenzoylbutane (I) by treatment with pyridine and then with dilute aqueous alkali resulted in a cleavage of the carbon chain and the production of benzoic acid. An investigation of this apparently novel reaction has shown it to be applicable to a number of phenacyl halides. This article is a preliminary report of these studies.

The first step in the reaction has been found to be the formation of the pyridinium halide. When 1,4-dibromo-1,4-dibenzoylbutane was heated with pyridine the dipyridinium bromide (II) was formed. The salt was



difficult to study because of its hygroscopicity but when allowed to stand in the air or when recrystallized from 95% alcohol, it took up two molecules of water and gave a dihydrate which was stable. This hydrated salt dissolved in cold 10% aqueous sodium hydroxide solution, giving a red-colored solution. The solution immediately deposited benzoic acid when acidified with hydrochloric acid.

In order to see if this type of cleavage was general for phenacyl halides, phenacyl chloride was treated with pyridine and alkali in the manner just described. In this case the pyridinium salt (III) formed a monohydrate. Decomposition gave benzoic acid in good yield. It should be mentioned at this point that a similar observation was recorded by Bamberger in 1887.[1] He found that phenacylpyridinium bromide when treated with concentrated aqueous alkali gave benzoic acid and ascribed the result to the action of alkali on phenacyl bromide reformed by dissociation of the salt into its original components. It is apparent that the results described in the present paper cannot be explained in this way. Neither phenacyl bromide nor its hydrolysis product, benzoylcarbinol, gives benzoic acid when treated with dilute aqueous alkali.[2]

[1] Bamberger, *Ber.*, **20**, 3344 (1887).

[2] Zincke, *Ann.*, **216**, 311 (1882).

The solubility of benzoic acid in water made it somewhat difficult to determine the yield accurately. Since *p*-bromobenzoic acid is only slightly soluble in water, it was thought that the cleavage of *p*-bromophenacyl bromide would be easier to study. *p*-Bromophenacylpyridinium bromide likewise formed a monohydrate which was found to undergo the cleavage and gave *p*-bromobenzoic acid in a yield of 89% of the theoretical.

The effect of steric hindrance on the cleavage has also been studied. ω-Chloroacetomesitylene has been found to react very slowly with pyridine to give 2,4,6-trimethylphenacylpyridinium chloride. This salt, however, does not form a hydrate and does not undergo cleavage when treated with cold alkali. From this it would appear that the hydration is necessary to the cleavage.

Sufficient data are available to indicate that phenacylpyridinium halides are in general cleaved by alkali to give the salts of the corresponding aromatic acids. The fate of the rest of the molecule is being investigated. The reaction is also being applied to a variety of similarly constituted compounds. It seems best to leave the question of mechanism entirely open until these studies shall have furnished more information as to the products of the reaction as well as to its limitations.

Experimental

1,4-Dibenzoyltetramethylenedipyridinium Bromide.—To 4.5 g. of 1,4-dibromo-1,4-dibenzoylbutane dissolved in 25 cc. of ethyl benzoate at 120° was added 10 g. of pyridine. The solution became turbid and 1,4-dibenzoyltetramethylenedipyridinium bromide immediately began to separate in the form of crystals. At the end of four or five minutes the solution became clear and the reaction was complete. The product when filtered had a variable melting point and rapidly absorbed moisture from the air to become a pasty mass which hardened within an hour to a friable solid. This when crystallized from 95% ethyl alcohol separated as a colorless crystalline powder melting at 212.5° (corr.). The yield was 4.5 g. or 74% of the theoretical.

Anal. Calcd. for $C_{28}H_{26}N_2O_2Br_2 \cdot 2H_2O$: Br, 25.9. Found: Br, 26.1, 25.7.

The Cleavage of 1,4-Dibenzoyltetramethylenedipyridinium Bromide.—To a solution of 2.5 g. of the salt dissolved in 10 cc. of cold water was added 15–20 cc. of a 5% sodium hydroxide solution. A brick-red color immediately developed. The addition of dilute hydrochloric acid to the red solution discharged the color and immediately caused the separation of a crystalline compound which melted at 121° and was proved by the method of mixed melting points to be benzoic acid.

Phenacylpyridinium Chloride.—To a solution of 13.2 g. of phenacyl chloride in 50 cc. of benzene 8 g. of pyridine was added. The reaction mixture was warmed and crystals separated. In this way 5 g. of phenacylpyridinium chloride melting at 109–110° was obtained.

The same quantities of phenacylchloride and pyridine were mixed without a solvent. Considerable decomposition occurred and the mixture became a solid black mass. This was combined with the mother liquor from the first run, the solvent was evaporated and the residue was recrystallized twice from 95% ethyl alcohol. In this manner an additional 12 g. of phenacylpyridinium chloride was obtained as a yellowish powder. Concentration of the mother liquors gave oils which were discarded.

Anal. Calcd. for $C_{13}H_{12}ONCl \cdot H_2O$: Cl, 14.1. Found: Cl, 14.0, 14.1.

Cleavage of Phenacylpyridinium Chloride.—A small amount of the salt was dissolved in water and treated with a dilute solution of sodium hydroxide. A deep red color immediately developed. Acidification of the mixture with dilute sulfuric acid discharged the color and caused the separation of crystals which were identified as benzoic acid.

***p*-Bromophenacylpyridinium Bromide.**—To a solution of 27.8 g. of *p*-bromophenacyl bromide in ether was added 10 g. of pyridine. The mixture was heated for an hour under reflux and the solid *p*-bromophenacylpyridinium bromide was removed by filtration. The salt separated from alcohol in long, colorless crystals melting at 225–230°. It was sparingly soluble in cold water and in alcohol.

Anal. Calcd. for $C_{13}H_{11}ONBr_2 \cdot H_2O$: Br, 21.3. Found: Br, 21.5, 21.7.

Cleavage of *p*-Bromophenacylpyridinium Bromide.—To 3.75 g. of the salt dissolved in 15 cc. of hot water was added 10 cc. of a 10% solution of sodium hydroxide. A dark red oil separated at once but redissolved after a few minutes. The solution upon acidification with dilute sulfuric acid deposited crystals which proved to be *p*-bromobenzoic acid.

The mother liquor was again made alkaline with sodium hydroxide and was warmed for half an hour. By acidification an additional crop of *p*-bromobenzoic acid was obtained. The whole process was repeated and a third crop of crystals was obtained. The total yield of *p*-bromobenzoic acid was 1.79 g. or 89% of the theoretical.

2,4,6-Trimethylphenacylpyridinium Chloride.—Twenty grams of ω-chloroacetomesitylene and 10 g. of pyridine were dissolved in 100 cc. of ether and the solution was heated under reflux. No reaction took place. The ether was evaporated and replaced by ethyl acetate. After this solution had been boiled for ten minutes it was cooled and 4.5 g. of unchanged ω-chloroacetomesitylene separated and was filtered.

The filtrate which now contained an excess of pyridine was heated under reflux on a steam cone for three and one-half hours, at the end of which time there was a small amount of a colorless crystalline product. When filtered and dried it weighed 0.5 g. and melted at 245–246°. It was extremely soluble in water.

The 4.5 g. of unchanged ω-chloroacetomesitylene was returned to the pyridine–ethyl acetate solution. Twenty-five cc. of pyridine was added and the mixture was heated under reflux for sixteen hours. In this way was obtained 7.5 g. of 2,4,6-trimethylphenacylpyridinium chloride melting at 245–246°.

Anal. Calcd. for $C_{16}H_{18}ONCl$: Cl, 12.9. Found: Cl, 12.9, 12.8.

Action of Alkali on 2,4,6-Trimethylphenacylpyridinium Chloride.—A small quantity of the salt was dissolved in cold water and a dilute (10%) sodium hydroxide solution was added. After the solution was allowed to remain alkaline for five minutes it was acidified with dilute sulfuric acid. There resulted a precipitate of a salt-like character having no definite melting point. There was no evidence of the formation of any isodurylic acid.

Summary

It has been shown that certain phenacylpyridinium halides are cleaved by alkali to give the corresponding aromatic acids. The evidence indicates that the cleavage is rapid and nearly quantitative and that it is greatly retarded by steric hindrance.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE ACTION OF SODIUM ETHYLATE ON LEVO-ETHYL-ALPHA-PHENYLSULFONEBUTYRATE

BY W. C. ASHLEY AND R. L. SHRINER

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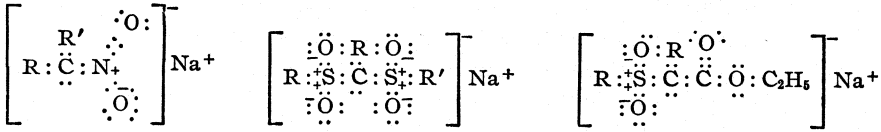
Studies of the sodium and potassium salts of secondary aliphatic nitro compounds have shown that they can exist in an optically active state.[1] If the structure suggested for these salts is that shown in formula A, then

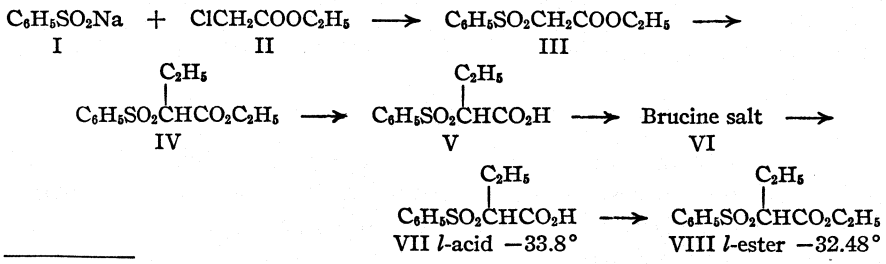


A B C

other types of salts with a similar constitution should likewise be capable of existing in optically active forms. Since a study of disulfones[2] indicated that they formed salts possessing the structure B, it seemed probable that an unsymmetrical disulfone of this structure should yield optically active sodium salts. The synthesis of compounds of this Type B is very difficult and no methods are available at present for the preparation of such a compound in an optically active condition. Pending the development of such methods, attention was turned to a closely related substance, ethyl-α-phenylsulfonebutyrate which has a carbethoxy group in place of one of the sulfone groups. This ester was prepared in the optically active state in order to determine whether it would yield optically active salts of Type C.

The condensation of sodium benzenesulfinate with chloroacetic ester yielded ethyl phenylsulfoneacetate, which was alkylated with ethyl iodide. Saponification and acidification gave racemic α-phenylsulfonebutyric acid. The latter was resolved by means of its brucine salt and the optically active acid obtained. The active ester was made from the acid through the acid chloride. The chart summarizes these reactions.

CHART I

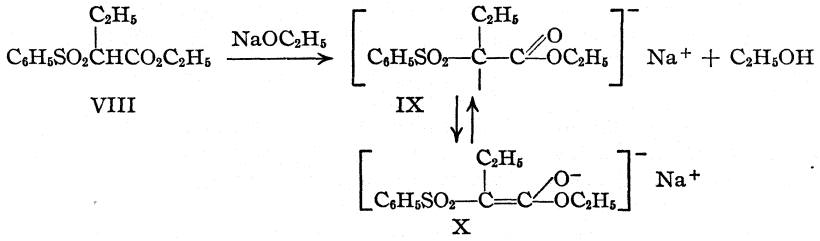


[1] Kuhn and Albrecht, *Ber.*, **60**, 1297 (1927); Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

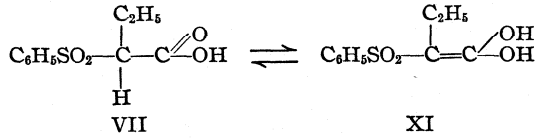
[2] Shriner, Struck and Jorison, *ibid.*, **52**, 2060 (1930).

When the active ester (VIII) was treated with one equivalent of sodium ethylate in absolute alcohol at −10° the solution of the sodium derivative of the ester was optically inactive although the solution was examined immediately.

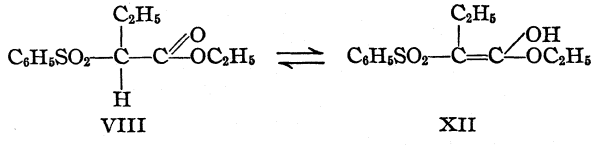
It was hoped that the active ion IX would have a life long enough for its existence to be detected but apparently a very rapid isomerization to the inactive form X occurred.



The rapid racemization of compounds with an asymmetric carbon atom carrying a hydrogen atom alpha to a keto or ester group in alkaline solutions[3] is well known. In support of the above explanation for the rapid racemization of the sodium derivative, the half-life periods of the active ester (VIII) and active acid (VII) were determined. It was found that the half-life period of the ester was eighty hours at 27° and of the acid 1350 hours at 27°. The slower racemization of the free acid is usually attributed to the fact that the hydrogen ion from the carboxyl group represses the tendency for the hydrogen on the alpha carbon to shift to form the enolic structure XI.



However, in the case of the ester (VIII) no such repression can occur and hence the inactive enol (XII) is formed much more readily and especially so in the presence of alkaline reagents.



The possibility of enolization on the sulfone group has been discussed previously[2] and shown to be untenable. The above difference in rates of racemization of the active acid and ester is additional evidence that the

[3] O. Rothe, *Ber.*, **47**, 843 (1914); McKenzie and Widdows, *J. Chem. Soc.*, **107**, 702 (1915); *ibid.*, **113**, 210 (1918); *ibid.*, **115**, 602 (1919).

sulfone group is not directly involved, although it certainly contributes to the mobility of the α-hydrogen atom.

Moreover, in the resolution of the acid V only the salt composed of *l*-brucine-*l*-acid could be obtained. Even the mother liquor, after filtering the salt which crystallized, on evaporation yielded more of the same salt, indicating that the (*d*) acid was transformed into the (*l*) form under the influence of the brucine. All of these facts indicate the tautomeric character of this acid and ester and lend support to the explanation of the optical inactivity of the sodium derivative of the *l*-ethyl-α-phenylsulfonebutyrate.

Experimental

Sodium Benzenesulfinate.—This compound was prepared by a modification of the directions for the preparation of sodium *p*-toluenesulfinate.[4] After the temperature of three liters of distilled water, placed in a large earthen jar, had been raised to 70° by the introduction of steam, the steam was turned off, and 315 g. (4.8 moles) of zinc dust was added. The temperature was now increased to 83°. Over a period of twenty minutes, 388 g. (2.15 moles) of benzenesulfonyl chloride was added in small portions with vigorous stirring. The stirring was continued for fifteen minutes. After further increasing the temperature to 90°, the steam was turned off, and 220 cc. of 12 normal sodium hydroxide solution was added to the hot solution. The solution was made strongly alkaline by the addition of sodium carbonate in 50-g. portions. The supernatant liquid was filtered and the residue extracted with one liter of water heated with steam as before. The combined filtrates were concentrated on the steam cone to a volume of 300 cc. After cooling and filtering, the precipitate was warmed with an additional 300 cc. of water, again cooled and filtered. The yield of crude sodium benzene sulfinate amounted to 334 g. or 94.6% of the theoretical.

Ethyl Phenylsulfoneacetate.—In a two-liter, three-necked, round-bottomed flask equipped with a stirrer, a condenser carrying a calcium chloride tube, and a dropping funnel, were placed 328 g. (2.0 moles) of the crude sodium benzenesulfinate and 1.25 liters of absolute alcohol. With stirring and slow refluxing, 306.3 g. (2.5 moles) of ethyl chloroacetate was added through the dropping funnel over a period of one hour. With continuous stirring, the solution was refluxed for eight hours, let stand overnight, and then refluxed for an additional two hours. One liter of alcohol was distilled and 800 cc. of water added. An oily layer separated. The oil was dissolved in ether and the aqueous solution extracted three times with this solvent. The combined ether extractions (including the solution containing the oil), amounting to about two liters, were washed and dried over anhydrous sodium sulfate. The dried solution was filtered through glass wool and the ether distilled. After removing the low boiling material under diminished pressure (water pump), the residue was distilled under vacuum (oil pump). The yield amounted to 215 g. of crude product, b. p. 175–205° at 5 mm. The oil readily crystallized to a solid mass, m. p. 40–43°. The low boiling fraction contained 83 g. of ethyl chloroacetate; the aqueous solution yielded 56 g. of crude sodium benzenesulfinate. The yield of crude product based on the ethyl chloroacetate used amounted to 51.8% of the theoretical.

Pure ethyl phenylsulfoneacetate may be obtained by one recrystallization from hot absolute alcohol, m. p. 42–43°.[5,6]

[4] "Organic Syntheses," 1922, Vol. II, p. 80.

[5] Michael and Comey, *Am. Chem. J.*, **5**, 116 (1883).

[6] Otto, *J. prakt. Chem.*, [2] **30**, 343 (1884).

Ethyl α-Phenylsulfonebutyrate.[7]—In a three-necked, one-liter, round-bottomed flask equipped with a stirrer, dropping funnel, and condenser carrying a calcium chloride tube was placed 750 cc. of absolute alcohol (commercial). Twenty-one and six-tenths grams (0.94 mole) of metallic sodium cut in small pieces was added at such a rate as to cause the alcohol to reflux slowly. By stirring and refluxing 215 g. (0.94 mole) of phenylsulfoneacetic ester (m. p. 40–43°) was dissolved into the solution of sodium alcoholate. To the hot solution 146.6 g. (0.94 mole) of ethyl iodide was added slowly (one hour) through the dropping funnel. The solution after six hours of stirring and refluxing reacted neutral to moist litmus. After distilling 500 cc. of alcohol, the residue was poured over cracked ice, whereby crystallization of the oil occurred at once. The yield of crystals, filtered and dried on a clay plate, amounted to 212 g., m. p. 52–55°, or 88.1% of the quantity calculated from theory. (Another run, using pure (m. p. 42–43°) phenylsulfoneacetic ester resulted in a yield of 91.8%, m. p. 57–59°.) A pure product may be obtained by recrystallization several times from acetone and water, m. p. 62–63°. An extraction with low-boiling petroleum ether and subsequent removal of the solvent yields a beautiful white product, m. p. 63–64°.

α-Phenylsulfonebutyric Acid.[8]—In 700 cc. of 95% alcohol placed in a three-necked one-liter flask equipped with a stirrer and condenser, was dissolved 100 g. of potassium hydroxide. Crude (m. p. 52–55°) α-phenylsulfonebutyric ester, 212 g. (0.83 mole), was added and the resulting solution refluxed and stirred for ten minutes. The solution, diluted with an equal volume of cold water, was poured rapidly with stirring into 500 cc. of cold (an ice–salt mixture surrounded the beaker) concentrated hydrochloric acid. The solution was extracted four times with ether, the ether extractions—amounting to 1.5 liters—washed, and the ether distilled. The oily residue readily crystallized when treated with 300 cc. of water. The yield of crude product amounted to 188 g. or practically 100%; m. p. 115–117°. Dissolving in acetone, treating with norite, filtering and precipitating by the addition of water gave a pure product, m. p. 123–124°. The amount of pure acid obtained was 122.6 g.

Anal. Subs., 0.3211: 12.98 cc. of 0.1082 *N* NaOH. Calcd. for $C_{10}H_{12}O_4S$: neut. equiv., 228.2. Found: 228.6.

Brucine Salt of α-Phenylsulfonebutyric Acid.—A solution consisting of 85.9 g. (0.376 mole) of α-phenylsulfonebutyric acid and 148.2 g. (the equivalent amount) of brucine dissolved in 400 cc. of hot acetone was filtered and set aside to cool. Rapidly the solution turned to a semi-solid mass of crystals. The crystals, filtered and washed with 50 cc. of acetone, amounted to 197 g. By concentrating the filtrate and washing, a second crop of 24.5 g. was obtained. The combined yield was 221.5 g.; theoretical for complete precipitation, 234.1 g. The filtrate was acidified and the free acid extracted with ether. For the brucine salt recrystallized from acetone α_D^{26} −25.4° (in chloroform); α_D^{28} −17.05° (in acetone).

Anal. Subs., 0.5951: $BaSO_4$, 0.2287 g. Calcd. for $C_{33}H_{38}N_2O_8S$: S, 5.16. Found: S, 5.27.

Anal. (Micro Dumas). Subs., 3.612 mg.: 0.157 cc. gas, at 742 mm. and 27.5°. Calcd. for $C_{33}H_{38}N_2O_8S$: N, 4.50. Found: N, 4.82.

***l*-α-Phenylsulfonebutyric Acid.**—Forty grams (0.064 mole) of the above brucine salt was covered with 300 cc. of water and 300 cc. of ether and 20 cc. of concentrated hydrochloric acid added with stirring. When all the salt had dissolved the aqueous layer was extracted twice with two portions of 200 cc. each of ether. After washing the combined ether extractions, the solvent was distilled on the steam cone to a volume

[7] Michael and Palmer, *Am. Chem. J.*, **7**, 66 (1885–1886).

[8] Troeger and Uhde, *J. prakt. Chem.*, [2] **59**, 322 (1899).

of 25 cc. The rest of the ether was removed under vacuum and the residue dried for twenty-four hours in a vacuum desiccator. The semi-solid was poured on a clay plate for crystallization (one week). The solid mass amounted to 5.07 g. or 34.7% of the theoretical. It softened at 60° and melted to a clear liquid at 105–107°; α_D^{27} −27.30° (in absolute alcohol).

Anal. Subs., 0.2406: 11.88 cc. of 0.0908 *N* NaOH. Calcd. for $C_{10}H_{12}O_4S$: neut. equiv. calcd., 228.2. Found: 223.1.

Anal. Subs., 0.4558: $BaSO_4$, 0.4745. Calcd. for $C_{10}H_{12}O_4S$: S, 14.06. Found: S, 14.30.

Ethyl *l*-α-Phenylsulfonebutyrate.—Eight grams of active acid was mixed with 15 cc. of thionyl chloride, whereby evolution of sulfur dioxide and hydrogen chloride occurred at once. After heating for twenty minutes in a water-bath just at the boiling point of the reagent, the oil had completely dissolved. The excess thionyl chloride was removed under vacuum and the residue treated with 15 cc. of absolute alcohol. After fifteen minutes the excess alcohol was removed by vacuum distillation. The residue, amounting to 6 g., was extracted several times with low boiling petroleum ether which dissolved the active ester. Evaporation of the ether left 2.8 g. of the ester which melted at 44–45° and had a rotation of −27.56°. Slow crystallization of the ester from petroleum ether gave a mass of beautiful colorless needles which melted at 44.5–45.5° and had α_D^{25} −32.48°.

Anal. (Micro). Subs., 4.605 mg.; $BaSO_4$, 4.28 mg. Calcd. for $C_{12}H_{16}O_4S$: S, 12.52. Found: S, 12.75.

Amide of α-Phenylsulfonebutyric Acid.—The acid chloride prepared as described above was dissolved in absolute ether and the solution saturated with ammonia. The precipitate of the amide and ammonium chloride was filtered. The amide was extracted by means of acetone and recrystallized twice from ethyl acetate. Colorless needles were obtained which melted at 169–170°. The amide was optically inactive.

Anal. Subs., 0.2845: $BaSO_4$, 0.2946. Calcd. for $C_{10}H_{13}O_3NS$: S, 14.12. Found: S, 14.22.

Sodium Salt of Ethyl *l*-α-Phenylsulfonebutyrate.—A solution consisting of 0.1803 g. (0.000704 mole) of ethyl *l*-α-phenylsulfonebutyrate dissolved in absolute alcohol was made up to a volume of 10 cc. and then cooled in an ice–salt mixture to −10°. The equivalent amount of sodium ethylate dissolved in absolute alcohol, 1.955 cc. containing 0.02450 g. per cc., was likewise cooled to −10°. The 1-dm. polariscope tube packed in ice and salt was given time to cool. The solutions were mixed rapidly, poured into the polariscope tube at −10° and readings taken within four minutes from the time of mixing the solutions. The solution was optically inactive. The experiment was repeated using more dilute solutions but no activity was ever observed.

Racemization of *l*-α-Phenylsulfonebutyric Acid and Ester.—The rate of racemization of an absolute alcoholic solution of the active acid was observed over a period of several weeks at 27°. The half-life period of the acid was 1350 hours.

The half-life period of the ester was found to be eighty hours at 27° and twenty-four hours at 47°.

Summary

The preparations of *l*-α-phenylsulfonebutyric acid and its ester are described. Treatment of the active ester with sodium ethylate yielded an inactive sodium derivative.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

DERIVATIVES OF PHENYLBORIC ACID, THEIR PREPARATION AND ACTION UPON BACTERIA. II. HYDROXYPHENYLBORIC ACIDS[1]

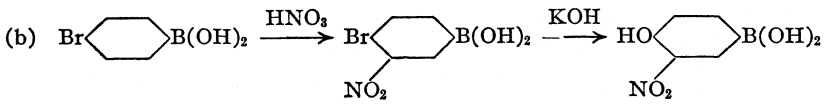
BY FREDERIC R. BEAN AND JOHN R. JOHNSON

RECEIVED JULY 5, 1932 PUBLISHED NOVEMBER 5, 1932

In an earlier investigation[2] various nitro and amino derivatives of phenylboric acid were prepared and their action on certain bacteria was tested. The present study was undertaken with the object of extending the work to other substituted aryl boric acids, particularly those containing a phenolic hydroxyl group.

Since the general methods for the preparation of aryl boric acids do not lend themselves to a direct synthesis of hydroxyphenylboric acids, it was necessary to introduce the phenolic hydroxyl by indirect methods. Of these, the following appeared to be the most promising.

(a) $NO_2C_6H_4B(OH)_2 \xrightarrow{H_2} NH_2C_6H_4B(OH)_2 \xrightarrow[+\text{ Hydrolysis}]{\text{Diazotization}} HOC_6H_4B(OH)_2$

(b) 

In addition to phenylboric acid, the following substituted boric acids were used as starting materials: *p*-tolyl-, *p*-anisyl- and *p*-bromophenylboric acids. These were prepared by the action of the corresponding organomagnesium bromides on *n*-butyl borate, at low temperatures. By substituting *n*-butyl borate[3] for methyl borate and effecting the reactions at −60° (instead of −15°),[2] the yields of these acids were improved markedly.

3-Hydroxyphenylboric acid was prepared through the reactions indicated above (a), from *m*-nitrophenylboric acid. The reduction of this and other nitroaryl boric acids was simplified by effecting a catalytic reduction with hydrogen in the presence of platinum[5] instead of using ferrous hydroxide.[6] *m*-Aminophenylboric acid was diazotized in the

[1] This article is an abstract of a thesis submitted by Frederic R. Bean to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in July, 1931.

[2] Seaman and Johnson, THIS JOURNAL, 53, 711 (1931).

[3] König and Scharrnbeck[4] have recently described the preparation of these aryl boric acids using isobutyl borate, but give no information concerning the yields obtained. They did not succeed in obtaining any nitro or amino derivatives of these acids.

[4] König and Scharrnbeck, *J. prakt. Chem.*, [2] 128, 157 (1930).

[5] Adams and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

[6] This modification enabled us to isolate *o*-aminophenylboric acid, which previously had been obtained only in solution.[2]

presence of sulfuric acid and the resulting diazonium salt was hydrolyzed in a current of steam. 3-Hydroxyphenylboric acid is a white crystalline solid, readily soluble in water and in ether. It gives a bluish-violet color with ferric chloride solution, and produces 3-hydroxyphenylmercuric chloride in practically quantitative yield on treatment with warm aqueous mercuric chloride solution.

The homolog, 3-hydroxy-4-methylphenylboric acid, was obtained by a similar series of reactions from 3-nitro-4-methylphenylboric acid. The latter was obtained readily by nitrating *p*-tolylboric acid with fuming nitric acid at −30°. The position of the nitro group was established by conversion into 4-bromo-2-nitrotoluene, and into 4-methyl-3-nitrophenylmercuric chloride. Catalytic reduction gave 3-amino-4-methylphenylboric acid, from which 3-hydroxy-4-methylphenylboric acid was obtained by diazotization and subsequent hydrolysis. The constitution of the hydroxy acid was established by conversion into *o*-cresol and into 4-methyl-3-hydroxyphenylmercuric chloride.

In the hope of obtaining a boric acid derivative of guaiacol, *p*-methoxyphenylboric acid was subjected to nitration. Fuming nitric acid, even at low temperatures, produced 2,4-dinitroanisole; likewise, in acetic anhydride, elimination of the boric acid residue occurred and 4-nitroanisole resulted. Difficulties were also encountered in the efforts to obtain derivatives of 4-hydroxyphenylboric acid. *p*-Bromophenylboric acid was used as a starting material in an attempt to use the second series of reactions indicated above (b). Nitration with fuming nitric acid at −15° gave 4-bromo-3-nitrophenylboric acid. The position of the nitro group was established through elimination of the boric acid group, and through replacement by bromine. The products were, respectively, 1,2-bromonitrobenzene and 1,4-dibromo-2-nitrobenzene. Various attempts to replace the bromine atom in the nitrated acid by hydroxyl were unsuccessful.

Work is now in progress on the preparation of substituted naphthylboric acids and diphenylboric acids.

Experimental Part

***n*-Butyl Borate.**—This ester was prepared by the interaction of boric anhydride and *n*-butyl alcohol, or merely by heating together boric acid and *n*-butyl alcohol under conditions such that the water produced in the reaction is eliminated continuously from the reaction mixture.[7] From 666 g. (9 moles) of *n*-butyl alcohol and 124 g. (2 moles) of boric acid there was obtained 410–435 g. (90–95% yield) of pure *n*-butyl borate; b. p. 103–105° (8 mm.), 114–115° (15 mm.), 234–238° (745 mm.), $d_{27.5}^{27.5}$ 0.856. Since *n*-butyl borate is hydrolyzed by atmospheric moisture, the product must be manipulated with a minimum exposure to the air. *n*-Butyl borate is more satisfactory than methyl borate for the preparation of organic boric acids since it is difficult to obtain methyl borate entirely free from methyl alcohol.

[7] W. J. Bannister, U. S. Patent 1,668,797, May 8, 1928; *Chem. Abstracts*, **22**, 2172 (1928).

Phenylboric Acid.—During the course of an hour, 0.25 mole of phenylmagnesium bromide (in approximately 1 molar solution) was added to a solution of 58 g. (0.25 mole) of *n*-butyl borate in 100 cc. of pure ether. During the reaction the solution was stirred mechanically and cooled in a slush of solid carbon dioxide and acetone, so that the internal temperature was maintained between −70 and −75°. As the Grignard reagent dropped into the solution, there formed immediately a white precipitate which slowly dissolved. After all of the Grignard reagent had been added, the reaction mixture was stirred (at −75°) until all of the precipitate had disappeared. The resulting yellow-orange solution was allowed to warm slowly to 0° in the cooling bath (preferably overnight). The reaction mixture was added slowly, while stirring vigorously, to 150 cc. of cold 10% sulfuric acid. The ether layer was separated and the aqueous layer was extracted twice with 100-cc. portions of ether. The original ether layer and the extracts were combined and the ether was removed by distillation from a steam-bath. The residual solution of phenylboric acid in *n*-butyl alcohol was made distinctly alkaline with potassium hydroxide solution and enough water was added to form a layer of about 150 cc. beneath the alcohol. The *n*-butyl alcohol was removed by steam distillation in vacuum by gentle heating (not above 45°); warm water was added slowly from time to time as needed and the distillation was continued until a mere trace of butyl alcohol remained. Toward the end a small amount of diphenyl distilled off, and a small amount of gummy solid separated in the aqueous solution in the distilling flask.

The residual solution was rendered acid to Congo paper by the addition of sulfuric acid and was diluted, if necessary, to a volume of 150–200 cc. Without separating the precipitate, the mixture was heated to the boiling point, with continuous stirring. After a short while the crystalline solid dissolved completely, leaving a heavy insoluble brown oil.[8] The hot aqueous solution was decanted through a fluted filter. The oil was extracted several times with 20-cc. portions of boiling water; the extracts were filtered while hot and added to the main solution. Phenylboric acid crystallized in white needles upon cooling the combined solutions. The product, after drying, weighed 14–17 g. (50–60% yield) and without further purification melted at 214–216° (corr.), in a capillary tube. An additional quantity of 1–2 g. of impure acid can be recovered from the mother liquors. When larger quantities were used in the preparation and more concentrated solutions of the Grignard reagent were employed, the yields were somewhat lower (42–47%).

***p*-Tolylboric Acid.**—*p*-Bromotoluene was converted into *p*-tolylmagnesium bromide in the conventional manner, and the method described for the preparation of phenylboric acid was used for the reaction with *n*-butyl borate. The yields of *p*-tolylboric acid were 43–48% of the theoretical (based upon the original *p*-bromotoluene).

p-Tolylboric acid crystallizes from water in slender needles, which melt at 258–259° (corr.) in a capillary tube heated from 20°. During the heating a fogginess appears in the capillary tube at 100–110°, apparently due to anhydride formation. On the Maquenne block[9] the substance melted without resolidification at 259–260° (decomp.); at lower temperatures it melts and instantly resolidifies, which indicates that the observed melting point is that of the anhydride (reported m. p. 259°).[4]

***p*-Methoxyphenylboric Acid.**—*p*-Anisylmagnesium bromide was prepared from *p*-bromoanisole in the customary manner, in yields of 90–95%. The general procedure described above gave the corresponding boric acid in yields of 30–35%. *p*-Methoxyphenylboric acid crystallizes from water in transparent plates which become opaque

[8] This is stated to contain the bis-arylboric acid, $(C_6H_5)_2B-OH$, formed by the action of a second molecule of C_6H_5MgBr upon $C_6H_5B(OC_4H_9)_2$.[4]

[9] *Cf.* Ref. 2, p. 714, footnote.

on drying in the air. The air-dried acid melted at 208.5–209.5° (corr.) in a capillary tube heated from 20°; on the Maquenne block it melted at 208° (decomp.). König and Scharrnbeck[4] reported the melting point 207° for this acid.

p-Bromophenylboric Acid.—*p*-Bromophenylmagnesium bromide was prepared by the action of a dilute ethereal solution of one mole of *p*-dibromobenzene upon one gram-atom of magnesium. The corresponding boric acid was obtained in the customary manner, in yields of 27–33% of the theoretical (based upon the original *p*-dibromobenzene). Since this acid is much less soluble in water than phenylboric acid, the quantity of water used in the last stage of the preparation was increased from 150 cc. to a volume of 600 cc., and the residual insoluble material was extracted with correspondingly larger quantities of hot water to remove the occluded *p*-bromophenylboric acid. From these solutions the acid crystallized in rough needles which melted at 276–281° (corr.) in a capillary tube heated from 20°. After recrystallization from 20% ethyl alcohol, with the addition of decolorizing charcoal, the substance melted with decomposition at 286–289° (corr.); a cloudiness appeared in the tube at about 100°. On the Maquenne block the compound melted without resolidification at 301–302°, which is probably the melting point of the anhydride since the material melts and resolidifies below this temperature. König and Scharrnbeck[4] reported the melting point 266° for this acid and Krause[10] reported 191°.

A sample of 0.5 g. of *p*-bromophenylboric acid was dissolved in hot water and treated with a concd. aqueous solution of 0.62 g. of mercuric chloride. There was precipitated 0.9 g. (95% yield) of *p*-bromophenylmercuric chloride, which after crystallization from 50% alcohol melted at 250°. This value agrees with the melting point of *p*-bromophenylmercuric chloride obtained from the corresponding sulfinic acid.[11] König and Scharrnbeck[4] reported the melting point 235° for the mercuri chloride obtained from their specimen of *p*-bromophenylboric acid.

3-Nitro-4-methylphenylboric Acid.—In a 150-cc. cylindrical Pyrex tube was placed 75 cc. of fuming nitric acid (1.50), to which a little urea had been added. The tube was cooled in a bath of liquid ammonia and 10 g. of finely pulverized, air-dried *p*-tolylboric acid was added slowly, with good mechanical stirring, during the course of one and one-half to two hours. The temperature was maintained at −28 to −30° during this addition and the solution was stirred at this temperature for thirty to forty-five minutes after all of the *p*-tolylboric acid had been added. The reaction mixture was carefully poured onto 150–200 g. of ice and the aqueous suspension was stirred thoroughly. The precipitated nitrotolylboric acid was filtered with suction, washed thoroughly with small portions of iced water, and recrystallized from a small volume of water (with the addition of decolorizing charcoal). The yield of the purified acid was 10 g. (75% of the theoretical). This acid proved to be pure 3-nitro-4-methylphenylboric acid; no isomeric nitro acid was isolated from the reaction products.

3-Nitro-4-methylphenylboric acid crystallizes from water in pale yellow needles; it is sparingly soluble in cold water, soluble in aqueous alkalies, alcohol and ether. In a capillary tube, heated from 20°, the acid darkened at 250° and melted at 260–264° (corr.); on the Maquenne block it melted sharply at 264°. For analysis an air-dried sample was crystallized twice from ethylene chloride. The analytical data indicate that this specimen was the anhydride, $NO_2C_7H_6B{=}O$.

Anal. Calcd. for $NO_2C_7H_6B(OH)_2$: N, 7.74. Calcd. for $NO_2C_7H_6BO$: N, 8.59. Found: N (Dumas), 8.48, 8.43.

A sample of 0.1 g. of the nitrotolylboric acid was refluxed for one to two hours with an excess of bromine dissolved in aqueous potassium bromide solution. The

[10] Krause, German Patent 371,467; *Chem. Abstracts*, **18**, 992 (1924).

[11] Hanke, THIS JOURNAL, **45**, 1321 (1923).

excess bromine was removed by adding a solution of sodium sulfite, and the bromonitrotoluene was purified by steam distillation. The purified product melted at 44.4–45°, and showed no depression of the melting point when mixed with an authentic specimen of 4-bromo-3-nitrotoluene, m. p. 45°.

On treatment with 0.3 g. of mercuric chloride in hot aqueous solution, 0.2 g. of the nitrotolylboric acid gave 0.35 g. of a nitrotolylmercuric chloride. After crystallization from 50% alcohol the product melted at 220–221°, in agreement with the m. p. 220.5–221° reported for 4-methyl-3-nitrophenylmercuric chloride.[12]

4-Bromo-3-nitrophenylboric Acid.—Ten grams of pulverized air-dried *p*-bromophenylboric acid was nitrated at −15° according to the procedure described above. The yield of purified product was 5.5–6.0 g. (45–50% of the theoretical). This acid proved to be pure 4-bromo-3-nitrophenylboric acid; no isomeric nitro acid was isolated from the reaction products.

4-Bromo-3-nitrophenylboric acid crystallizes from water in pale yellow needles. It is sparingly soluble in cold water, moderately soluble in hot water; it is soluble in aqueous alkalies and in alcohol and ether. In a capillary tube, heated from 20°, the acid melted at 300–301° (corr.); on the Maquenne block it melted at 320°. Bromine determinations were made by the method of Drogin and Rosanoff,[13] on samples that had been dried in air for ten to twelve hours and then in a desiccator over sulfuric acid for three to four hours. The composition corresponded to that of the acid, $RB(OH)_2$, and not the anhydride.

Anal. Calcd. for $C_6H_5O_4NBrB$: Br, 31.24. Found: Br, 31.23, 31.34.

A sample of 0.5 g. of the acid upon treatment with an excess of bromine, in the customary manner, gave 0.3 g. of 1,4-dibromo-2-nitrobenzene. After purification this product melted at 84° and was identified by comparison with an authentic sample of 1,4-dibromo-2-nitrobenzene.

Upon boiling 0.3 g. of the acid with an excess of aqueous silver nitrate solution and steam distilling the mixture, there was obtained 0.2 g. of *o*-bromonitrobenzene. After further purification the product melted at 41.5–42.5°, and showed no depression of the melting point when mixed with an authentic specimen of *o*-bromonitrobenzene, m. p. 42–43°.

***m*-Aminophenylboric Acid.**—A solution of 16.7 g. (0.1 mole) of *m*-nitrophenylboric acid[2] in 40 cc. of methyl alcohol was diluted with 100 cc. of distilled water, and after transferring to a reduction bottle was treated with 0.2 g. of platinum oxide.[5] On shaking with hydrogen under 2–3 atmospheres pressure, in the usual way,[14] the theoretical quantity of hydrogen was taken up in thirty to forty-five minutes. After allowing the catalyst to settle, the solution was decanted through a filter. For the preparation of *m*-hydroxyphenylboric acid the amino acid was not isolated.

A solution of the sulfate of *m*-aminophenylboric acid was prepared by acidifying the filtrate with sulfuric acid and distilling off the methyl alcohol under reduced pressure. Toward the end of the distillation, white crystals of the sulfate separated. To ensure complete removal of methyl alcohol, 100 cc. of water was added and the solution was again evaporated, under reduced pressure, to a small volume. The amount of sodium nitrite solution required for diazotization indicated a yield of about 85–90% of the amino acid.

A small portion of the resulting solution was converted to *m*-benzoylaminophenylboric acid by treatment with benzoyl chloride[2] in the presence of sodium bicarbonate. The product melted at 289° (corr.) in a capillary tube heated from 20°, in good agree-

[12] Coffey, *J. Chem. Soc.*, **129**, 639 (1926).

[13] Drogin and Rosanoff, THIS JOURNAL, **38**, 711 (1916).

[14] "Organic Syntheses," 1928, Vol. VIII, pp. 10, 66.

ment with the reported value (290°). The quantity of the benzoylated product varied in several reductions from 50–53% of the theoretical, based upon the nitro acid.

o-Aminophenylboric Acid.—Five grams of *o*-nitrophenylboric acid[2] was reduced catalytically as described above and the theoretical quantity of hydrogen was taken up. After filtering from the catalyst, the solution of the amino acid was evaporated in vacuum (below 30°) in a slow current of hydrogen. The sirupy residue was treated with 150 cc. of pure acetone and the solution was again evaporated, under the same conditions, until a sirup remained. This operation was repeated with two 100-cc. portions of anhydrous ether. The viscous, sirupy mass obtained finally, when allowed to stand overnight, yielded 1.0 g. of almost colorless crystals of the desired amino acid.

Upon recrystallization from anhydrous ether containing a small amount of acetone, *o*-aminophenylboric acid separated in colorless crystals which melted at 179–180° (corr.), in a capillary tube heated from 20°. The acid gives the usual qualitative tests for boron and nitrogen. It is quite soluble in acetone and in methyl alcohol, sparingly soluble in anhydrous ether. The observation that this substance dissolves slowly in water and in aqueous alkalies, indicates that it is an anhydride. By analogy with *m*-aminophenylboric acid, it would be expected to form an anhydride of the formula $(NH_2C_6H_4BO)_2O$.

Solutions of the amino acid decompose on warming or on long standing in the air. The mother liquors from which the acid had crystallized gradually turned brown on being exposed to the air, and after standing for some time had a distinct odor of aniline. On benzoylation there were obtained 1.5 g. of benzanilide, and 0.5 g. of an unidentified substance melting at approximately 270–275°.

For identification, *o*-aminophenylboric acid was benzoylated. The product melted at 283.6–285.6° (corr.), in good agreement with the value, 283–284° (corr.), reported for *o*-benzoylaminophenylboric acid.[2]

4-Methyl-3-aminophenylboric Acid.—A solution of 10 g. of 4-methyl-3-nitrophenylboric acid in 40 cc. of methyl alcohol and 100 cc. of water was reduced catalytically as described above, and took up the theoretical quantity of hydrogen. After removal of the catalyst the solution was evaporated to a small volume, under reduced pressure, in a current of hydrogen. The residue was treated with 100 cc. of water and warmed gently until all the crystalline material had dissolved. The solution was heated with decolorizing charcoal for several minutes, at 60–70°, and filtered. The filtrate was concentrated, under reduced pressure, to a volume of about 25 cc.; during this period a considerable quantity of white crystals of the amino acid had separated. These were filtered with suction and weighed 7 g. (85% of the theoretical). The mother liquor upon further concentration gave a small additional quantity (0.2–0.4 g.). The amino acid was purified by recrystallization from hot water; it crystallizes in small white cubes, which soften at 200° and melt at 209–212° (corr.) without apparent decomposition, in a capillary tube heated from 20°. On the Maquenne block it melts slowly at 267–270°, and instantly at 285°.

4-Methyl-3-aminophenylboric acid is soluble in dilute aqueous alkalies, alcohol, and hot water, but is only sparingly soluble in ether. It gives the usual qualitative tests for boron and nitrogen. A sample for analysis was dried for two days over concd. sulfuric acid; the analyses indicate that anhydride formation did not occur.

Anal. Calcd. for $C_7H_{10}O_2BN$: N, 9.26. Found: N (Kjeldahl), 9.04, 9.37.

Treatment of the amino acid with acetic anhydride produced an acetyl derivative; after crystallization from hot water this melted at 244–246°, in a capillary tube. On warming the acetyl derivative with silver nitrate solution, *o*-acetotoluidide was obtained. Upon benzoylation the amino acid gave 4-methyl-3-benzoylaminophenylboric acid. The latter melts and resolidifies at 95–100° and remelts at 315° (corr.). The benzoyl

derivative upon boiling with aqueous silver nitrate solution gave *o*-benzotoluide. The latter after purification melted at 143–144° (corr.); a mixed melting point determination with a known sample of benzoyl-*o*-toluidine (m. p. 142.6–143.6°) gave the value 142.6–143.5° (corr.).

***m*-Hydroxyphenylboric Acid.**—An aqueous solution of the sulfate of *m*-aminophenylboric acid was prepared from the product of reduction of 16.7 g. (0.1 mole) of *m*-nitrophenylboric acid, and freed of methyl alcohol as described under *m*-aminophenylboric acid. The solution was diluted with water to a volume of 200–250 cc. and an additional 0.1 mole of 50% sulfuric acid was added. The strongly acid solution was cooled to −2° in an ice–salt mixture and a solution of 0.1 mole of sodium nitrite in 50 cc. of water was introduced slowly beneath the surface, with mechanical stirring. Throughout the addition of the nitrite the temperature was maintained between 0 and −2°, and the rate of inflow was controlled so that no large excess of free nitrous acid was present. If oxides of nitrogen appeared, the addition of the nitrite solution was stopped until a test with starch–iodide paper was negative. Addition of the nitrite solution was continued until the starch–iodide test was positive after standing for five to ten minutes. This usually required nearly all of the nitrite solution. At this point the solution had acquired a reddish-brown color and a small amount of tarry material was present. After the diazotization was completed the slight excess of nitrous acid was destroyed by adding a 20% solution of urea, until the starch–iodide test was negative. The solution of the diazonium salt was immediately hydrolyzed in an apparatus previously prepared for this purpose.

A 3-liter round-bottomed Pyrex flask was fitted with a water-cooled condenser, supported in a vertical position, and a jacketed air-cooled condenser bent at an angle of 30° from the vertical. The upper enlarged end of the inclined condenser was bent back to the vertical, and was fitted with a cork bearing a 150-cc. separatory funnel and a 6-mm. steam inlet tube drawn out to a 2-mm. capillary, which extended 2–3 cm. below the stem of the separatory funnel.

Hydrolysis of the diazonium salt was accomplished by allowing the solution to drop at a fairly rapid rate into a strong current of dry steam which entered through the capillary tube. The diazonium salt was decomposed immediately (with frothing) upon striking the steam and the products of decomposition were blown through the air-cooled condenser into the flask. The time required for adding the diazonium solution was thirty to forty minutes and at the end about 500 cc. of a red solution was present in the flask.

The hot solution was treated with decolorizing charcoal and the warm filtrate was saturated with sodium chloride. This caused the separation of a small amount of tarry material, which was filtered off in a fluted filter. The filtrate was cooled to 20° and extracted with three 150-cc. portions and two 75-cc. portions of ether. The ethereal extracts were evaporated over a water-bath and left a viscous, reddish-brown mass. On standing for several hours this solidified and was broken up into a coarse powder. The weight of the crude product was 4.3 g., which is a 30% yield based upon the original *m*-nitrophenylboric acid.

The crude acid was recrystallized from ethylene chloride containing a small amount of acetone. From the concentrated solution the acid separated in faintly pink crystals. After two or three recrystallizations the pink color was removed entirely and 2.5–3.0 g. of the pure acid was obtained. In a capillary tube heated from 20°, the substance softened at 219° (corr.) and melted with decomposition at 225°; on the Maquenne block it did not melt up to 380°.

m-Hydroxyphenylboric acid is very soluble in water, alcohol, acetone and ether; sparingly soluble in ethylene chloride and chloroform. It gives the usual qualitative

test for boron, and gives a bluish-violet color on treatment with ferric chloride solution. An aqueous solution of the acid shows the characteristic reactions with silver nitrate and with mercuric chloride. Analyses indicated that the product obtained by crystallization from ethylene dichloride is a mixture of about equal amounts of the acid and the anhydride R—B=O or double anhydride of the composition $(HO—C_6H_4—B—OH)_2O$.

Anal.[15] Calcd. for $HOC_6H_4B(OH)_2$: C, 52.21; H, 5.89. Calcd. for $HOC_6H_4B=O$: C, 60.07; H, 5.89. Calcd. for $(HOC_6H_4BOH)_2O$: C, 55.87; H, 4.69. Found: C, 56.50, 56.63; H, 4.62, 4.82.

A few tenths of a gram of the acid was boiled with an excess of aqueous silver nitrate solution and the mixture was steam distilled. The distillate upon treatment with bromine gave instantly a milky precipitate, which after purification melted at 91–92°. The melting point was not lowered by mixture with known 2,4,6-tribromophenol (m. p. 91.5–92°).

***m*-Hydroxyphenylmercuric Chloride.**—A solution of 0.3 g. of *m*-hydroxyphenylboric acid in 100 cc. of water, at 50°, was treated dropwise with a saturated solution of mercuric chloride, until no further precipitation occurred. After ten minutes the precipitate was filtered with suction and washed with hot water to remove excess mercuric chloride. The yield of *m*-hydroxyphenylmercuric chloride was practically quantitative. The substance was recrystallized from 30% alcohol, from which it separated as a white powder, m. p. 240.5–241.5° (corr.). The isomeric *o*- and *p*-hydroxyphenylmercuric chlorides melt, respectively, at 152.5 and 224–225°.[16]

Anal. Calcd. for C_6H_5OClHg: Cl, 10.77. Found: Cl, 10.61, 10.66

4-Methyl-3-hydroxyphenylboric Acid.—This acid was obtained from 4-methyl-3-nitrophenylboric acid, by catalytic reduction, diazotization and hydrolysis of the diazonium salt, following the general procedure used for the preparation of *m*-hydroxyphenylboric acid. From 10 g. (0.55 mole) of the nitro acid there was obtained 4 g. (45% yield) of the crude hydroxy acid. After two crystallizations from ethylene chloride + acetone, 3.3 g. of pure material was obtained; m. p. 266–268° (corr.) with decomposition, in a capillary tube. On the Maquenne block the substance does not melt up to 380°.

4-Methyl-3-hydroxyphenylboric acid is moderately soluble in water, from which it crystallizes in small cubes. It is soluble in alcohol, acetone and ether. The acid gives a boron flame test, and gives a violet color with ferric chloride solution. It gives the characteristic reactions with silver nitrate and mercuric chloride. Analyses indicate that the product obtained by crystallization from ethylene chloride is the anhydride, R—B=O.

Anal. Calcd. for $C_7H_7O_2B$: C, 62.74; H, 5.27. Found: C, 62.75, 62.64; H, 5.53, 5.46.

On boiling this acid with silver nitrate solution, and following the procedure outlined under *m*-hydroxyphenylboric acid, there was obtained a dibromocresol, m. p. 53–54°. A mixture of this product with authentic 3,5-dibromo-2-hydroxytoluene (m. p. 55°) melted at 54–55°.

4-Methyl-3-hydroxyphenylmercuric Chloride.—This substance was prepared in almost quantitative yield from the corresponding boric acid by the method described under *m*-hydroxyphenylmercuric chloride. After recrystallization from 40% alcohol, the pure substance melted at 143.6–144.6° (corr.), with darkening.

Anal. Calcd. for C_7H_7OClHg: Cl, 10.30. Found: Cl, 10.34, 10.44.

[15] Microanalyses by Schoeller.

[16] Dimroth, *Ber.*, 32, 761 (1899).

Bacteriological Tests[17]

Bactericidal Tests by the Reddish Method.[18]—Two series of experiments were made with *Staphylococcus aureus*, at 37°, using 5 cc. of the "antiseptic" in the dilutions noted and 0.5 cc. of a twenty-four hour bouillon culture of the organism. In one series the test solution was allowed to act for five minutes, and in a second series for fifteen minutes. The results of these tests are given in Table I.

Bacteriostatic Tests.[19]—To each mixture of organisms and "antiseptic" solutions used in the bactericidal tests, an equal volume of standard plain broth was added and the mixture was incubated for forty-eight hours at 37°. The results of these tests are given in Table I.

TABLE I

	Bactericidal tests[b]										Bacteriostatic tests[b]				
	Five minutes					Fifteen minutes									
S[a]	100[c]	200	500	1000	2000	100	200	500	1000	2000	200	400	1000	2000	4000
I	−	+	+	+	+	−	+	+	+	+	−	−	+	+	+
II		+	+	+	+		+	+	+	+		−	+	+	+
III			−	+	+			−	−	+			−	−	−
IV			+	+	+			+	+	+			−	−	+
V		−	−	+	+		−	−	+	+	−	−	−	−	+
VI	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
VII	+	+	+	+	+	+	+	+	+	+	−	+	+	+	+
VIII	+	+	+	+	+	+	+	+	+	+	−	+	+	+	+

[a] (I) *p*-Tolylboric acid; (II), *p*-methoxyphenylboric acid; (III), *p*-bromophenylboric acid; (IV), 4-methyl-3-nitrophenylboric acid; (V), 4-bromo-3-nitrophenylboric acid; (VI), 4-methyl-3-aminophenylboric acid; (VII), *m*-hydroxyphenylboric acid; (VIII), 4-methyl-3-hydroxyphenylboric acid.

[b] A minus sign indicates a positive effect (killing or inhibition of growth); a plus sign indicates continued growth.

[c] Dilution of the test solution; *i. e.*, 1/100.

Discussion of Bacteriological Tests.—While the chemistry of disinfection—that is, the mechanism of the process—may be explained by a general theory,[20] a consideration of many observations shows that there is little, if any, obvious relation between the antiseptic potency of a sub-

[17] The authors wish to express their thanks to Dr. E. H. Volwiler, Chemical Director, and to Mr. E. B. Carter, Director of Biologic Laboratories, of the Abbott Laboratories, North Chicago, Illinois, for their kind coöperation in carrying out the tests described in this communication.

[18] An antiseptic solution in the dilution recommended must kill a *Staphylococcus aureus* culture, under the conditions of the Reddish test, in five minutes. The culture of *Staphylococcus aureus* when tested against phenol should be killed by a 1:70 dilution in ten minutes, and may or may not be killed by a 1 : 60 dilution in five minutes.

[19] The term bacteriostatic action denotes the property of hindering the growth of organisms without killing them. This is commonly called an antiseptic effect but does not conform to the official ruling of the Bureau of Chemistry.

[20] Bancroft and Richter, *J. Phys. Chem.*, **35**, 511 (1931).

stance and its molecular structure and physical properties. Certain groups introduced into a structure of recognized antiseptic potency (such as phenol) diminish its effectiveness and others augment it. Prediction of the antiseptic value of a particular substance depends upon deductions drawn from analogy and upon empirical rules derived from a large number of observations.

In the present study, *m*-hydroxyphenylboric acid and 4-methyl-3-hydroxyphenylboric acid were of particular interest. They can be regarded from the two aspects: as derivatives of phenol and *o*-cresol, whence the effects of the boric acid group can be compared with that of other substituents, or as derivatives of phenyl and *p*-tolyboric acids, whence the effect of introducing the phenolic hydroxyl can be observed.

Both of these substances were found to have practically no bactericidal action (toward *Staphylococcus aureus*) and to exert very little bacteriostatic effect. From the first point of view, this marked decrease in antiseptic action with the introduction of the boric acid group into the phenolic structure in the *m*-position appears to parallel that produced by a carboxyl, or a second phenolic hydroxyl, in the *m*-position.[21] The relative potency of these hydroxyarylboric acids and other substituted phenylboric acids can be deduced approximately by comparing the maximum dilutions at which the substances exhibit bacteriostatic action. Using phenylboric acid as standard, the effect of the substituents can be expressed simply by means of a "phenylboric acid index,"[23] which is the ratio of the maximum bacteriostatic dilution of the test substance to that of phenylboric acid.

TABLE II

COMPARISON OF SUBSTITUTED PHENYLBORIC ACIDS

Substituents	Maximum bacteriostatic dilution	Index	Substituents	Maximum bacteriostatic dilution	Index
3-NH_2	>1:200	<0.5	2-NO_2	1:2000	5.0
3-NH_2, 4-CH_3	>1:200	<0.5	3-NO_2	1:2000	5.0
3-OH	1:200	0.5	4-NO_2	1:2000	5.0
3-OH, 4-CH_3	1:200	0.5	3-NO_2, 4-CH_3	1:2000	5.0
4-CH_3	1:400	1.0	3-NO_2, 4-Br	1:2000	5.0
4-OCH_3	1:400	1.0	4-Br	1:4000	10.0
None	1:400	1.00			

[21] *m*-Hydroxybenzoic acid has practically no antiseptic action; resorcinol has a good phenol coefficient (*B. typhosus*) of 0.29.[22]

[22] Morgan and Cooper, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, **19**, 243 (1912); *Chem. Abstracts*, **6**, 2944 (1912).

[23] This notation is used rather than the conventional phenol coefficient because we were concerned primarily with the effect of introducing substituents into the parent structure, phenylboric acid. The phenol coefficient of phenylboric acid is approximately 0.5 against *B. typhosus* (20°) and *Staph. aureus* (37°).

The relatively high bacteriostatic action of the nitrophenylboric acids and of *p*-bromophenylboric acid indicates that the effect of introducing these substituents into phenylboric acid parallels the effect produced in phenol, since the nitrophenols and *p*-bromophenol have a stronger antiseptic action than phenol itself. The effects are not quantitatively the same since *p*-tolylboric acid has an index of approximately one and *p*-cresol has a phenol coefficient of two. In view of the fact that the indices used in the present work are based upon bacteriostatic effects and phenol coefficients are based upon bactericidal effects, this discrepancy is not surprising.

It is unwise to draw any generalization from the limited numbers of compounds tested but it does not seem unreasonable to assume, as a guide for the selection of other substituted aryl boric acids for study, that the effect of introducing a substituent into phenylboric acid will be of the same general nature as that produced in phenol.

Summary

3-Hydroxyphenylboric acid and 3-hydroxy-4-methylphenylboric acid were prepared from phenyl- and *p*-tolylboric acids. Several substituted aryl boric acids used in their preparation have been described and characterized.

The preparation of aminoaryl boric acids from the corresponding nitro acids has been improved by the use of catalytic reduction in the presence of platinum. This modification made possible the isolation of *o*-aminophenylboric acid, which had been obtained previously only in solution.

The bacteriostatic effects of a number of substituted phenylboric acids upon *Staphylococcus aureus* were determined. The effect of introducing various substituents appears to be analogous to that produced by the same substituents in phenol.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYLS.[1] XXV. THE RELATIVE INTERFERING EFFECTS OF THE GROUPS F, OCH_3, Cl, Br AS DETERMINED BY THE RELATIVE RATES OF RACEMIZATION OF THE 2'-SUBSTITUTED 2-NITRO-6-CARBOXYDIPHENYLS

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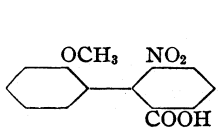
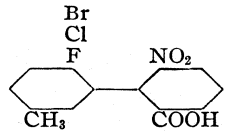
The observation that 2-nitro-6-carboxy-2',5'-dimethoxydiphenyl racemized readily at room temperature made evident that a study of the rates of racemization of various 2'-substituted 2-nitro-6-carboxydiphenyls might lead to a satisfactory method for determining the relative interfering effects of various groups.

In this investigation the 2-nitro-6-carboxy-2'-methoxydiphenyl (I) and the 2'-fluoro, chloro and bromo derivatives (II) of 2-nitro-6-carboxy-5'-methyldiphenyl have been synthesized and compared.



I



II

The 2-nitro-6-carboxy-2'-methoxydiphenyl was of particular interest since it contained the same 2,2',6-substituents as were present in 2-nitro-6-carboxy-2',5'-dimethoxydiphenyl reported by Yuan and Adams.[1b] The only modification is the elimination of the methoxyl group in the 5'-position of the latter compound. Both products showed exactly the same phenomenon in that merely one alkaloidal salt could be isolated and this showed mutarotation. The active forms obtained from the salts racemized with the same half-life period. It is apparent, then, that the additional methoxyl group in the previously reported compound has no appreciable influence on the interference effect of the 2,2',6 groups. The corresponding 2-nitro-6-carboxy-2'-methoxy-5'-methyldiphenyl has also been synthesized, a description of which is published in the succeeding paper and it also showed mutarotation of the single salt which could be isolated and a half-life period for the active acid essentially the same as that for the unsubstituted or 5'-substituted 2-nitro-6-carboxy-2'-methoxydiphenyl. Since the 5'-methyl group had no influence on the molecule, the halogen derivatives, 2'-fluoro, chloro and bromo of the 2-nitro-6-

[1] The last three papers in this series: (a) Roll and Adams, THIS JOURNAL, **54**, 2494 (1932); (b) Yuan and Adams, *ibid.*, **54**, 2966 (1932); (c) Becker and Adams, *ibid.*, **54**, 2973 (1932).

[2] This communication is an abstract of a thesis submitted by R. W. Stoughton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

carboxy-5′-methyldiphenyl were used for comparison since they were considerably simpler to prepare than those not containing the methyl group.

The 2-nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl formed only a single salt. However, unlike the methoxyl derivative, the salt showed no mutarotation at room temperature. Whether this indicated that the fluoro acid was incapable of resolution or that the mutarotation of the salt was so rapid that it could not be observed experimentally, was determined as follows. The brucine salt was dissolved in chloroform, not at room temperature but at 0°, and retained at that temperature in a polarimeter tube. Under these conditions a gradual change in rotation was noted from an initial reading of $[\alpha]_D^0$ +13° to a final constant reading of $[\alpha]_D^0$ −3.4°, which corresponds to a half-life period at 0° of forty-two minutes. If the brucine salt was dissolved at room temperature and then cooled to 0°, a rotation was obtained the same as that of a solution of the salt prepared originally at 0° and allowed to stand till constant rotation resulted. From these experiments it may be concluded that a single form of the brucine salt of the fluoro compound was in hand, but that it mutarotated with such rapidity that only at low temperatures could it be observed in the laboratory. The acid from this salt would certainly be extremely sensitive to racemization and in fact, in spite of all precautions, no active acid could be obtained by decomposition of the salt even at −5°.

The corresponding chlorine and bromine derivatives showed normal properties. Both salts were isolated and both active forms of each compound were obtained. The rates of racemization of the active acids were slow. The chloro compound did not racemize appreciably in hot ethyl alcohol and had a half-life period in boiling butyl alcohol of one hundred and forty-one minutes as compared with seventy hours for the bromo compound under similar conditions. More complete data are given in Table III. In every instance the bromo compound racemized much more slowly than the chloro.

From all these results it appears that the relative interference effects of the four groups studied would be in the following order—bromine > chlorine > methoxyl > fluorine, with marked differences between each. It is unlikely that any other factors in the molecule could modify the rates of racemization to such a degree that these groups would fall out of the order indicated. The corresponding methyl, carboxyl and nitro derivatives are now under investigation.

The average interference on each side of the molecule from x-ray data, based on the values previously assigned to the individual groups (with the exception that 1.45 Å. was substituted for 1.54 Å. for the methoxyl group)[1c] was as follows: for the F, OCH_3, Cl, Br: +0.01 Å., +0.04 Å.,

+0.25 Å., +0.37 Å. Assuming the rings to be coaxial at all times, the minimum interference value in each molecule would be, respectively, as follows: 0.05 Å., 0.11 Å., 0.55 Å., 0.78 Å. As the order from the two methods of computation is the same, either method might be adopted. The authors at present favor the second and recognize the fact that any calculated interferences in the 2,2′,6-trisubstituted diphenyls have less influence on racemization rates in these compounds than the same interference in the 2,2′,6,6′-tetrasubstituted diphenyls.

The compounds were prepared by condensing 1-nitro-2-bromo-3-carbomethoxybenzene with the intermediates *o*-iodoanisole, 1-methyl-3-iodo-4-chlorobenzene, 1-methyl-3-iodo-4-bromobenzene and 1-methyl-3-iodo-4-fluorobenzene by means of copper, saponification of the reaction product and isolation of the desired diphenyls. The salts of the acids showed a marked tendency to retain water, possibly in the form of water of crystallization. The anhydrous salts were hygroscopic and consequently the rotations were taken on the hydrated salts which had been analyzed for water content.

Experimental

1-Nitro-2-bromo-3-carbomethoxybenzene.—A solution of 130 g. of 1-nitro-2-bromo-3-carboxybenzene[3] in one liter of dry methyl alcohol was saturated with dry hydrogen chloride and refluxed for eight hours. This solution was poured into 6 liters of ice water, filtered, washed with sodium carbonate solution and recrystallized from a liter of 30% alcohol. A yield of 131 g. (95%) of white plates melting at 78.0–78.5° was obtained.

Anal. Calcd. for $C_8H_6BrNO_4$: Br, 30.76. Found: Br, 30.3.

1-Methyl-3-iodo-4-chlorobenzene.—A solution of 50 g. of 1-methyl-3-iodo-4-aminobenzene hydrochloride[4] in 350 cc. of glacial acetic acid, 90 cc. of water and 30 cc. of concentrated hydrochloric acid was cooled in an ice–salt bath and to it was added with constant stirring a solution of 17.5 g. of sodium nitrite in 90 cc. of water. At the same time a cuprous chloride solution was prepared by refluxing a mixture composed of 80 g. of potassium chloride, 44 g. of crystallized copper sulfate, 30 cc. of concentrated hydrochloric acid, 17 cc. of concentrated sulfuric acid, 50 g. of copper turnings and 250 cc. of water until it turned colorless. After the diazotized solution had stood for one and one-half hours in the cold, it was added to the hot cuprous chloride solution and the reaction mixture was immediately steam distilled. The distillate was extracted with ether and purified by vacuum distillation. The product amounted to 36 g. (76%) boiling at 157–159° at 50 mm. Ullmann and Glenck[5] prepared it by diazotizing chloro-*m*-toluidine and replacing with iodine. They give the boiling point at 249° at atmospheric pressure.

1-Methyl-3-iodo-4-bromobenzene.—A solution of 90 g. of 1-methyl-3-iodo-4-aminobenzene[4] in 600 cc. of glacial acetic acid, 90 cc. of water and 18 cc. of concentrated sulfuric acid was cooled in an ice–salt bath and to it was added with constant stirring

[3] "Organic Syntheses," John Wiley and Sons, Inc., New York City, 1927, Vol. VII, p. 12.

[4] Wheeler and Liddle, *Am. Chem. J.*, **42**, 445 (1909).

[5] Ullmann and Glenck, *Ber.*, **49**, 2493 (1916).

a solution of 26 g. of sodium nitrite in 150 cc. of water. At the same time a cuprous bromide solution was prepared by refluxing a mixture composed of 192 g. of sodium bromide, 90 g. of crystallized copper sulfate, 70 cc. of concentrated sulfuric acid, 70 g. of copper turnings and 500 cc. of water until it turned light yellow. After the diazotized solution had stood for one and one-half hours in the cold it was added to the hot cuprous bromide and the reaction mixture was immediately steam distilled. The distillate was extracted with ether and purified by vacuum distillation. A yield of 46 g. (40%) of a yellow oil was obtained boiling at 145–150° at 20 mm.

Anal. Calcd. for C_7H_6BrI: Br + I, 69.68. Found: Br + I, 69.39.

1-Methyl-3-iodo-4-fluorobenzene.—To a solution of 100 g. of 1-methyl-3-iodo-4-aminobenzene[4] hydrochloride in 50 cc. of concentrated hydrochloric acid and 80 cc. of water, cooled in an ice–salt bath, 35 g. of sodium nitrite was added slowly over a period of three hours. After standing for two hours in the cold, the diazotized solution was filtered and to it was added 90 cc. of fluoroboric acid solution. This solution was prepared according to the directions of Balz and Schiemann[6] by adding slowly 73 g. of boric acid to 190 g. of a cold 48% hydrogen fluoride solution in a copper flask. The solution was kept in a wax bottle. Upon the addition of the fluoroboric acid a heavy yellow crystalline precipitate of diazonium borofluoride separated. This was filtered and washed first with alcohol and then with a little ether. A yield of 90 g. (70%) was obtained. This substance decomposes at 110° and upon standing for several weeks becomes dark colored.

The diazonium borofluoride was decomposed by placing in a distilling flask, loosely fitted with a cork stopper and connected to a condenser and receiver. A stream of air was drawn through the apparatus by a suction pump through a water trap. The flask was heated gently with a free flame until decomposition started. A large amount of boron trifluoride was liberated and if heated too strongly escaped into the room in spite of the suction. After the salt was decomposed, the flask was heated more strongly in order to distil over the iodofluorotoluene. As soon as iodine vapors appeared in the flask the heating was discontinued. Some of the product was always carried over to the water trap. This was added to the main product and washed with sodium hydroxide and water. It was finally vacuum distilled. A yield of 45 g. (70% based on the borofluoride) of a colorless liquid was obtained: b. p. (30 mm.) 122–125°, d_{20}^{20} 1.8337, n_D^{18} 1.5757.

Anal. Calcd. for C_7H_6FI: I, 53.8. Found: I, 53.0.

Condensation of 1-Nitro-2-bromo-3-carbomethoxybenzene with Halogenated Benzenes to Form Substituted 2-Nitro-6-carboxydiphenyls.—In a 200-cc. 3-necked flask fitted with a mechanical stirrer and reflux condenser was placed 20–30 g. of 1-nitro-2-bromo-3-carbomethoxybenzene and an excess of half a mole of the aryl halide. The mixture was heated in a metal bath and as soon as the contents began to boil 40–60 g. of copper bronze was added slowly over a period of three-quarters of an hour. During the addition of the copper, the bath temperature was maintained just below the refluxing point and then raised 25° for fifteen minutes. After cooling, the mixture was thoroughly extracted with 200–300 cc. of hot alcohol and filtered. To this alcohol extract 100–150 cc. of 10% sodium hydroxide was added, the solution diluted to 500–750 cc. and refluxed for five hours. At the end of this time an oil remained which consisted of a mixture of unreacted halide and any diphenyl formed from its symmetrical coupling. This was recovered by steam distillation.

The aqueous layer was then acidified with dilute hydrochloric acid. The brown solid that separated was collected and dissolved in 150–200 cc. of hot glacial acetic acid.

[6] Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

On cooling, any 2,2′-dinitro-6,6′-dicarboxybenzene that had been formed, separated. This was removed and the filtrate was diluted to 400–500 cc. with water and heated until solution was complete. On cooling, the crude acid was deposited. It was then recrystallized from a suitable solvent. The pure acid may also be obtained by extracting the crude product from the saponification with warm benzene as the 2,2′-dinitro-6,6′-dicarboxybenzene is nearly insoluble in benzene even when warm. The benzene solution is then extracted with sodium hydroxide and recrystallized.

TABLE I

PROPERTIES OF DIPHENYLS

The products were purified by dissolving in hot alcohol and adding water up to the point of cloudiness. The 2-nitro-6-carboxy-2′-bromo-5′-methyldiphenyl, however, was crystallized from either alcohol or glacial acetic acid.

Acid	Aryl halide condensed with 1-nitro-2-bromo-3-carbomethoxy-benzene	Temp. of coupling bath, °C.	Yield, pure, %	Form and color	M. p. (corr.), °C.	Analyses, %	Calcd.	Found
2-Nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl	1-Methyl-3-iodo-4-fluoro-benzene	200–210	16	Yellow plates	187–188	C,	61.10	61.19
						H,	3.64	3.69
2-Nitro-6-carboxy-2′-chloro-5′-methyldiphenyl	1-Methyl-3-iodo-4-chlorobenzene	230–240	11	Yellow plates	234–234.5	C,	57.63	57.89
						H,	3.62	3.57
2-Nitro-6-carboxy-2′-bromo-5′-methyldiphenyl	1-Methyl-3-iodo-4-bromobenzene	240–250	10	Yellow plates	228–229	Br,	23.78	23.59
2-Nitro-6-carboxy-2′-methoxydiphenyl	1-Iodo-2-methoxy-benzene	240–250	21	Yellow needles	196.5–197	C,	61.53	61.73
						H,	4.08	3.88

2,2′-Dichloro-5,5′-dimethyldiphenyl.—The oil recovered from the saponification process in the preparation of 2-nitro-6-carboxy-2′-chloro-5′-methyldiphenyl was steam distilled. At first the unreacted chloroiodotoluene came over but near the end of the distillation a white solid was obtained. This was recrystallized from dilute alcohol. It melted at 85–86°.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: Cl, 28.25. Found: Cl, 28.35.

Resolution of 2-Nitro-6-carboxy-2′-methoxydiphenyl.—To a warm solution of 1.86 g. of 2-nitro-6-carboxy-2′-carboxydiphenyl in 150 cc. of alcohol was added a solution of 2.79 g. of brucine in 75 cc. of alcohol and the mixture filtered. Upon standing overnight at 0°, 1.2 g. of yellow solid deposited. Due to the instability of this salt no attempt was made to purify it by recrystallization. It melted at 219–220°. This salt contained water which corresponded to one-half a molecule of water of crystallization. The anhydrous form melts at 223–224°. (See Table II for rotations and mutarotations of the hydrated salt.)

The mother liquors were evaporated under an air jet in the cold and 1.5 g. more obtained with the same melting point and rotation.

Anal. Calcd. for $C_{37}H_{37}N_3O_9$: C, 66.54; H, 5.59. Found: C, 66.85; H, 5.65. Calcd. for $C_{37}H_{37}N_3O_9 \cdot 0.5H_2O$: H_2O, 1.33. Found: 1.57.

***d*-2-Nitro-6-carboxy-2′-methoxydiphenyl.**—The active acid was obtained by treating 1 g. of the salt with 50 cc. of ice cold 6 *N* hydrochloric acid in a flask cooled in an ice–salt bath for one hour. It was filtered, treated with a second portion of hydrochloric acid and allowed to stand in an ice box overnight. It was then filtered and washed, first with dilute acid and then with water until the washings gave no test for brucine. Until the acid was obtained in the solid state the temperature was kept at 0°. A yield of 0.3 g. was obtained melting at 196–197°. (See Table II for rotations and racemization experiments.)

TABLE II

ROTATIONS OF *d*-2-NITRO-6-CARBOXY-2'-METHOXYDIPHENYL AND ITS BRUCINE AND SODIUM SALTS

Compound	Wt.,[a] g.	Solvent	Temp., °C.	Rotations in degree[b] Initial α_D	Initial $[\alpha]_D$	Final α_D	Final $[\alpha]_D$	Average K	Average deviation of K	Half-life period in min.
Brucine salt[e]	0.1827	Chloroform	0	+1.08	+88.7	−0.11	−9.0	0.0010	±0.001	301.0
Brucine salt	.1016	Chloroform	26	+0.40	+29.5	− .11	−8.1	.025	± .002	12.0
d-Acid	.2057	Alcohol	26	+ .81	+29.5	Not carried to completion[d]		.032	± .003	9.4
Sodium salt	.1260	0.1 *N* NaOH	26	+ .80	+47.5	Not carried to completion[d]		.015	± .002	20.0
Sodium salt	.1414	Dil. Na ethylate[c]	26	+ .94	+49.9	Not carried to completion[d]		.091	± .005	3.3

[a] Made up to 15 cc. [b] $l = 2$. [c] Solution of 0.5 g. of sodium in 50 cc. of absolute alcohol was used. [d] Six to eight readings were taken during the period of partial racemization and from these half-life periods were calculated. [e] The brucine salt at 0°: $l = 1$ but all the others $l = 2$.

Resolution of 2-Nitro-6-carboxy-2'-chloro-5'-methyldiphenyl.—To a warm solution of 3.0 g. of 2-nitro-6-carboxy-2'-chloro-5'-methyldiphenyl in 125 cc. of ordinary ethyl alcohol was added a solution of 4.15 g. of anhydrous brucine in 75 cc. of alcohol. Upon standing for five hours 4.2 g. of white plates was deposited. These were collected and after three recrystallizations from alcohol 1.5 g. of salt of constant rotation was obtained melting at 200° with previous softening at 150°. This less soluble salt was found to contain water which corresponded to three-fourths of a molecule of water of crystallization. The melting point of the anhydrous form is 215–217°.

Rotation. Hydrated less soluble salt: 0.1270 g. made up to 15 cc. with chloroform at 20° gave α_D −0.32°; $l = 2$; $[\alpha]_D^{20}$ −25.3°.

Anal. 0.2681 g. lost 0.0052 g. on drying. Calcd. for $C_{37}H_{36}ClN_3O_8 \cdot 0.75H_2O$: H_2O, 1.85. Found: H_2O, 1.94. Calcd. for $C_{37}H_{36}ClN_3O_8$: C, 64.75; H, 5.29. Found: C, 64.75, H, 5.39.

The mother liquors were evaporated under an air jet and the solid obtained was recrystallized three times from *n*-butyl alcohol. This yielded 2.0 g. of more soluble salt. It melted at 220–221°.

Rotation. More soluble salt: 0.1398 g. made up to 15 cc. with chloroform at 20° gave α_D +0.43°; $l = 2$; $[\alpha]_D^{20}$ +22.8°.

Anal. Calcd. for $C_{37}H_{36}ClN_3O_8$: C, 64.75; H, 5.29. Found: C, 65.52; H, 5.47.

***l*- and *d*-2-nitro-6-carboxy-2'-chloro-5'-methyldiphenyl.**—The active acids were liberated from their salts by treatment with hydrochloric acid in the cold as previously described. The organic acids were obtained as fine cream-colored powders.

The active acids were recrystallized from dilute alcohol. The *l*-acid from the less soluble salt was obtained melting at 234.5° with slight softening at 180°. The *d*-acid from the more soluble salt melted at 234° with slight softening at 180°. (See Table III for rotations and racemization experiments on *l*-acid.) The rotation of the *l*-acid in boiling ethyl alcohol remained constant.

Rotation. *d*-Acid: 0.1213 g. made up to 15 cc. with ethyl alcohol at 20° gave α_D +0.30; $l = 2$; $[\alpha]_D^{20}$ +18.6°.

Resolution of 2-Nitro-6-carboxy-2'-bromo-5'-methyldiphenyl.—To a warm solution of 1.68 g. of 2-nitro-6-carboxy-2'-bromo-5'-methyldiphenyl in 50 cc. of alcohol was added a solution of 1.97 g. of anhydrous brucine in 50 cc. of alcohol and the mixture filtered. Upon standing overnight 1.6 g. of white plates was deposited. These were collected

and after two recrystallizations from alcohol 1.0 g. of salt of constant rotation remained. It melted at 203° with previous softening at 150°. This salt on drying was found to contain water which corresponded to one molecule of water of crystallization. The anhydrous form melted at 219°.

Rotation. Hydrated less soluble salt: 0.1226 g. made up to 15 cc. with chloroform at 20° gave α_D −0.52°; $l = 2$; $[\alpha]_D^{20}$ −31.8°.

Anal. 0.3424 g. lost 0.0088 g. on drying. Calcd. for $C_{37}H_{36}BrN_3O_8 \cdot H_2O$: H_2O, 2.47. Found: H_2O, 2.57. Calcd. for $C_{37}H_{36}BrN_3O_8$: Br, 10.95. Found: Br, 10.88.

The mother liquors were evaporated under an air jet and the solid obtained was recrystallized three times from *n*-butyl alcohol. This yielded 0.5 g. of pure more soluble salt. It contained no water and melted at 228–229°.

Rotation. Anhydrous more soluble salt: 0.1463 g. made up to 15 cc. with chloroform at 20° gave α_D +0.75°; $l = 2$; $[\alpha]_D^{20}$ +38.4°.

Anal. Calcd. for $C_{37}H_{36}BrN_3O_8$: Br, 10.95. Found: Br, 11.17.

l- and d-2-Nitro-6-carboxy-2′-bromo-5′-methyldiphenyl.—The active acids were liberated from their salts by treatment with hydrochloric acid in the cold. The organic acids were obtained as fine cream-colored powders. The active acids were purified from dilute alcohol. The *l*-acid from the less soluble salt melted at 227–228° with very distinct softening at 177°. The *d*-acid from the more soluble salt melted at 226.5–228° with softening at 177°. (See Table III for rotations and racemization experiments on *l*-acid.)

Rotation. d-Acid: 0.1337 g. made up to 15 cc. with ethyl alcohol at 20° gave α_D +0.49°; $l = 2$; $[\alpha]_D^{20}$ +27.5°.

TABLE III

RACEMIZATION EXPERIMENTS OF *l*-2-NITRO-6-CARBOXY-2′-CHLORO-5′-METHYLDIPHENYL AND *l*-2-NITRO-6-CARBOXY-2′-BROMO-5′-METHYLDIPHENYL

Wt.,[a] g.	Solvent	Temp., °C.	Rotations in degree[b] Initial α_D	Initial $[\alpha]_D^{20}$	Partially racemized Time, min.	Partially racemized α_D	Partially racemized $[\alpha]_D^{20}$	Average $K \times 10^3$	Average deviation of $K \times 10^3$	Half-life period in min.
2-Nitro-6-carboxy-2′-chloro-5′-methyldiphenyl										
0.1868	Butyl alcohol	117	−0.61	− 40.8	360	−0.10	− 6.7	2.14	±0.03	141
.2342	Acetic acid	118	−1.29	− 68.9	340	−0.29	− 15.5	1.95	± .03	154
.1604	0.1 *N* NaOH	80	+1.61	+125	390	+1.41	+110	0.12	± .03	2510
.1190	0.1 *N* NaOH	100	−0.93	− 97.6[c]	330	−0.39	− 41.0	1.4	± .2	218
.1505	Dil. Na ethylate[d]	78	+1.4	+116	240	+1.27	+105	0.17	± .01	1770
2-Nitro-6-carboxy-2′-bromo-5′-methyldiphenyl										
0.2495	Butyl alcohol	117	−0.74	− 37.1	1500	−0.58	− 29.1	0.69	±0.001	4350
.1478	Acetic acid	118	−0.69	− 58.4	1080	− .55	− 46.5	.88	± .005	3240
.1816	0.1 *N* NaOH	100	+1.20	+ 82.6	1080	+ .97	+ 66.8	.85	± .002	3540
.1094	Dil. Na ethylate[d]	78	+0.76	+ 85.9	300	+ .66	+ 75.3	.13	± .01	2340

[a] Made up to 25 cc. [b] $l = 2$. [c] Partially active. [d] Solution of 0.5 g. of sodium in 50 cc. of absolute alcohol was used.

Resolution of 2-Nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl. Brucine Salt.—To a warm solution of 2.75 g. of 2-nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl in 50 cc. of ordinary ethyl alcohol was added a solution of 3.94 g. of anhydrous brucine in 100 cc. of alcohol. Upon standing overnight in an ice box 5.1 g. of a white solid was deposited. Upon evaporation of the mother liquors in the cold 1 g. of a yellow viscous oil remained which solidified on standing. On recrystallization, a salt of similar rotation to the first fraction was obtained.

The salt gave a constant rotation at 20° but if made up at 0° a rotation was at first

observed which gradually decreased through mutarotation until a constant value resulted. This final constant value was the same as that obtained by cooling to 0° the sample that had been first dissolved at 20°. Recrystallization of this salt did not change the rotation. It melted at 213–214.5° with slight softening at 150°. This salt retained water which corresponds to one-fourth of a molecule of water of crystallization. The melting point of the anhydrous form is 214–215°.

Rotation. Hydrated salt: 0.2846 g. made up to 15 cc. with chloroform at 20° gave α_D −0.12°; $l = 2$; $[\alpha]_D^{20}$ −3.2°. 0.1464 g. made up to 10 cc. with chloroform at 0° and allowed to remain at 0°; $l = 1$.

Time in minutes	α_D	$[\alpha]_D^0$	k	Av. k
0	...	+15.0° (calcd.)	....	
10	+0.19°	+13.0°	....	
30	+ .10°	+ 6.8°	0.0093	
60	+ .05°	+ 3.4°	.0072	0.0083
115	− .02°	− 1.4°	.0084	
5 hours	− .05°	− 3.4°	....	

Half-life period, 42 minutes.

Anal. 0.2154 g. lost 0.0015 g. on drying. Calcd. for $C_{37}H_{36}FN_3O_8 \cdot 0.25H_2O$: H_2O, 0.68. Found: H_2O, 0.70. Calcd. for $C_{37}H_{36}FN_3O_8$: C, 66.34; H, 5.42. Found: C, 66.41; H, 5.45.

Quinine Salt.—To a warm solution of 3.24 g. of quinine in 30 cc. of ordinary ethyl alcohol was added a solution of 2.75 g. of 2-nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl in 30 cc. of alcohol and the mixture filtered. At the end of four hours 2.6 g. of yellow crystals was deposited. Upon standing overnight 2.5 g. more was obtained which gave the same rotation as the first fraction. This salt behaved as did the brucine salt in showing a constant rotation at 20° but mutarotation at 0°. Likewise recrystallization did not affect the rotation. This salt melts at 135–140°. It was found to contain solvent of crystallization which corresponds to two molecules of water. The anhydrous form melts at 138–140°.

Rotation. Hydrated salt: 0.114 g. made up to 15 cc. with chloroform at 20° gave α_D −1.40°; $l = 2$; $[\alpha]_D^{20}$ −94.5°.

Mutarotation. Hydrated salt: 0.0703 g. was made up to 10 cc. with chloroform at 0° and allowed to stand at 0°; $l = 1$.

Time in minutes	α_D	$[\alpha]_D^0$	k	Av. k
0	...	−125.0° (calcd.)	....	
5	−0.82°	−116.6°	....	
35	− .65°	− 92.4°	0.0178	0.0187
60	− .60°	− 85.3°	0.0196	
5 hours	− .58°	− 82.5°	....	

Half-life period, 16 minutes.

Anal. 0.3099 g. lost 0.0173 g. on drying. Calcd. for $C_{34}H_{34}FN_3O_8 \cdot 2H_2O$: H_2O, 5.67. Found: H_2O, 5.58. Calcd. for $C_{34}H_{34}FN_3O_6$: C, 68.08; H, 5.71. Found: C, 67.12; H, 5.81.

Strychnine Salt.—A mixture of 2.26 g. of 2-nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl and 3.18 g. of strychnine was dissolved in 100 cc. of ordinary ethyl alcohol. Upon standing for two days 4.4 g. of white crystals was deposited. This salt showed no mutarotation at 0° and recrystallization did not change the rotation. The melting point is 194–196°.

Rotation. 0.2030 g. made up to 15 cc. with chloroform at 20° gave α_D −0.67°; $l = 2$; $[\alpha]_D^{20}$ −24.5°. 0.1342 g. made up to 10 cc. with chloroform at 0° gave α_D −0.42°; $l = 1$; $[\alpha]_D^0$ −31.2°.

Anal. Calcd. for $C_{35}H_{32}FN_3O_6$: C, 68.93; H, 5.29. Found: C, 67.84; H, 5.67.

Attempt to Obtain Active 2-Nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl.—The organic acid was obtained by treating one gram of the brucine salt with 50 cc. of dilute hydrochloric acid at −5° for twelve hours. This was filtered and washed, first with dilute hydrochloric acid and then with cold water. Until the acid was obtained in the pure state, the temperature was kept at −5°. Three-tenths of a gram obtained in this manner melted at 185–186°. However, this acid showed no rotation when dissolved in ethyl alcohol at 0°. Similar results were obtained from the quinine and strychnine salts.

1-Methyl-4-fluoro-5-nitrofluorenone.—A solution of 0.5 g. of 2-nitro-6-carboxy-2′-fluoro-5′-methyldiphenyl in 10 cc. of concentrated sulfuric acid was warmed on the steam cone for ten minutes. The solution turned red as soon as the diphenyl dissolved. This was poured into ice water. The solid that separated was recrystallized from alcohol. A quantitative yield of yellow needles was obtained melting at 204–205°.

Anal. Calcd. for $C_{14}H_8FNO_3$: C, 65.35; H, 3.11. Found: C, 65.60; H, 3.27.

Summary

1. 2-Nitro-6-carboxy-2′-methoxydiphenyl and the 2′-fluoro, chloro and bromo derivatives of 2-nitro-6-carboxy-5′-methyldiphenyl have been prepared and resolved. The rates of racemization of the active forms have been compared.

2. The differences between the individual compounds are very marked and lead to the conclusion that the interfering effect of the 2′-substitution is in the following order: Br > Cl > OCH_3 > F.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STEREOCHEMISTRY OF DIPHENYLS.[1] XXVI. THE EFFECT OF SUBSTITUTION ON THE RATE OF RACEMIZATION OF CERTAIN OPTICALLY ACTIVE DIPHENYLS

BY H. C. YUAN[2] AND ROGER ADAMS

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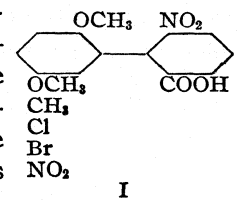
It is generally accepted that the two phenyl rings in diphenyl compounds have a common axis of rotation, and that the phenomenon of stereoisomerism in variously substituted 2,2′,6,6′ derivatives is due to restriction of free rotation of one ring with respect to the other by those groups, thus causing the two rings to be non-coplanar and giving the molecule a spatial asymmetric configuration. No experimental evidence is as yet available

[1] For the last three papers in this series see (a) Yuan and Adams, THIS JOURNAL, **54**, 2966 (1932); (b) Becker and Adams, *ibid.*, **54**, 2973 (1932); (c) Stoughton and Adams, *ibid.*, **54**, 4426 (1932).

[2] This communication is a portion of a thesis submitted by H. C. Yuan in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

in regard to the effect of substituents at positions other than 2,2′,6,6′ on the resolvability of certain diphenyl compounds or on the stability of the active molecules. The present investigation had the object in view of getting information on this problem. Since the ortho tetrasubstituted derivatives, with the exception of a few types, present molecules which cannot be racemized at all or only with great difficulty, the 2,2′,6-trisubstituted diphenyls offer the most promising field for this study.

The specific compounds prepared were four substituted 2-nitro-6-carboxy-2′-methoxydiphenyls with the groups methyl, chloro, bromo and nitro in position 5′ (I). Together with the 2-nitro-6-carboxy-2′,5′-dimethoxydiphenyl described in a previous article,[1a] five analogous diphenyls are available for comparison with the unsubstituted 2-nitro-6-carboxy-2′-methoxydiphenyl.[1c] Conclusions may thus be drawn in regard to the effect of different types of groups in the 5′-position.



I

As observed in the case of 2-nitro-6-carboxy-2′,5′-dimethoxydiphenyl and 2-nitro-6-carboxy-2′-methoxydiphenyl, only one brucine salt could be isolated for each of the diphenyls prepared. The second salt was apparently converted through mutarotation to the less soluble form during the process of concentration of the solution. Moreover, all the salts mutarotated and the active acids obtained from the salts racemized readily in organic solvents at room temperature. On the assumption that the size of the ortho substituents was the only factor involved, the rates of mutarotation of the various salts should be identical and the rates of racemization of the active acids should be the same. Experimentally, however, this was found not to be true. The half-life periods calculated from the velocity constants were taken as a means for comparison of the stabilities. The half-life periods are given in Table I. For complete data see Table III.

TABLE I

HALF-LIFE PERIODS AT 26° OF THE ACTIVE FORMS OF SUBSTITUTED 2-NITRO-6-CARBOXY-2′-METHOXYDIPHENYLS AND THEIR SALTS

Compound group at 5′	Half-life period in minutes			
	Free acid in alcohol	Brucine salt in chloroform	Sodium salt in water	Sodium salt in alcohol
—OCH_3[1a]	10.8	16.7	27.4	3.7
—CH_3	11.5	15.8	30.1	3.8
—Cl	31.0	16.7	40.2	9.7
—Br	32.0	16.7	43.6	11.5
—NO_2	35.4	7.7	35.0	16.7

The average deviation of the individual velocity constants was less than 10%. The values could be readily duplicated.

The following conclusions may be drawn from these data. (1) A comparison of the rates of racemization of the free acids indicates that the

stabilities of 5′-methoxy and 5′-methyl derivatives are practically the same, the stabilities of the 5′-chloro and 5′-bromo are also identical and they are more stable than the first two. The 5′-nitro is the stablest of all the derivatives. This can be seen more clearly from Fig. 1. Line A is parallel to B and C to D and line E has the smallest slope. (2) The brucine salts, which, unlike the acids, contain an additional asymmetric influence, have essentially similar stability with the exception of the nitro derivative. The brucine salt of the 5′-nitro mutarotates twice as fast as the others (Fig. 2). (3) The brucine salts of the 5′-methoxy and the 5′-methyl derivatives in chloroform are more stable than the corresponding acids in alcohol while the salts of the 5′-chloro, bromo or nitro derivatives in chloroform are less stable. (4) The sodium salts in water racemize less readily but in alcohol more readily than the free acids in organic solvents.

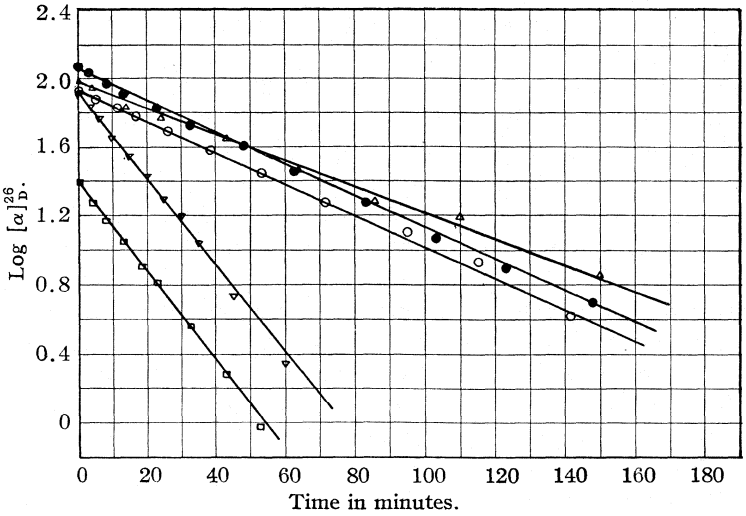


Fig. 1.—Rates of racemization of five 5′-substituted 2-nitro-6-carboxy-2′-methoxydiphenyls: □, CH_3; ▽, OCH_3; ○, Br; ●, Cl; △, NO_2.

The first point constitutes the main theme of the present investigation, the effect of substituents on the rate of racemization of the active acids when determined under similar conditions. Although the exact mechanism of this phenomenon is still obscure, there are several factors, any or all of which may influence the molecules.

First, it has been demonstrated by Ingold,[3] Debye[4] and Smyth[5] and many others through different methods that the valence angle of carbon

[3] Ingold, *J. Chem. Soc.*, **121**, 2676 (1922), and other papers.

[4] Debye, *Z. Elektrochem.*, **36**, 612 (1930).

[5] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Company, New York, 1931, p. 112.

is not a constant value 109.5°, but varies with the nature of atoms or groups present in the molecule. The introduction of the 5′ groups into the diphenyl molecules may be sufficient to change the valence angles of the groups in the 2,2′,6-positions and thus diminish or increase the interference in a molecule.

Second, the 5′ groups may cause the linkage between the two rings to bend in such a way that the rings are no longer coaxial. The interference of the 2,2′,6 groups would certainly be affected by such a change.

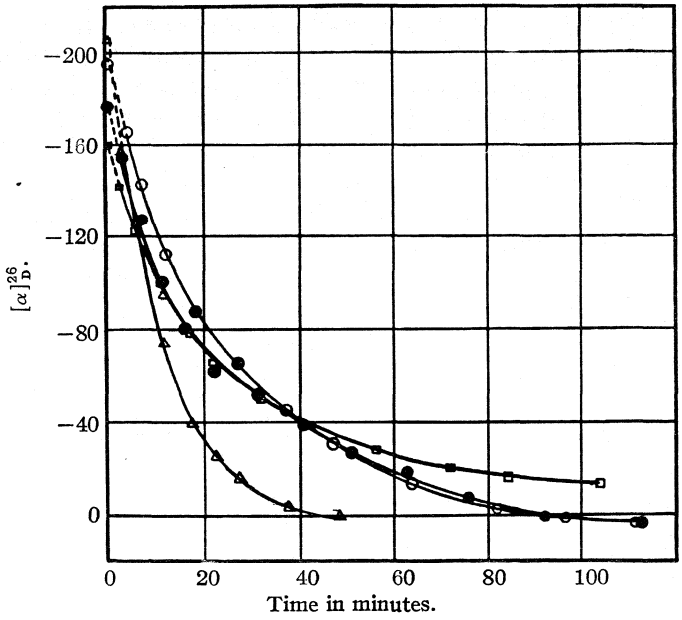


Fig. 2.—Mutarotation curves of the brucine salts of four 5′-substituted 2-nitro-6-carboxy-2′-methoxydiphenyls: □, CH_3; ○, Br; ●, Cl; △, NO_2.

Third, the frequency of semi-circular oscillation of the two rings may vary with the nature of the substituents and hence may change the rate of racemization. It is reasonable to expect that heavy substituents might slow down the oscillation, and thus diminish the rate of racemization. In the compounds under investigation, however, this factor apparently cannot play more than an unimportant role since both 5′-chloro and 5′-bromo derivatives racemize at the same rate.

Fourth, the distance between 1,1′ carbon atoms may vary with the nature of the substituents. The vertical distance between the 2,2′ carbon atoms in the phenyl rings was estimated as 2.90 Å. based upon the x-ray measurement of the distance between two carbon atoms. In the study of

the stereoisomerism of diphenyls, this value of 2.90 Å.[6] was assumed to be essentially constant for all substituted diphenyls. This assumption can only be approximately true, since much evidence[7] is available that the interatomic distance does vary more or less with the nature of the compound. For substituted diphenyls it is very probable that the distance between the 1,1′-carbon atoms varies by at least a few hundredths of an Å. due to the nature of the substituents. Such a change, though small, may affect considerably the rate of racemization if the groups in the 2,2′,6-positions are of such a size as barely to permit restricted rotation.

There appears to be some parallelism between the dipole moments and the rates of racemization.[8] No data are available on the dipole moments of resolvable diphenyls and it is questionable whether these values would be significant on account of the complicated structure of such molecules. The dipole moment, however, is more or less an additive property in a molecule. One half of each of the diphenyls under investigation remains the same, 2-nitro-6-carboxyphenyl, which may be assumed to have a constant moment. In regard to the other half of the molecules, it is of interest to consider moments of the corresponding substituted anisoles (Table II).

TABLE II

DIPOLE MOMENTS OF SUBSTITUTED ANISOLES AND HALF-LIFE PERIODS OF ANALOGOUS DIPHENYLS

Substituted anisole	Moment $\times 10^{18}$	5′-Substituted 2-nitro-6-carboxy-2′-methoxydiphenyls	Half-life period in minutes
No subs.	1.2	No subs.[10]	9.4
p-CH_3	1.2[9]	CH_3	11.5
p-OCH_3	1.8	OCH_3	10.8
p-Cl	2.24	Cl	31.0
p-Br	2.24	Br	32.0
p-NO_2	4.3	NO_2	35.4

[6] The value 2.90 Å. originally adopted as the approximate distance between the 2,2′ carbon atom in diphenyl should perhaps have been more accurately considered to be 2.96 Å. by the addition of the linkage of the diphenyls 1.54 Å. and 1.42 Å. (the aromatic C—C distance).

[7] The distance between two carbon atoms was found to be 1.54 Å. in diamond, 1.6 Å. in solid ethane, 1.55 Å. in the side-chains of hexamethylbenzene, 1.58 Å. in long-chain paraffins, 1.42 Å. in graphite, 1.45 Å. in naphthalene, 1.35 Å. in solid stilbene.

[8] Dr. C. P. Smyth has kindly calculated the energy differences involved in the different reaction rates as given by the half-life periods in Table II. He has found that the energies involved are of the same magnitude as the potential energies which must exist between the dipoles in the two halves of the molecule. This offers the possibility of explaining the variation in rate of racemization (at least semi-quantitatively) in terms of the mutual potential energies of the dipoles.

[9] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Company, New York, 1931, p. 196; see also Bergmann and Engel, *Z. physik. Chem.*, **15B**, 94 (1931); Smyth in a private communication reports a value of 2.24×10^{18} for *p*-bromoanisole.

The rate of racemization diminishes as the dipole moment becomes larger. If this is approximately true, prediction can be made concerning other substituted 2-nitro-6-carboxy-2′-methoxydiphenyls. *p*-Anisidine, for example, has a moment of 1.8, then the half-life period of the active 2-nitro-6-carboxy-2′-methoxy-5′-aminodiphenyl should be between ten and fifteen minutes at room temperature. Substituted anisoles always decrease in moment from para to meta to ortho. Therefore, the 3′ or 4′ substituted 2-nitro-6-carboxy-2′-methoxydiphenyls should racemize more readily than those in the 5′-position, if dipole moments are significant.

Apart from this semi-quantitative consideration, there appears to be some correlation between the polarity and the relative rate of racemization. The 5′-methyl- and 5′-methoxydiphenyls have the same stability and the two groups are practically non-polar. The chloro and bromo are two groups with the same polarity and the corresponding substituted diphenyls racemized at the same rate. The nitro is more strongly polar and the 5′-nitro derivative was the stablest of the five.

The rate of mutarotation of the brucine salts, as pointed out above, does not parallel the rates of racemization of the active acids. The presence of other points of asymmetry adds materially to the complexity of the molecule and no attempt to explain the facts will be made at this

TABLE III

ROTATIONS OF FOUR SUBSTITUTED 2-NITRO-6-CARBOXY-2′-METHOXYDIPHENYLS AND OF THEIR BRUCINE SALTS AND SODIUM SALTS

Compound group at 5′	Wt.[a] in g.	Temp., °C.	Rotations in degrees[b] Max. $[\alpha]_D$ by extrap.	Min.	Initial α_D	Initial $[\alpha]_D$	Min.	Final α_D	Final $[\alpha]_D$	Average K	Average deviation of K	Half-life period in min.
Brucine salts in chloroform												
—CH_3	0.0378	26.5	−160	3	−1.07	−142	104	−0.10	−13	0.019	±0.001	15.8
—Cl	.0320	26.5	−177	3	−1.00	−156	113	+0.02	+ 3.1	.018	± .002	16.7
—Br	.0402	26.5	−196	4	−1.33	−166	112	+0.03	+ 3.7	.018	± .001	16.7
—NO_2	.0381	26.5	−206	3	−1.20	−157	45	0.0	0.0	.039	± .004	7.7
Free acids in absolute alcohol												
—CH_3	0.1532	26	− 26	4	−0.62	− 20	68	0	0	0.026	±0.002	11.5
—Cl	.0440	27	−125	3	− .99	−115	193	0	0	.0097	± .0004	31.0
—Br	.0449	26	− 93	5	− .76	− 84	191	0	0	.0094	± .0006	32.0
—NO_2	.0270	26.5	−101	4	− .50	− 93	195	0	0	.0085	± .0006	35.4
Sodium salts in water[c]												
—CH_3	0.0525	26	− 33	3	−0.32	− 30.5	130	0	0	0.010	±0.0006	30.1
—Cl	.0342	26.5	−173	6	−1.07	−156	260	0	0	.0075	± .0005	40.2
—Br	.0491	26	−141	6	−1.25	−127	264	0	0	.0069	± .0005	43.6
—NO_2	.0300	27	−196	3	−1.09	−183	246	0	0	.0086	± .0004	35.0
Sodium salts in absolute alcohol[d]												
—CH_3	0.0502	26	− 46	3	−0.24	− 24	25	0	0	0.079	±0.002	3.8
—Cl	.0328	26.5	−316	4	−1.58	−241	59	0	0	.031	± .001	9.7
—Br	.0408	26	−262	2	−1.90	−233	87	0	0	.026	± .002	11.5
—NO_2	.0275	26.5	−291	2	−1.50	−273	102	0	0	.018	± .001	16.7

[a] Made up to 10 cc. [b] $l = 2$. [c] 0.1 *N* NaOH solution used. [d] Solution of 0.1 g. of sodium in 100 cc. of absolute alcohol was used.

time. The greater rates of mutarotation of the brucine salts of 5′-chloro, 5′-bromo and 5′-nitrodiphenyls than the rates of racemization of the corresponding active acids is also puzzling. This is not without precedent, however, as Mills and Elliott[10] made the same observation in regard to N-benzenesulfonyl-8-nitro-1-naphthylglycine and its salts.

From the data in this and in previous communications the axially asymmetrical diphenyls may be classified into four groups: (1) resolvable and non-racemizable; (2) resolvable but racemizable at higher temperatures; (3) resolvable but racemizable at room temperature (the alkaloidal salts of these compounds mutarotate in solution); (4) non-resolvable. To which group a diphenyl belongs is primarily determined by the number and size of the 2,2′,6,6′ substituents. In the second or the third classes, differences in rate of racemization are due not only to the number and size of the ortho groups but to the nature of other substituents also. For those compounds on the border line, the nature of other substituents may be a deciding factor.

The compounds in this investigation were prepared by condensing 1-nitro-2-bromo-3-carbomethoxybenzene by means of copper with the proper halogen compounds, 1-iodo-2-methoxy-5-methylbenzene, 1-iodo-2-methoxy-5-chlorobenzene, 1-iodo-2-methoxy-5-bromobenzene, 1-iodo-2-methoxy-5-nitrobenzene, saponification of the condensation products and separation of the desired acids from the by-products.

Experimental

2-Nitro-6-carboxy-2′-methoxy-5′-methyldiphenyl.—A mixture of 30 g. of 1-iodo-2-methoxy-5-methylbenzene[11] and 18 g. of 1-nitro-2-bromo-3-carbomethoxybenzene was placed in a 200-cc., three-necked flask fitted with a mechanical stirrer and a reflux condenser. The flask was heated in a metal bath and as soon as the bath temperature reached 240°, 45 g. of copper bronze was introduced in portions. The addition of copper took about one-half to three-quarters of an hour and during this period the bath temperature was held between 240 and 260°. About fifteen minutes after all the copper had been added, the flask was removed from the bath and cooled to room temperature. The product was then extracted from the copper and copper halides with 100 cc. of warm alcohol and filtered. The filtrate was transferred to a 2-liter flask, concentrated to about 50 cc. and refluxed with 500 cc. of 5% sodium hydroxide for four hours. After cooling, the aqueous solution was decanted from the unsaponified oil and acidified slowly with dilute hydrochloric acid. A brownish-black tar separated which solidified upon standing.

The crude product was dissolved in sodium bicarbonate solution, filtered and reprecipitated with dilute hydrochloric acid. The precipitate weighed 11 g. It was then dissolved in 50 cc. of warm glacial acetic acid and treated with norite. Less than 1 g. of 2,2′-dinitro-6,6′-dicarboxydiphenyl crystallized out upon standing. The mother liquor was diluted with an equal amount of water, warmed to bring all the precipitate into solution and treated further with norite. Crystals of 2-nitro-6-carboxy-2′-meth-

[10] Mills and Elliott, *J. Chem. Soc.*, 1291 (1928).

[11] Davis, Magers and Steiner, THIS JOURNAL, **52**, 1570 (1930).

oxy-5'-methyldiphenyl were obtained after standing at room temperature overnight. They were collected and recrystallized twice from 50% alcohol. The yield was 3.5 g.

The pure 2-nitro-6-carboxy-2'-methoxy-5'-methyldiphenyl forms greenish-yellow plates melting at 182–183°, soluble in the common organic solvents, but insoluble in water.

Anal. Calcd. for $C_{15}H_{13}NO_5$: neut. equiv., 287.1; N, 4.88. Found: neut. equiv., 288.7; N (micro Dumas), 4.92.

Resolution of 2-Nitro-6-carboxy-2'-methoxy-5'-methyldiphenyl. Brucine Salt.—A solution of 1.200 g. of 2-nitro-6-carboxy-2'-methoxy-5'-methyldiphenyl in 30 cc. of warm alcohol was mixed with a solution of 1.647 g. of anhydrous brucine in 40 cc. of warm alcohol. No salt was obtained after standing in the ice box for three days. After addition of 20 cc. of water and further cooling, small white crystals were obtained. The first fraction weighed 0.985 g. The mother liquor was concentrated *in vacuo* to 50 cc. A second fraction of 0.816 g. of the brucine salt resulted. Further concentration of the solution to about 10 cc. yielded a third fraction of 0.648 g. The different fractions of the brucine salt had the same appearance, the same melting point, 146–150°, and the same rotation (see Table III and Fig. 2).

Anal. Calcd. for $C_{38}H_{39}N_3O_9$: N, 6.16. Found: N (micro Dumas), 6.31.

A mixture of 0.2014 g. of the racemic acid and 0.2765 g. of anhydrous brucine was made up to 25 cc. with chloroform at 26°. After the solid had been wetted for eight minutes, it gave the initial rotation α_D −0.36°, l = 2, $[\alpha]_D^{26}$ −9.6° and in thirty minutes a final value α_D −0.28°, $[\alpha]_D^{26}$ −7.4°. The final specific rotation is a little lower than the final value obtained from the *l*-salt. This is due, possibly, to the higher concentration of this solution.

***l*-2-Nitro-6-carboxy-2'-methoxy-5'-methyldiphenyl.**—One and four-tenths grams of the brucine salt was ground to a fine powder in an agate mortar and transferred to a 125-cc. Erlenmeyer flask surrounded with ice. Then 50 cc. of 6 *N* ice-cold hydrochloric acid was added. The flask was immersed in an ice-water bath with occasional shaking. In three to four hours the hydrochloric acid was filtered off and replaced by fresh acid of the same strength. After standing overnight in an ice box the active acid was filtered by suction and washed thoroughly with ice-cold water until both the filtrate and the precipitate showed a negative test for brucine. The dried acid weighed 0.56 g. It melted at 180–182° (see Table III and Fig. 1 for rotation).

2-Nitro-6-carboxy-2'-methoxy-5'-chlorodiphenyl.—A mixture of 36 g. of 1-iodo-2-methoxy-5-chlorobenzene[12] and 18 g. of 1-nitro-2-bromo-3-carbomethoxybenzene was heated to 240° and then 40 g. of copper bronze was introduced in small portions. The reaction product was extracted with two portions of 250 cc. of warm alcohol. The alcoholic solution was transferred to a 2-liter flask and the alcohol was distilled. The residue was then saponified with 5% sodium hydroxide solution, the unsaponified oil separated from the water solution, and the solution acidified with dilute hydrochloric acid. A light yellow precipitate formed which weighed 13 g.

The crude product was dissolved in 60 cc. of warm glacial acetic acid and treated with some norite. Upon standing for several hours, 2 g. of 2,2'-dinitro-6,6'-dicarboxydiphenyl crystallized out. The mother liquor was diluted with 50 cc. of water and the solution was warmed on a hot-plate to bring all the precipitate into solution. Pale yellow leaflets were obtained after standing at room temperature for a few hours. The crude product, which amounted to 8.5 g., was recrystallized twice from 70% alcohol. The yield of pure 2-nitro-6-carboxy-2'-methoxy-5'-chlorodiphenyl was 6.5 g., m. p. 174–175°.

[12] Ingold, Smith and Vass, *J. Chem. Soc.*, 1248 (1927).

Anal. Calcd. for $C_{14}H_{10}ClNO_5$: neut. equiv., 307.5; Cl, 11.52; N, 4.55. Found: neut. equiv., 309.1; Cl, 11.64; N (micro Dumas), 4.67.

The unsaponified oil solidified upon standing. It was washed with water and then cold methanol and recrystallized three times from 95% alcohol. About 6 g. of pure product was obtained. It was 2,2'-dimethoxy-5,5'-dichlorodiphenyl, one of the symmetrical coupling products.

The pure 2,2'-dimethoxy-5,5'-dichlorodiphenyl forms colorless needles melting at 144.5–145.5°.

Anal. Calcd. for $C_{14}H_{12}Cl_2O_2$: C, 59.33; H, 4.27. Found: C, 59.24; H, 4.37.

Resolution of 2-Nitro-6-carboxy-2'-methoxy-5'-chlorodiphenyl. Brucine Salt.—A solution of 1.6847 g. of 2-nitro-6-carboxy-2'-methoxy-5'-chlorodiphenyl in 40 cc. of warm absolute alcohol was mixed with a solution of 2.16 g. of anhydrous brucine in 40 cc. of warm absolute alcohol and then filtered. Upon standing, crystals began to deposit and in five hours 2.81 g. of brucine salt was obtained. The mother liquor was placed in an ice box overnight and a second fraction of 0.858 g. of the salt crystallized. These two fractions together amounted to 98% of the theoretical yield. They were both the same salt.

The product forms light yellow leaflets melting at 148–153°. It contains one molecule of water of crystallization (see Table III and Fig. 2 for rotations).

Anal. Calcd. for $C_{37}H_{36}ClN_3O_9 \cdot H_2O$: H_2O, 2.50; N, 5.84. Found: H_2O, 2.42; N (micro Dumas), 5.89.

***l*-2-Nitro-6-carboxy-2'-methoxy-5'-chlorodiphenyl.**—The salt was finely pulverized and decomposed in a similar manner as the brucine salt of 2-nitro-6-carboxy-2'-methoxy-5'-methyldiphenyl. The product was dried over phosphorus pentoxide and weighed 0.62 g., m. p. 173–175° (see Table II and Fig. 1 for rotations).

2-Nitro-6-carboxy-2'-methoxy-5'-bromodiphenyl.—A mixture of 26 g. of 1-iodo-2-methoxy-5-bromobenzene[13] and 16 g. of 1-nitro-2-bromo-3-carbomethoxydiphenyl was heated at 200–215°, then 40 g. of copper bronze was introduced by portions. The reaction product was extracted with two 100-cc. portions of boiling alcohol. Upon cooling of the alcoholic solution, 5.8 g. of white crystals of 2-nitro-6-carbomethoxy-2'-methoxy-5'-bromodiphenyl melting at 148–149° separated. The ester was saponified by refluxing with 200 cc. of 5% aqueous sodium hydroxide solution for four hours. The solution was filtered and acidified with dilute hydrochloric acid. The crude product was recrystallized twice from 50% alcohol.

The pure 2-nitro-6-carboxy-2'-methoxy-5'-bromodiphenyl forms pale yellow plates melting at 186–187°.

Anal. Calcd. for $C_{14}H_{10}BrNO_5$: neut. equiv., 352; N, 3.98. Found: neut. equiv., 354.4; N (micro Dumas), 4.02.

Resolution of 2-Nitro-6-carboxy-2'-methoxy-5'-bromodiphenyl. Brucine Salt.—A solution of 1.3305 g. of the diphenyl in 30 cc. of alcohol was treated with a solution of 1.4910 g. of anhydrous brucine in 30 cc. of warm alcohol. The solution was diluted with 40 cc. of water. After standing for several hours 1.14 g. of the brucine salt deposited. By concentrating the mother liquor to 60 cc., 0.97 g. more of the salt was obtained. Further concentration gave a third fraction of 0.62 g. They were the same in melting point and rotation.

The brucine salt of 2-nitro-6-carboxy-2'-methoxy-5'-bromodiphenyl forms pale yellow needles, m. p., 162–165° (see Table III and Fig. 2 for rotations).

Anal. Calcd. for $C_{37}H_{36}BrN_3O_9$: N, 5.63. Found: N (micro Dumas), 5.51.

[13] Hirtz, *Ber.*, **29**, 1410 (1896).

l-**2-Nitro-6-carboxy-2′-methoxy-5′-bromodiphenyl.**—One and four-tenths grams of the finely powdered brucine salt was decomposed by the ice-cold hydrochloric acid in the manner previously described. The product weighed 6.2 g., m. p. 185–187° (see Table III for rotations and Fig. 1).

2,5′-Dinitro-6-carboxy-2′-methoxydiphenyl.—The procedure was similar to that for the other three diphenyls. The bath temperature was carefully controlled between 230 and 240°. (In the first run when the temperature was raised higher than 250°, all of the 1-iodo-2-methoxy-5-nitrobenzene decomposed.) Since the coupling product was not very soluble in alcohol, it was extracted with acetone and the acetone was distilled off before saponification. The separation of 2,2′-dinitro-5,5′-dicarboxydiphenyl was carried out as usual through the fractional crystallization from acetic acid. From 30 g. of 1-iodo-2-methoxy-5-nitrobenzene,[14] 18 g. of 1-nitro-2-bromo-3-carbomethoxybenzene and 40 g. of copper bronze, 3.5 g. of the crude 2,5′-dinitro-6-carboxy-2′-methoxydiphenyl was obtained. It was purified by recrystallizing twice from 70% alcohol. The yield was 2.5 g.

The pure 2,2′-dinitro-6-carboxy-2′-methoxydiphenyl forms pale yellow prisms melting at 202–203°.

Anal. Calcd. for $C_{14}H_{20}N_3O_7$: neut. equiv., 318; N, 8.80. Found: neut. equiv., 316.8; N (micro Dumas), 8.69.

Resolution of 2,5′-Dinitro-6-carboxy-2′-methoxydiphenyl. Brucine Salt.—A solution of 1.0528 g. of 2,5′-dinitro-6-carboxy-2′-methoxydiphenyl in 20 cc. of warm alcohol was treated with a solution of 1.3052 g. of anhydrous brucine in 30 cc. of warm alcohol. No salt was obtained after standing for several days. Then 40 cc. of water was added and the solution was allowed to stand at room temperature overnight. One and twenty-four hundredths grams of brucine salt separated as golden yellow crystals. When the mother liquor was concentrated to 30 cc., a second fraction of 0.61 g. of the brucine salt was obtained. A resinous residue was left after the mother liquor evaporated to dryness. The residue was dissolved in 50 cc. of boiling water and more crystalline brucine salt was obtained.

Different fractions of the brucine salt had the same appearance, the same melting point, 179–183° and the same rotation (see Table III for rotations and Fig. 2). Its chloroform solution is colorless.

Anal. Calcd. for $C_{37}H_{36}N_4O_{11}\cdot 3H_2O$: H_2O, 7.05; N, 7.31. Found: H_2O, 6.89; N (micro Dumas), 7.25.

l-**2,5′-Dinitro-6-carboxy-2′-methoxydiphenyl.**—One and five-tenths grams of the finely powdered brucine *l*-salt was decomposed in the usual manner with ice-cold hydrochloric acid. The dried *l*-acid weighed 0.61 g. It melted at 201–202° (see Table III for rotations and Fig. 1).

Summary

1. Five 5′-substituted 2-nitro-6-carboxy-2′-methoxydiphenyls have been prepared containing the OCH_3, CH_3, Cl, Br and NO_2 groups. These have been resolved and the rates of racemization of the active acids compared with the results on 2-nitro-6-carboxy-2′-methoxydiphenyl.

2. The rates of racemization have been shown to be affected. A discussion is given of the possible mechanism of the changes produced by the 5′-substitution.

URBANA, ILLINOIS

[14] Reverdin, *Ber.*, **29**, 997 (1896).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HOLY CROSS COLLEGE]

PHENACYL AND PARA-BROMOPHENACYL ESTERS OF DIBASIC ORGANIC ACIDS[1]

BY T. LEONARD KELLY AND PIERRE A. KLEFF

RECEIVED JULY 6, 1932 PUBLISHED NOVEMBER 5, 1932

The use of phenacyl and *p*-bromophenacyl esters was introduced by Reid and co-workers[2] as a means of identifying acids. Since derivatives of acids are desirable as an aid in their identification the present investigation was undertaken.

Experimental

The procedure for the preparation of the esters was essentially the same as that of Reid. All melting points are uncorrected, having been taken in a Fisher melting point apparatus, with the aid of a set of Anschütz thermometers which gave correct melting points with various pure reagents.

Results

The results are expressed in tabular form, the first column giving the melting point of the ester and the second the percentage yield obtained.

TABLE I

PHENACYL ESTERS

Ester	M. p., °C.	Yield, %	Ester	M. p., °C.	Yield, %
Adipate	87.6	82	Suberate	102.4	93
Pimelate	72.4	90	Azelate	69.7	84
Sebacate	80.4	100	Phthalate	154.4	78
Isophthalate	191	57	Terephthalate	192.2	38

TABLE II

p-BROMOPHENACYL ESTERS

Ester	M. p., °C.	Yield, %	Ester	M. p., °C.	Yield, %
Glutarate	136.8	80	Phthalate	152.8	62
Adipate	154.5	85	Isophthalate	179.1	53
Pimelate	136.6	78	Terephthalate	225	71
Suberate	144.2	84	Itaconate	117.4	70
Azelate	130.6	86	*l*-Malate	179	65

It was found impossible to prepare a crystalline ester of malonic acid with either of the reagents, both giving an oil. In general the solubility of the phenacyl esters is much higher than that of the *p*-bromophenacyl esters. The *p*-bromophenacyl esters of the aliphatic acids have higher melting points than the phenacyl esters of these same acids. Acetone was used as solvent for the recrystallization of all the *p*-bromophenacyl esters. Two

[1] This paper is constructed from a thesis submitted by Pierre A. Kleff to the Faculty of Holy Cross College in partial fulfilment of the requirements for the degree of Master of Science.

[2] Reid and co-workers, THIS JOURNAL, **41**, 75 (1919); **42**, 1043 (1920).

of the *p*-bromophenacyl esters, *viz.*, those of adipic and suberic acids, were analyzed for bromine by means of the Parr peroxide bomb and the results checked with the calculated percentages.

Summary

A number of dibasic organic acids have been converted to the phenacyl and *p*-bromophenacyl esters and their melting points determined.

WORCESTER, MASSACHUSETTS

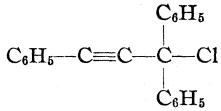
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

REARRANGEMENTS OF POLYINES. II. TETRAPHENYLDIPHENYLETHINYLETHANE

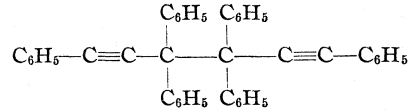
BY H. E. MUNRO AND C. S. MARVEL

RECEIVED JULY 7, 1932 PUBLISHED NOVEMBER 5, 1932

Several years ago a hydrocarbon, $C_{42}H_{30}$, was prepared by the action of iron on diphenylphenylethinylchloromethane (I) and assigned the formula tetraphenyldiphenylethinylethane[1] (II).

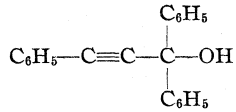


I

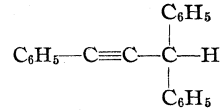


II

The preparation of this same hydrocarbon has also been reported by Wieland and Kloss,[2] who used not only the original method of treating diphenylphenylethinylchloromethane with a metal, but two other methods, namely, the reduction of diphenylphenylethinylcarbinol (III) with titanium trichloride and the oxidation of phenylethinyldiphenylmethane (IV) with potassium permanganate solution.



III



IV

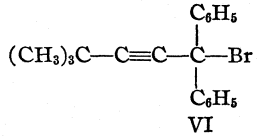
Some recent work[3] in this Laboratory on the closely related hydrocarbon tetraphenyl-di-*tert.*-butylethinylethane (V) has demonstrated that it has properties which are altogether unlike those reported for Moureu's hydrocarbon. The *tert.*-butyl derivative is easily cleaved by 40% sodium amalgam, absorbs oxygen rapidly and undergoes rearrangement in solution at room temperature to give an isomeric hydrocarbon, $C_{38}H_{38}$. This re-

[1] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

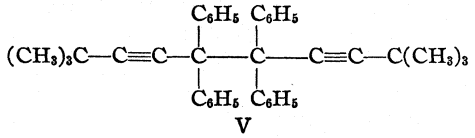
[2] Wieland and Kloss, *Ann.*, **470**, 217 (1929).

[3] Stampfli and Marvel, THIS JOURNAL, **53**, 4057 (1931).

arranged hydrocarbon, whose structure has been under investigation[4] in this Laboratory for some time, is more nearly analogous to the hydrocarbon $C_{42}H_{30}$ which Moureu obtained. It has been found[4a] also that the action of metals on diphenyl-*tert.*-butylethinylbromomethane (VI) leads not to the ethane (V) but to the rearrangement product, $C_{38}H_{38}$. More recently it has been shown[5] that titanium trichloride reduces di-



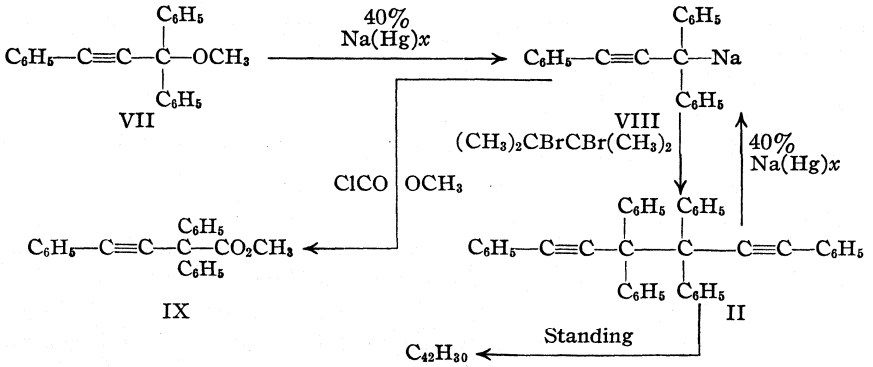
VI



V

phenyl-*tert.*-butylethinylcarbinol to this same rearranged hydrocarbon instead of the ethane. These facts coupled with the wide variation between the properties of Moureu's hydrocarbon and the tetraaryldialkylethinylethane which has been prepared in this Laboratory have led to a further investigation of tetraphenyldiphenylethinylethane.

The preparation of this compound has now been accomplished by using the general method of Ziegler and Schnell.[6] Diphenylphenylethinylcarbinol (III) has been converted to the methyl ether (VII) by the procedure described by Moureu, Dufraisse and Blatt.[7] By treating this ether with 40% sodium amalgam the alkali metal alkyl (VIII) is obtained. The ethane (II) is obtained from this sodium derivative by the action of tetramethylethylene bromide. The ethane is very unstable and has not been isolated in a pure condition. In solution, it is readily cleaved by 40% sodium amalgam to give the metal alkyl (VIII), which has been identified by conversion to the methyl ester of diphenylphenylethinylacetic acid (IX); it absorbs oxygen very rapidly, but does not form a



[4] (a) Salzberg and Marvel, THIS JOURNAL, **50**, 2840 (1928); (b) Althausen and Marvel, *ibid.*, **54**, 1174 (1932).

[5] Sweet and Marvel, *ibid.*, **54**, 1184 (1932).

[6] Ziegler and Schnell, *Ann.*, **437**, 244 (1924).

[7] Moureu, Dufraisse and Blatt, *Bull. soc. chim.*, [4] **35**, 1412 (1924).

stable peroxide; and it rearranges to give Moureu's hydrocarbon, $C_{42}H_{30}$. In spite of the fact that the ethane has not been isolated in a crystalline condition, these reactions show that it is strictly analogous to the corresponding *tert.*-butyl derivative (V) in its behavior.

The reactions of Moureu's hydrocarbon have been investigated to some extent. That it does not absorb oxygen has been demonstrated by the earlier work.[1,2] It is not cleaved by 40% sodium amalgam but it does add sodium, apparently producing a disodium derivative, $C_{42}H_{30}Na_2$, which on treatment with water gives a solid hydrocarbon $C_{42}H_{32}$ and with methyl chlorocarbonate gives an impure solid ester.

The evidence is thus rather conclusive that the hydrocarbon reported by Moureu does not have the structure which was assumed for it but is analogous to the hydrocarbon, $C_{38}H_{38}$, which is formed by the rearrangement of tetraphenyl-di-*tert.*-butylethinylethane. A diindene formula has been suggested for the isomeric $C_{38}H_{38}$ hydrocarbon but the evidence now available makes this formula seem very unlikely.[8]

Experimental

Diphenylphenylethinylmethyl-sodium.—This sodium alkyl was first obtained from diphenylphenylethinylchloromethane which was prepared by the procedure described by Moureu, Dufraisse and Mackall.[9] However, better yields of the sodium derivative based on the carbinol were obtained by treating the methyl ether[7] with 40% sodium amalgam. The procedure using either starting material was that described previously for diphenyl-*tert.*-butylethinylmethyl-sodium.[3] The sodium alkyl was not isolated but was used in the succeeding experiments.

Methyl Diphenylphenylethinylacetate.—In order to identify the sodium alkyl an attempt was made to convert it to diphenylphenylethinylacetic acid by treatment with carbon dioxide. The acid thus obtained was apparently unstable and did not crystallize well. However, the methyl ester was obtained by treating the sodium alkyl with methyl chlorocarbonate.

The calculated amount of methyl chlorocarbonate (6 g.) was added to an ether solution of the sodium alkyl prepared from 9.0 g. of the methyl ether. Considerable heat was evolved by the reaction mixture. The red color of the solution disappeared and sodium chloride precipitated. The solution was filtered to remove the salt and the ether was evaporated. A thick reddish oil remained. After two distillations under reduced pressure a product boiling at 98–105° (2–3 mm.) and weighing 3.5 g. (35% of the theoretical amount) was obtained.

This product decolorized bromine in carbon tetrachloride solution, reduced an aqueous solution of potassium permanganate and gave a distinct red color to concentrated sulfuric acid; d_4^{20} 1.0621; n_D^{20} 1.5790; M_D, calcd. for methyl diphenylphenylethinylacetate, 102.26; found, 102.06.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.85; H, 5.66.

It may be of interest to report here that treatment of a solution of this sodium alkyl and also the sodium addition product of Moureu's hydrocarbon with phenyl isocyanate in the hope of obtaining crystalline anilides of the corresponding acids gave instead

[8] Halley and Marvel, THIS JOURNAL, **54**, 4450 (1932).

[9] Moureu, Dufraisse and Mackall, *Bull. soc. chim.*, [4] **33**, 934 (1923).

triphenylisocyanurate, m. p. 281–282°, which has previously been obtained by heating phenyl isocyanate with sodium acetate.[10]

Tetraphenyldiphenylethinylethane.—To an ether solution of the sodium alkyl prepared from 10 g. of the methyl ether was added enough of a 10% ether solution of tetramethylethylene bromide to discharge the deep red color of the mixture. The ether was removed under reduced pressure while the temperature was held at about 0°. The residue was treated with about 200 cc. of water to wash out the sodium bromide, the remaining oily material was dissolved in petroleum ether (b. p. 25–40°) and the solution was dried over anhydrous magnesium sulfate. These operations were carried out at room temperature and as rapidly as possible (about ten minutes). The petroleum ether solution was cooled in an acetone–solid carbon dioxide cooling bath and a heavy liquid separated. The petroleum ether was decanted. The oil was then redissolved in fresh petroleum ether at room temperature and again cooled to cause the hydrocarbon to separate. After two such treatments the hydrocarbon separated in white flocculent crystals which melted and turned red when an attempt was made to isolate them by filtration.

When the petroleum ether solution of this substance was allowed to stand for an hour at room temperature and then chilled, a hydrocarbon melting at 160–165° was obtained. This was identical with Moureu's hydrocarbon as demonstrated by mixed melting point determinations.

In order to establish definitely the presence of the unstable ethane cleavage experiments with forty per cent. amalgam were carried out on the material which separated when the solutions were cooled in carbon dioxide–acetone baths. About 1 g. of this oily material was taken up in 30 cc. of dry ether and treated with 5 cc. of 40% sodium amalgam. The deep red color of the diphenylphenylethinylmethyl-sodium was apparent within three minutes. After three hours the mixture was treated with methyl chlorocarbonate and the reaction mixture was worked up for methyl diphenylphenylethinylacetate. Only a few drops were obtained, but this had a refractive index of 1.5820 whereas the ester prepared from the known alkyl gave the value 1.5790.

To further establish this point, the metal alkyl from 8 g. of the methyl ether was coupled with tetramethylethylene bromide and then the decolorized solution treated with 15 cc. of 40% sodium amalgam. The deep red color reappeared in a few minutes and after treatment with methyl chlorocarbonate 2.5 g. (30% of the theoretical amount) of product was obtained; d_4^{20} 1.058; n_D^{20} 1.5790 boiling at 122–23° (8 mm.).

From the residues left on the distillation of this ester was isolated a product melting at 93–96° which was identical with the one obtained from the sodium addition product of Moureu's hydrocarbon on treatment with methyl chlorocarbonate.

In the early experiments it was found that Moureu's hydrocarbon could be obtained readily by treating a solution of diphenylphenylethinylmethyl-sodium with tetramethylethylene bromide, and then working up the colorless solution without keeping the temperature low. The product thus obtained on recrystallization from alcohol melted at 165–167° and as much as 2 g. at a run was isolated. Samples of Moureu's hydrocarbon were prepared by each of the methods which have been described[1,2] and were found to melt at 169°. A mixture of this material prepared from the sodium alkyl melted at 165–167°.

On one occasion the impure ethane prepared from 10 g. of the methyl ether was dissolved in 50 cc. of 95% alcohol and heated on the steam cone for fifteen minutes. An orange-red solid separated and was filtered. After recrystallization from alcohol this melted at 233–234°. The yield was 0.56 g. This compound is another isomer in the series.

[10] Hofmann, *Ber.*, **18**, 765 (1885).

Anal. Calcd. for $C_{42}H_{30}$; C, 94.34; H, 5.66. Found: C, 94.0, 94.1; H, 5.61, 5.55.

The mother liquors from the above preparation yielded 0.25 g. of Moureu's hydrocarbon which melted at 168–169°.

Treatment of a solution of the ethane with 1% sodium amalgam did not give the desired alkyl but from such solutions Moureu's hydrocarbon was obtained. Apparently rearrangement proceeded more rapidly than combination with the dilute amalgam.

A solution of the crude ethane (from 2 g. of the methyl ether) in 100 cc. of dry ether was connected with a gas buret filled with dry oxygen. The gas was absorbed quite rapidly at first and then the rate of absorption dropped off gradually. By flushing out the flask above the ether solution with fresh oxygen, further rapid absorption of oxygen was resumed. No accurate estimates of oxygen absorption were attempted because the hydrocarbon was so impure. However, this experiment showed that 135 cc. of oxygen was taken up and this is a sufficient quantity to prove that the new ethane will oxidize with gaseous oxygen. From the oxidized reaction mixture, no peroxide could be isolated but some of the rearrangement product, Moureu's hydrocarbon, was obtained. Moureu's hydrocarbon does not oxidize in gaseous oxygen under the conditions of this experiment. A solution of the new ethane decolorizes a carbon tetrachloride solution of bromine very rapidly. An ether solution of Moureu's hydrocarbon under the same conditions did not decolorize a carbon tetrachloride solution of bromine.

Some Reactions of the Sodium Derivative of Moureu's Hydrocarbon, $C_{42}H_{30}$.— In order to be certain that the sodium alkyl obtained from methyl diphenylphenylethinylmethyl ether and from the cleavage of tetraphenyldiphenylethinylethane was really different from the sodium addition product of Moureu's hydrocarbon, some comparative experiments were performed.

An ether solution of the true ethane prepared from 0.15 g. of the methyl ether was treated with 5 cc. of 40% sodium amalgam and a bright reddish-purple color developed within twenty minutes. Under exactly similar conditions 0.075 g. of Moureu's hydrocarbon in 100 cc. of ether gave no color with 40% sodium amalgam in twenty minutes but within forty minutes a reddish-brown color developed. The color of the solution was distinctly different.

The sodium addition product was prepared by shaking an ether solution of 4 g. of Moureu's hydrocarbon with 15 cc. of 40% sodium amalgam. To the reddish-brown solution was carefully added a few cc. of boiled distilled water. When the color of the metal derivative had disappeared, 200 cc. more of water was added, the ether solution was separated and evaporated. The residue was a brown sticky mass which was very insoluble. By purification with petroleum ether a product melting at 239–241° was obtained. It was apparently a dihydro derivative of Moureu's hydrocarbon although a satisfactory molecular weight was not obtained.

Anal. Calcd. for $C_{42}H_{32}$: C, 94.03; H, 5.97. Found: C, 93.33, 93.44; H, 5.98, 5.93. *Mol. wt.* (Rast). Calcd. for $C_{42}H_{32}$: 536. Found: 394.

The sodium addition product prepared from 6 g. of Moureu's hydrocarbon and 15 cc. of 40% sodium amalgam in dry ether was treated with enough methyl chlorocarbonate to discharge the color of the solution. On working up the reaction mixture as described under methyl diphenylphenylethinylacetate, a thick gummy product which did not distil at 275° (2 mm.) was obtained. When this residue was treated with alcohol, a reddish-brown precipitate was formed. Attempts to purify this material by recrystallization from various organic solvents were unsuccessful. A light tan powder was obtained by dissolving the dark material in hot glacial acetic acid, filtering off the insoluble tarry material and adding water. After drying in a desiccator under reduced

pressure, this material melted at 90–93°. The melting point was not changed by further treatment. The material was evidently not a single product but analysis indicated a formula $C_{42}H_{30}(COOCH_3)_2$.

Anal. Calcd. for $C_{48}H_{36}O_4$: C, 84.7; H, 5.52. Found: C, 85.4; H, 5.68.

This product requires further study but it is of interest because it shows that the true ethane and its rearrangement product give distinctly different compounds when treated with sodium amalgam.

Summary

Tetraphenyldiphenylethinylethane has been prepared in solution. This hydrocarbon is oxidized by oxygen, is cleaved by 40% sodium amalgam, and readily rearranges to an isomeric hydrocarbon, $C_{42}H_{30}$, which is identical with the hydrocarbon which has previously been prepared by the action of metals on diphenylphenylethinylchloromethane.

URBANA, ILLINOIS

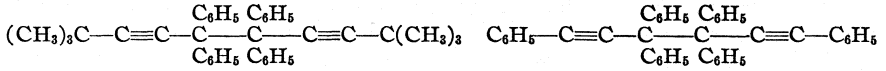
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

REARRANGEMENTS OF POLYINES. III. THE SYNTHESIS OF BIS-1,1'-(1,3-DIPHENYLINDYL)

BY L. F. HALLEY AND C. S. MARVEL

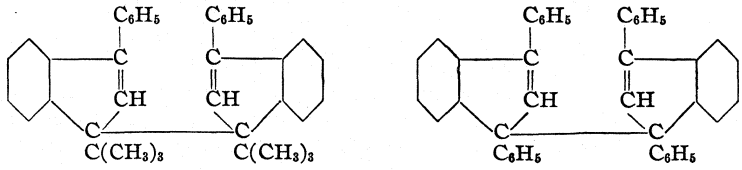
RECEIVED JULY 7, 1932 PUBLISHED NOVEMBER 5, 1932

Recent investigations[1] have shown that certain tetraaryl-diethinylethanes readily undergo rearrangement and yield isomeric hydrocarbons of unknown structures. The two compounds which have been studied thus far are *sym.*-tetraphenyldi-*tert.*-butylethinylethane (I) and *sym.*-tetraphenyldiphenylethinylethane (II). While these ethanes exhibit a reactivity which resembles that of the hexa-arylethanes, the isomeric



I II

hydrocarbons obtained by their rearrangement are much more stable compounds. A study of the reactions of the hydrocarbon, $C_{38}H_{38}$, obtained by the rearrangement of tetraphenyldi-*tert.*-butylethinylethane (I) led to the suggestion that it might have a diindene structure (III).



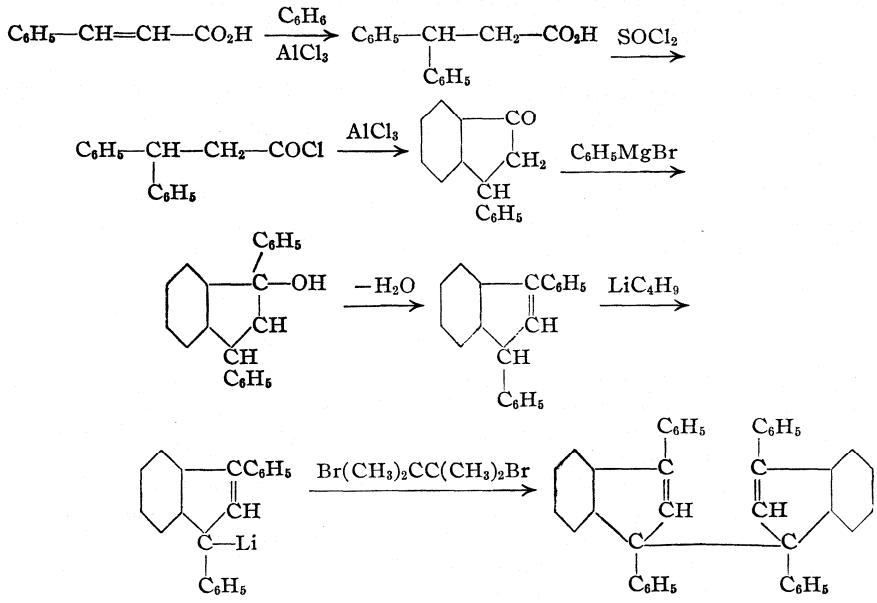
III IV

[1] (a) Stampfli and Marvel, THIS JOURNAL, **53**, 4057 (1931); (b) Althausen and Marvel, *ibid.*, **54**, 1174 (1932); (c) Munro and Marvel, *ibid.*, **54**, 4445 (1932).

If tetraphenyldiphenylethinylethane (II) rearranges in an analogous manner it might be expected to produce bis-1,1′-(1,3-diphenylindyl) (IV). That the two hydrocarbons, $C_{38}H_{38}$ and $C_{42}H_{30}$, obtained by the respective rearrangements of the ethanes (I and II), do have similar structures is indicated by the work which has been reported previously.[1b,1c] A further indication of the resemblance in structure has been found in the oxidation of $C_{42}H_{30}$ to *o*-benzoylbenzoic acid, a product which had previously been obtained by the oxidation of the hydrocarbon, $C_{38}H_{38}$.

The preparation of bis-1,1′-(1,3-diphenylindyl) seemed to offer the most satisfactory method of checking up on the suggestion that diindenes are produced when the polyines undergo spontaneous rearrangement.

The synthesis has been accomplished by the following reactions



β,β-Diphenylpropionic acid was prepared by the method of Vorländer and Czensny[2] from cinnamic acid, benzene and anhydrous aluminum chloride. β,β-Diphenylpropionyl chloride has been mentioned in the literature[3] but details for its preparation have not been given. It was obtained readily by the action of thionyl chloride on the acid. The ring closure to give 3-phenylindanone was accomplished by the method of Kohler.[3] 1,3-Diphenylindene was prepared according to the procedure of Ziegler, Grabbe and Ulrich[4] and converted to the lithium derivative by the method

[2] Vorländer and Czensny, *Ber.*, **56**, 1131 footnote (1923).

[3] Kohler, *Am. Chem. J.* **31**, 649 (1904).

[4] Ziegler, Grabbe and Ulrich, *Ber.*, **57**, 1983 (1924).

recently used by Blum–Bergmann.[5] This lithium derivative was coupled to give the diindene.[6]

The bis-1,1′-(1,3-diphenylindyl) thus obtained does not agree in its properties with the hydrocarbon, $C_{42}H_{30}$, obtained by the rearrangement of tetraphenyldiphenylethinylethane.[1c] The diindene has a higher melting point (190–191°) and the melting point is greatly depressed (158–163°) when this compound is mixed with the hydrocarbon, $C_{42}H_{30}$ (m. p. 172–173°).

Two stereochemical forms (meso and racemic) of the diindene are theoretically possible. In the work[1b] on the hydrocarbon, $C_{38}H_{38}$, obtained by spontaneous rearrangement of tetraphenyl-di-*tert.*-butylethinylethane, it was found possible to produce a further isomerization to a higher melting compound by the prolonged action of heat on a solution of the hydrocarbon in glacial acetic acid in the presence of dry hydrogen chloride. The hydrocarbon, $C_{42}H_{30}$, was also found to yield a higher melting product when it was heated with hydrogen chloride in acetic acid but this compound melted at about 261° and was not identical with the diindene which had been synthesized.

Thus it seems doubtful that molecules of the diindene type are produced by the spontaneous rearrangement of tetra-aryldiethinylethanes and further work is needed before definite structures can be assigned to these rearrangement products.

Experimental

Bis-1,1′-(1,3-diphenylindyl).—Lithium *n*-butyl was prepared according to the procedure of Ziegler and Colonius[7] from 9.3 g. (0.1 mole) of *n*-butyl chloride and about 3.5 g. (0.5 mole) of lithium shavings in 100 cc. of dry benzene. The benzene solution was decanted into a second flask while an atmosphere of dry nitrogen was maintained over the solution. Then a solution of 7 g. (0.026 mole) of 1,3-diphenylindene was added slowly. A yellow precipitate formed almost at once but the flask was stoppered tightly and shaken for about thirty-six hours. At the end of this period the solution was filtered through an alundum filter plate and to the precipitate was added a solution of 5 g. (0.02 mole) of tetramethylethylene bromide in 100 cc. of dry benzene. An atmosphere of dry nitrogen was maintained over the solutions during all of these operations. A reaction between the lithium derivative of the indene and the bromide was indicated by the liberation of some heat and a change in the nature of the insoluble material. After about one-half hour the solution was again filtered through an alundum plate, washed with a little water, dried over sodium sulfate and the solvent was evaporated by drawing a current of air through the solution under reduced pressure. The crystalline residue was purified by dissolving in alcohol and ether and concentrating this solution under reduced pressure until crystals began to appear. The solution was then cooled in an ice-bath and filtered. The crystals were washed with three small portions of low

[5] Blum–Bergmann, *Ann.*, **484**, 36 (1930); see also Schlenk and Bergmann., *ibid.*, **463**, 192 (1928).

[6] Ziegler and Schnell, *ibid.*, **437**, 244 (1924).

[7] Ziegler and Colonius, *ibid.*, **479**, 135 (1930).

boiling petroleum ether to remove any excess tetramethylethylene bromide. The product thus obtained weighed 3.5 g. (50% of the theoretical amount) and melted at 185–186°. Three further crystallizations from alcohol raised the melting point to 190–191° where it remained unchanged by further purification.

Anal. Subs., 0.2216, 0.1883: CO_2, 0.7590, 0.6517; H_2O, 0.1140, 0.0930. Calcd. for $C_{42}H_{30}$: C, 94.38; H, 5.62. Found: C, 93.41, 94.39; H, 5.76, 5.53. *Mol. wt.* (Rast). Subs., 0.0051; camphor, 0.52; Δ^t, 8°. Calcd. for $C_{42}H_{30}$: mol. wt., 534. Found: mol. wt., 486.

The Hydrocarbon, $C_{42}H_{30}$.—The hydrocarbon was prepared by the action of silver on diphenylphenylethinylchloromethane[8] and also by the two methods more recently described,[9] namely, the reduction of diphenylphenylethinylcarbinol with titanium trichloride and the oxidation of the 1,1,3-triphenylpropine with potassium permanganate solution. The product from the first reaction was not readily purified. The best product melted at 172–173°.

Oxidation of the Hydrocarbon, $C_{42}H_{30}$.[10]—To a solution of 0.55 g. of the hydrocarbon in 15 cc. of glacial acetic acid was added 1.1 g. of chromium trioxide. The solution was boiled under a reflux condenser for about eight hours, allowed to stand for forty hours and then poured into 75 cc. of water. The aqueous solution was extracted twice with ether. The ether extracts were combined and extracted with 5% sodium hydroxide solution. The first extract removed most of the acetic acid, and when it was evaporated and acidified no insoluble acids precipitated. A second extraction with 5% sodium hydroxide was then made and on concentration and acidification, 0.1785 g. of air-dried water-insoluble acid was obtained. This material melted at 70–112°. On drying in an Abderhalden dryer at 76° at 40 mm., some crystals sublimed and collected in the cooled portion of the dryer. This sublimate weighed 0.085 g. and proved to be benzoic acid, m. p. 120–121°. The residual material in the dryer was recrystallized from carbon tetrachloride and again dried in an Abderhalden dryer at 100° (3 mm.) for about twenty hours. It then melted at 127.5–128.5° and did not depress the melting point of an authentic specimen of anhydrous *o*-benzoylbenzoic acid.

Rearrangement of the Hydrocarbon, $C_{42}H_{30}$.—A solution of 5 g. of the hydrocarbon, $C_{42}H_{30}$, in 100 cc. of glacial acetic acid was heated to boiling and a current of dry hydrogen chloride was passed through the boiling solution for about four hours. A precipitate separated and after filtering and recrystallizing from glacial acetic acid this product melted at 261–262°. The yield was about 1 g. This material was not thoroughly investigated but a molecular weight determination (Rast method) showed the material was not polymerized (mol. wt. 503). A smaller fraction of material melting at 290° was obtained.

Summary

1. Oxidation of the hydrocarbon, $C_{42}H_{30}$, obtained by the action of metals on diphenylphenylethinylchloromethane or by the rearrangement of tetraphenyldiphenylethinylethane has yielded *o*-benzoylbenzoic acid.

2. Bis-1,1′-(1,3-diphenylindyl) has been synthesized and it is not identical with the hydrocarbon, $C_{42}H_{30}$, obtained by the methods mentioned above.

3. These results make it seem unlikely that the compound obtained

[8] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

[9] Wieland and Kloss, *Ann.*, **470**, 217 (1928).

[10] We are indebted to Mr. J. Harmon for this portion of the experimental work.

by the spontaneous rearrangement of tetraphenyl-di-*tert.*-butylethinylethane has the diindene structure which was recently suggested for it.

URBANA, ILLINOIS

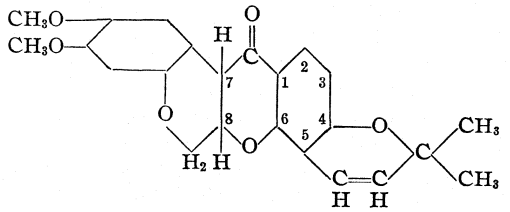
[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TEPHROSIN. II. ISOTEPHROSIN

BY E. P. CLARK AND H. V. CLABORN

RECEIVED JULY 9, 1932 PUBLISHED NOVEMBER 5, 1932

In a recent communication[1] formula I was proposed as representing the structure of deguelin, and it was also indicated that tephrosin is an hydroxydeguelin in which the hydroxyl group replaces one of the hydrogen atoms attached to either carbon atom 7 or 8.



I. Deguelin

In the course of the preparation of tephrosin from a recent shipment of Peruvian cubé root a white crystalline material separated which after purification melted at 252°. The substance was an isomer of tephrosin, as shown by its molecular composition, its methoxyl content, and the ease with which it was converted to dehydrodeguelin by the loss of a molecule of water. The material has been designated as isotephrosin.

Isotephrosin is a colorless crystalline material which like tephrosin is optically inactive. It is considerably less soluble in ordinary solvents than is tephrosin, and it is oxidized by potassium permanganate to a dicarboxylic acid isomeric with tephrosindicarboxylic acid.

While the ready conversion of isotephrosin into dehydrodeguelin, through the loss of a molecule of water, leaves no doubt that the difference between tephrosin and isotephrosin consists in the orientation of the hydrogen and hydroxyl groups on carbon atoms 7 and 8, no definite information is available as to the exact configurations existing at these carbon atoms. The most plausible assumption is that if in tephrosin the hydroxyl group is on carbon atom 7, then in isotephrosin the hydroxyl group would be on carbon atom 8 or *vice versa*.

Although there appears to be no immediate prospect of reaching a definite decision concerning these configurations, it is, nevertheless, an interesting fact that the two isomeric forms of this compound exist.

[1] Clark, THIS JOURNAL, **54**, 3000 (1932).

Experimental

Preparation of Isotephrosin.—Two kilograms of ground cubé root was extracted with ether. After separating the rotenone and removing the solvent from the mother liquors as completely as possible by vacuum distillation, 250 g. of non-crystalline extractives was obtained. This material was dissolved in 3 liters of methanol, and 180 cc. of 10% sodium hydroxide was added. After standing for a day, 12.8 g. of practically pure deguelin (m. p. 166°) separated. Upon removing this material further crystallization of the filtrate soon occurred, yielding three different fractions. The first, 19.6 g., consisted of somewhat impure deguelin, m. p. 164–174°. The second fraction, 17.5 g., was a mixture of deguelin and tephrosin, m. p. 187°. The third fraction, 10.5 g., was composed essentially of isotephrosin, m. p. 250°. This was recrystallized first from its solution in chloroform by the addition of methanol, and finally it was purified to a constant melting point of 252° by recrystallization from boiling *n*-butanol.

The material consisted of plate-like rhombs many of which extinguished sharply in parallel polarized light (crossed nicols); others, however, were only partly extinguished and in convergent polarized light showed biaxial interference figures; α, 1.547 (common); β, indeterminate, apparently perpendicular to the broad face of the plates; γ, 1.582 (common); both ± 0.003.[2]

Anal. Calcd. for $C_{23}H_{22}O_7$: C, 67.30; H, 5.41; OCH_3 (2), 15.1. Found: C, 67.31; H, 5.61; OCH_3, 15.2.

Dehydrodeguelin from Isotephrosin.—A mixture of 0.5 g. of isotephrosin, 0.25 g. of sodium acetate and 4 cc. of acetic anhydride was boiled for ten minutes. The condenser was then disconnected, and two-thirds of the anhydride was removed by distillation. The remainder of the anhydride was then decomposed with methanol, after which 10 volumes more of methanol was added. Crystallization of dehydrodeguelin began at once and was soon completed. The material was recrystallized from its solution in chloroform by the addition of methanol. Thus obtained it melted at 233° and was proved by comparison with an authentic sample to be dehydrodeguelin.

The same reaction involving the loss of a molecule of water was obtained by boiling 0.2 g. of isotephrosin with 10 cc. of 5% absolute ethanolic hydrochloric acid. The yield of dehydrodeguelin was 80% and after recrystallization as described before the material had the same melting point, mixed melting point and optical properties as recorded for dehydrodeguelin.

Isotephrosindicarboxylic Acid.—A constantly stirred solution of 2 g. of isotephrosin in 300 cc. of acetone, maintained at a temperature between 15 and 20°, was treated with 4 g. of potassium permanganate until the solution became colorless. The resulting manganese dioxide was extracted with boiling water and the solution filtered from the residue. The aqueous extract was acidified to Congo red with sulfuric acid and the acid allowed to crystallize. There was obtained 0.9 g. of material which melted at 185°. The crude substance was dissolved in the necessary quantity of alkali, the solution was diluted to 75 cc., then acidified with acetic acid and filtered through norit. The filtrate was heated to boiling and made acid to Congo red with sulfuric acid. The isotephrosindicarboxylic acid separated as thin colorless irregular-shaped plates which when air-dried melted at 185°. When dried in a high vacuum it melted at 187°. The plates invariably extinguished sharply with crossed nicols, precluding distinct interference figures (convergent polarized light), but the substance appears to be biaxial; α, 1.485; β, not determined but apparently shown when the plates are tipped on edge; γ, 1.660; both ± 0.003.

[2] The optical data here recorded were determined by George L. Keenan of the Food and Drug Administration, U. S. Department of Agriculture.

Anal. Calcd. for $C_{23}H_{22}O_{11}\cdot 0.5\ H_2O$: mol. wt., 492.6; C, 57.13; H, 4.80; OCH_3 (2), 12.8. Found: mol. wt. (titration, 482); C, 57.29; H, 4.93; OCH_3, 12.9.

Tephrosinmonocarboxylic Acid.—When isotephrosindicarboxylic acid was boiled for one-half minute with diphenyl ether, tephrosinmonocarboxylic acid was formed in essentially the same yield as recorded for tephrosindicarboxylic acid.[1]

As obtained from the cooled diphenyl ether solution upon the addition of methanol the acid melted at 266–268°, and when it was mixed with an authentic sample of tephrosinmonocarboxylic acid no depression of the melting point occurred. It also gave the characteristic scarlet color with ferric chloride that is obtained with tephrosinmonocarboxylic acid.

Summary

A crystalline material, shown by its composition and certain of its derivatives to be an isomer of tephrosin, has been obtained from a sample of Peruvian cubé root. This substance has been designated as isotephrosin. The structural difference between tephrosin and isotephrosin exists in the orientation of the hydrogen and hydroxyl groups on carbons 7 and 8 in the structure given in the text.

WASHINGTON, D. C.

NOTES

The Nitration of 4,4′-Dichlorodiphenyl

BY CLARENCE C. VERNON, A. REBERNAK AND H. H. RUWE

Shaw and Turner have recently published an article[1] which concerns in part the exhaustive nitration of 4,4′-dichlorodiphenyl. In it they have shown that the three nitro groups entered the 2,3′,5′ positions.

Without knowledge that the problem was being investigated elsewhere, this study has been in progress in this Laboratory for the past two years. The results attained are in agreement with those of Shaw and Turner, as the following brief account shows. Direct nitration of 4,4′-dichlorodiphenyl at 100°, using a mixture of fuming nitric and fuming sulfuric acids, resulted in the formation of a trinitro derivative with a melting point which corresponded to that of the 4,4′-dichloro-2,3′,5′-trinitrodiphenyl reported by Shaw and Turner. The yield was lower than that secured by them, but the product, precipitated by pouring the filtered reaction mixture over cracked ice, melted at 164–165° without further purification. Nitration of 4,4′-dichloro-2,3′-dinitrodiphenyl under these conditions resulted in the formation of the same compound, as was shown by the melting point of a mixture of the two.

The lability of the chlorine atoms was determined by hydrolysis with dilute sodium hydroxide solutions in the presence of metallic copper, and under quantitative conditions.[2] Only one chlorine atom was found to be

[1] Shaw and Turner, *J. Chem. Soc.*, 285–297 (1932).

[2] Hale and Britton, *Ind. Eng. Chem.*, **20**, 114 (1928).

labile. In the case of the 4,4′-dichloro-2,3′-dinitrodiphenyl, neither of the chlorine atoms was labile under these conditions. This was considered evidence supporting the conclusion that the third nitro group was in the 5′-position.

As a whole, our results confirmed the conclusions arrived at by Shaw and Turner. The fact that they were secured by somewhat different methods renders them still more valuable as supporting evidence.

THE UNIVERSITY OF LOUISVILLE
LOUISVILLE, KENTUCKY

RECEIVED JUNE 20, 1932
PUBLISHED NOVEMBER 5, 1932

Preparation of Diethylisopropylamine

BY SAUL CASPE

No appreciable reaction takes place between isopropyl bromide and diethylamine on boiling under atmospheric pressure. In the early experiments[1] it was found that a yield of 10% was obtained on heating these reactants for forty-two hours in the presence of copper and sodium bromide. The yield was increased to 30% by the use of an autoclave, with the above accelerators, at 140° for six hours. The reaction was promoted to an even greater extent by the presence of glycerol. A mixture of 123 g. of isopropyl bromide, 94.9 g. of diethylamine and 50 g. of glycerol was gently heated under reflux for seventy-two hours; the resulting amines were liberated with alkali, dried with potassium hydroxide and fractionally distilled, when 67 g. (60% of the theoretical amount) of a product boiling at 108° was obtained. A similar yield was obtained when the glycerol was replaced by an equal weight of ethylene glycol; with half that quantity of mannitol, the yield amounted to only 25 g.

Diethylisopropylamine is a colorless liquid, miscible in all proportions with water. Its specific gravity is 0.75.

Anal. Calcd. for $C_7H_{17}N$: C, 73.00; H, 14.80; N, 12.20. Found: C, 73.41; H, 14.82; N, 12.16.

260 WEST 73D ST.
NEW YORK CITY

RECEIVED JULY 9, 1932
PUBLISHED NOVEMBER 5, 1932

[1] W. F. Whitmore and S. Caspe, unpublished data, 1930.

COMMUNICATIONS TO THE EDITOR

A CORRECTION

Sir:

In the note on the use of ammonium acetate as a buffer [THIS JOURNAL, 54, 1911 (1932)], the implication was made that an ordinary good grade product was suitable for this purpose. Unfortunately the matter was treated by us as a passing observation and no more experimentational work was done than that reported. Subsequently we have tested other samples of ammonium acetate. An unopened Kahlbaum sample gave a P_H of 6.93, which is close to neutrality, but other samples were very much more acid. Ammonium acetate recrystallized by dissolving the dry salt in five times its weight of methanol, adding a slight excess of ammonia (using as little water as possible), then adding an equal volume of acid-free ether, is reasonably stable and has always in our hands yielded a solution nearly neutral. In one case, however, the P_H value of a solution of crystals prepared approximately in this way was 6.85. Our original supply of ammonium acetate was therefore, by coincidence, somewhat unique in possessing the theoretically anticipated neutrality. We have not had time for a thorough study, but hope others may carry out such studies. We are regretful that a fuller experimental study was not made previous to the publication of our note.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON

ROGER J. WILLIAMS
CARL M. LYMAN

RECEIVED JULY 13, 1932
PUBLISHED NOVEMBER 5, 1932

A PROPOSAL TO ADOPT THE STEM "XEN" OF A. W. HOFMANN'S XENYL AS BASIS FOR NOMENCLATURE OF BIPHENYL (DIPHENYL) AND ITS DERIVATIVES

Sir:

The study of condensed nuclei involving benzene has been materially aided through the employment of generic names for each particular grouping. In those cases, however, where two or more benzene rings are singly linked we have encountered an increasing difficulty in finding suitable terminology that is both clear and brief.

The name biphenyl (or diphenyl) has long been in use to designate the first step in the condensation of two benzene rings. It is only when we come to the consideration of well-known derivatives of biphenyl that we encounter a growing cumbersomeness in nomenclature.

For hydroxylated biphenyl compounds, the designations of ortho, meta and para phenylphenol are now meeting with favor over the correctly formed yet less euphonious corresponding terms ortho, meta and para hydroxybiphenyl; yet there is no reason why we should continue in use such

long terms as phenylphenol when we refer to a group of compounds which are of growing worth in the chemical industry and, as far as we can discern, will be of far greater worth in the future than the simple, old-time phenol.

Xenylamine, later identified as *p*-aminobiphenyl, was isolated by A. W. Hofmann from the high-boiling bases (over 330°) found in commercial aniline. This same compound was called martylamine by the same author [*Proc. Roy. Soc.* (London), **12,** 389 (1862)] but only the former name seems to have persisted in the literature.

The confusion that arises today in the use of "biphenyl" or "biphenylyl" as a univalent group in contradistinction to "diphenyl" designating two phenyl groups is not easily dispelled. For example, *o*-aminobiphenyl—sometimes termed *o*-biphenylamine, must be readily discernible from diphenylamine and this notwithstanding that the hydrocarbon phenylbenzene remains "diphenyl" as well as "biphenyl." It would seem advisable, therefore, that we adopt some simpler means of representing a hydrocarbon base when made up of separate benzene rings singly linked.

For the present, it is hardly necessary to look beyond groupings containing more than two benzene rings singly linked, and for this reason the proposal by A. W. Hofmann [*Compt. rend.*, **55,** 901 (1862); *Jahrest. Fort. Chem.*, 344 (1862)] of the name "xenyl" for the biphenylyl radical is here considered sufficient. Its meaning should be extended to include the ortho and meta as well as the para series. The hydrocarbon of which xenyl is the univalent radical naturally must become "xenene"; the hydroxyl derivative will become "xenenol" or in abbreviated form "xenol."

The preparation of ortho and para xenylamines is reported in several articles by Morgan and Walls [*J. Soc. Chem. Ind.*, **49,** 15T (1930); **50,** 94 (1931)]. "Beilstein" has adopted this term in the new editions. *Chemical Abstracts* since 1917 has used the term "xenyl" as an equivalent for *p*-biphenylyl in the name xenylamine. Hurd, in the "Pyrolysis of Carbon Compounds," page 28, makes brief mention of "xenyl" in contradistinction to phenyl and other radicals.

The diamino derivatives of "xenene" now should be looked upon as "xenylenediamine" compounds and the well-known 4,4′-biphenylenediamine or benzidine, will become 4,4′-xenylenediamine. The monocarboxylated xenene derivative would become xenenecarboxylic acid or *o*-, *m*- or *p*-xenoic acid (by analogy with benzoic, naphthoic, etc., acids).

The hydroxyl derivatives of xenene thus become xenyl hydroxides or xenols and of these *o*-xenol and *p*-xenol are now meeting with extensive use in the chemical industry. Among the halogen derivatives we would have, for example, *o*-, *m*- or *p*-chloroxenene and other halides similarly named.

THE DOW CHEMICAL COMPANY WILLIAM J. HALE
MIDLAND, MICHIGAN

RECEIVED AUGUST 13, 1932
PUBLISHED NOVEMBER 5, 1932

AN EQUATION RELATING VISCOSITY AND SURFACE TENSION

Sir:

An equation relating viscosity and surface tension can be obtained by combining the following equations of Batchinski [*Z. physik. Chem.*, **84**, 643 (1913)] and McLeod [*Trans. Faraday Soc.*, **19**, 38 (1923)], respectively,

$$\eta = \frac{C'}{v - w} \qquad \frac{\gamma}{(D - d)^4} = C$$

where η is the viscosity, v the specific volume, w the limiting volume or approximately van der Waals b, γ the surface tension, D the density of the liquid, d the density of the vapor, and C' and C are constants for a given liquid. Below the boiling point the density of the vapor may be neglected in comparison with the density of the liquid. Neglecting d and equating v to $1/D$, we obtain

$$\gamma^{-1/4} = A\frac{1}{\eta} + B$$

where A and B are constants characteristic of the liquid.

If this equation is correct, a straight line will be obtained when $\gamma^{-1/4}$ is plotted against fluidity. When such plots were made for twenty-five liquids, water included, the deviations of the points from a straight line were within the experimental error except in the cases of ethyl ether and the alcohols, in which the surface tension at low fluidities was less than the straight-line requirements, the deviation increasing as fluidity decreases.

LABORATORY OF PHYSICAL CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

DANIEL SILVERMAN
W. E. ROSEVEARE

RECEIVED SEPTEMBER 26, 1932
PUBLISHED NOVEMBER 5, 1932

THE PHOTOCHEMICAL FORMATION OF HYDROGEN PEROXIDE

Sir:

In previous communications [*J. Phys. Chem.*, **30**, 34 (1926); THIS JOURNAL, **49**, 2763 (1927)] the author has reported the quantum yield for the formation of hydrogen peroxide from hydrogen and oxygen by light of wave length 2536 Å. when photosensitized by mercury vapor. In making these measurements, a quartz filter containing chlorine and bromine was used. The manufacturers gave the transmission of this filter for 2536 Å. as 80%. Since these papers were published Frankenburger and Klinkhardt [*Z. physik. Chem.*, **B15**, 421 (1932)] have also reported work on this reaction in which they obtain a yield of 1.2 molecules of H_2O_2 and 1.5–2.5 molecules of H_2O per quantum absorbed. The author originally reported 6.6 molecules of H_2O_2 formed per quantum absorbed. In attempting to account for this discrepancy the filter originally used was borrowed from Princeton University and its transmission measured by Mr. Frank Benford,

in this Laboratory, using a Bausch and Lomb monochromator and receiving the transmitted energy on a thermopile. The transmissions measured are given in the accompanying table.

Wave length in Å.	Fraction of incident light transmitted	Wave length in Å.	Fraction of incident light transmitted
2475	0.24	3650	0.00
2536	.31	4047	.00
2650	.36	4350	.03
2804	.17	4916	.25
2967	.00	5461	.60
3024	.00	5770	.53

These results agree fairly well with measurements on a similar filter reported by Villars [THIS JOURNAL, **48,** 1874 (1926)]. As a result of these measurements the quantum yield reported by the author will have to be reduced from 6.6 to *2.5*.

In previous experiments (Ref. 1) using a closed circulatory system the author was able to show that the product of the reaction was predominantly hydrogen peroxide. Due to an unfortunate accident, this was only an estimate, but a careful check on the volume of the system made from a photograph shows that the yield was at least 75% H_2O_2 and probably much greater. It is thus possible to say that in these experiments where the gas was saturated with water vapor at 20° the yield of water vapor in the reaction is not at all in agreement with the results of Frankenburger, who found more water formed than peroxide. His objection to the mechanism postulated

$$H + O_2 = HO_2 \quad (1)$$
$$HO_2 + H_2 = H_2O_2 + H \quad (2)$$

on account of the endothermic nature of reaction (2) is not necessarily valid since the original product HO_2 may react with oxygen before it loses the 69 k. cal. acquired in its formation.

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY, N. Y.
A. L. MARSHALL

RECEIVED SEPTEMBER 29, 1932
PUBLISHED NOVEMBER 5, 1932

DERIVATIVES OF DIOXANE

Sir:

The recent article of C. L. Butler and L. H. Cretcher [THIS JOURNAL, **54,** 2987 (1932)] and the communication of R. K. Summerbell and R. Christ [*ibid.*, **54,** 3777 (1932)], both connecting with our first article [Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50,** 909 (1931) and *Proc. R. Acad.*, **34,** 631 (1931)] cause us to give a brief preliminary report of the continuation of our research. While chlorinating 2,3-dichlorodioxane, we obtained

the liquid asymmetrical tetrachlorodioxane, described by Butler and Cretcher, a crystalline hexachlorodioxane and more highly chlorinated derivatives which are under investigation. More properties of the isomeric naphthodioxanes have been determined and the inquiry has been enlarged to include the derivatives with 1,3-propanediol, pyrocatechol, benzyl alcohol, ester of tartaric acid, etc. By treatment with potassium acetate we made and investigated the diacetate. We are very much astonished that our first communication, intended *inter alia* to save double work, has apparently been understood as an invitation to continue our research. After this explanation we think it will be clear that we ourselves will continue our research in all directions. The results obtained since our last article will be communicated in the near future.

DEPARTMENT OF ORGANIC CHEMISTRY
DELFT TECHNICAL UNIVERSITY
DELFT, HOLLAND

J. BÖESEKEN
F. TELLEGEN
P. COHEN HENRIQUEZ

RECEIVED OCTOBER 13, 1932
PUBLISHED NOVEMBER 5, 1932

THE REACTION OF CARBOXYLIC ACIDS WITH PHOSPHORUS PENTOXIDE

Sir:

Certain aliphatic ketones have been made by the action of phosphorus pentoxide with acids [Gal and Étard, *Compt. rend.*, **82**, 457 (1876); Kipping, *J. Chem. Soc.*, **57**, 532, 980 (1890); **63**, 452 (1893)]. An attempt to apply this reaction to trimethylacetic acid gave no ketone nor carbon dioxide but instead gave carbon monoxide and polymers of isobutylene. *n*-Butyric and isobutyric acids with excess of phosphorus pentoxide gave both carbon dioxide and carbon monoxide and formed tars. The yields and ratios of these gases were determined.

Acid	% Yield of CO and CO_2	Ratio CO : CO_2
n-Butyric	7	1:5
Isobutyric	10	5:1
Trimethylacetic	60	∞

Use of xylene as a solvent for the first two acids cut the yields of gas to 0.07 and 0.14%, respectively, but did not change the ratio of CO:CO_2. No gas was evolved when benzoic acid was treated in boiling xylene with an excess of phosphorus pentoxide.

This process is being studied as a possible means of distinguishing tertiary aliphatic acids from other types of acids.

PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

KENNETH C. LAUGHLIN
FRANK C. WHITMORE

RECEIVED OCTOBER 20, 1932
PUBLISHED NOVEMBER 5, 1932

THE REACTION BETWEEN NEUTRAL LEAD MERCAPTIDES AND SULFUR

Sir:

The reaction between neutral lead mercaptides and sulfur in benzene solution leads to the formation of lead disulfide and organic polysulfides [W. E. Duncan and Emil Ott, THIS JOURNAL, **53**, 3940 (1931)].

Preliminary work on the similar reaction with basic lead mercaptides indicated an analogous reaction with the formation of basic lead polysulfides of the type $HOPbS_x \cdot PbOH$ [Emil Ott and E. E. Reid, *Ind. Eng. Chem.*, **22**, 884 (1930); **22**, 878 (1930)].

This reaction was now studied more extensively with basic *sec.*-butyl lead mercaptide. The relatively stable yellow-orange (light reddish-brown when dry) precipitate obtained by the addition of sulfur in benzene solution was definitely established to be a mixture of basic lead polysulfides of the type mentioned above. Most mixtures may simply be described as containing the compounds with $x = 3$ and $x = 4$, but in some cases $x = 5$ is additionally present.

Thorough qualitative tests and quantitative analyses for lead, sulfur, hydrogen and carbon established composition and constitution of the products.

Since the basic *sec.*-butyl lead mercaptide cannot be prepared entirely free from neutral *sec.*-butyl lead mercaptide, a certain amount of lead disulfide is also formed, the amount of which can be predicted accurately from the analysis of the mercaptide solution. Thus no uncertainty is introduced into the final analyses. It lies in the nature of the problem that no individual compounds could be isolated; for the same reason this abreviated communication seemed necessary.

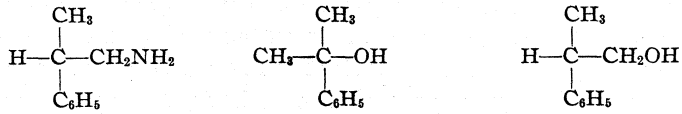
DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND
WALLACE E. DUNCAN
EMIL OTT

RECEIVED OCTOBER 21, 1932
PUBLISHED NOVEMBER 5, 1932

REARRANGEMENTS BY THE ACTION OF NITROUS ACID ON AMINES OF THE TYPE $CH_3CH(C_6H_5)CH_2NH_2$

Sir:

The amine I on treatment with nitrous acid should form, on the basis of observations made on aliphatic amines of this type, two isomeric carbinols,

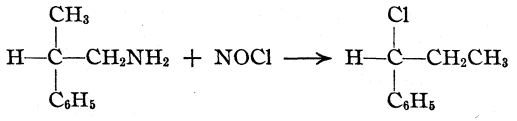


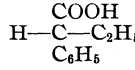
I II III

II in predominating proportion and III in much smaller proportion. In the case of the optically active amine, the first carbinol should be optically

inactive. Similar effects should be expected from the action on the amine of NOCl or NOBr. The active halides should be expected to be the primary. This assumption was made by Levene, Mikeska and Passoth [*J. Biol. Chem.*, **88**, 27 (1930)] and was made the basis of the correlation of the substituted phenylacetic to phenylpropionic acids by Levene and Marker [*ibid.*, **93**, 749 (1931)].

We now find that the active halide obtained by the action of nitrosyl halides on the amine is not a primary but a secondary halide. Thus, in course of the reaction an unexpected rearrangement takes place



inasmuch as this halide leads to  .

A similar rearrangement takes place in the case of 1,1-ethylphenylethylamine (Ref. 2).

It may be mentioned here that the dextrorotatory substituted phenylacetic acids are now correlated to levorotatory substituted 3-phenylpropionic acids on the basis of new evidence. The details will be published in the *Journal of Biological Chemistry*.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
NEW YORK, N. Y.

P. A. LEVENE
R. E. MARKER
ALEXANDRE ROTHEN

RECEIVED OCTOBER 21, 1932
PUBLISHED NOVEMBER 5, 1932

THE COLORIMETRIC DETERMINATION OF FLUORINE IN WATER WITH FERRIC THIOCYANATE

Sir:

In the determination of fluorine in water it has been found most satisfactory to use a colorimetric method based on the fact that the complex ion formed in the reaction between a fluoride and ferric chloride does not give the characteristic iron color with ammonium thiocyanate. Thus, with more iron than is necessary to react with the fluoride, the color is less than that produced by the same amount of iron without fluoride. By determining colorimetrically the quantity of iron reacting with the ammonium thiocyanate, the quantity withdrawn by the fluoride may be found by difference and its equivalent in fluoride read from a curve which has been made by plotting the effect of definite amounts of fluoride upon the amount of iron used in the determination.

The alkalinity of the sample of water must be neutralized and if the volume of the sample is much over 50 cc., it must be evaporated to about

this volume. By using 5 cc. of ferric chloride solution (0.1 g. of iron and 30 cc. of *N* hydrochloric acid in 1 liter) with 10 cc. of ammonium thiocyanate solution (24 g. in 1 liter) in a volume of 75 cc., as little as 0.025 mg. of fluorine in 100 cc. of the sample of water may be determined. If the sample contains more than 0.4 mg. of fluoride, a smaller sample should be taken or more iron used, which necessitates making a new curve for the larger amount of iron. It is important that the acidity, temperature, and volume be more carefully controlled than in the usual thiocyanate determination.

Sulfate produces a similar but very much smaller effect upon the red color but this is also quantitative and a curve showing the effect of definite amounts of sulfate in terms of iron or of fluorine may be made. Then, for each sample, the effect of the sulfate present may be subtracted to obtain the true fluoride content. For example, 200 parts per million of sulfate produced a fading effect equivalent to 0.5 part of fluorine when a 100-cc. sample was used. If the fading of the sample containing this amount of sulfate indicated a fluoride content of 3.7 parts per million, 0.5 part must be subtracted to obtain the true fluoride content of the sample.

Chloride produces a slight fading but for quantities below 500 parts per million this is so small that it may be ignored in a 100-cc. sample. For quantities above 500 parts per million, about 0.1 part per million of fluorine must be subtracted for each 500 parts of chloride present. The chloride added as hydrochloric acid to neutralize the alkalinity must, of course, be taken into consideration. The effect of sulfate and chloride is the same whether they are present as calcium, magnesium, or sodium salts. The amount of nitrate usually found in natural waters has no effect.

This method is particularly adapted to the determination of the small amounts of fluoride to be expected in most natural waters.

U. S. Geological Survey
Washington, D. C.
Margaret D. Foster

Received October 21, 1932
Published November 5, 1932

NEW BOOKS

Annual Survey of American Chemistry. Volume VI, 1931. Edited by CLARENCE J. WEST, Director, Research Information Service, National Research Council. Published for the National Research Council by The Chemical Catalog Company, Inc., 419 Fourth Ave., New York, 1932. 573 pp. 13.5 × 21.5 cm. Price, $4.50.

The "Survey" for the year 1931 contains thirty-seven chapters varying in length from three pages (Properties of Compressed Gases) to thirty-three pages (Colloids). The selection of subjects follows along the line of the previous volumes and is sufficiently broad to include practically all research work that would naturally fall within the domain of chemistry. One misses the chapters on carbohydrates and dyes, but undoubtedly they will appear in the "Survey" for 1932 and cover a two-year period. Very complete bibliographies are included; for example, the chapter on Analytical Chemistry lists 265 different references and that on Colloids 250. The large amount of work being done in the field of insecticides and fungicides is indicated by 240 different references. The total number of references listed in the thirty-seven chapters is 3961, which gives some idea of the extent of the research work being done in the various fields covered by the "Survey." In addition to the bibliography, a number of chapters list important patents, either granted or applied for, while others suggest important problems for research.

A new member in the family of fundamental particles, the neutron, has made its appearance—at least in name. In commenting on the neutron proposed by Pauli, the authors of the chapter on "Subatomic Phenomena" write as follows: "There appears to be no definite evidence for the existence of such particles, but there is no conclusive proof that they do not exist." Attention is also called to the large number of isotopes recently added to the list—42 new ones. Probably the most interesting is the discovery of the predicted isotope of hydrogen of mass number 2. According to the "Survey," this isotope is present to the extent of about one part in 4000. More recent investigations, however, have changed this figure to one part in from 30,000 to 40,000, which shows how difficult it is for a book to keep up with the times, some statements being out of date before the book can be printed.

In reading the "Survey," one cannot help being impressed not only with the large amount of research work being done in our country but also with the fundamental character of the work. Our chemists owe a debt of gratitude to the authors of the different chapters included in the "Survey." Some of these authors have no hesitation in referring to work done in other countries and one cannot help hoping that the time may soon come when the "Survey" will become international in scope, and so take its place along with *Chemical Abstracts*, which knows no national boundaries.

WM. MCPHERSON

Outlines of Theoretical Chemistry. By FREDERICK H. GETMAN, Ph.D. Fifth Edition, Revised and Largely Rewritten by Farrington Daniels, Professor of Chemistry in the University of Wisconsin. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1931. ix + 643 pp. 180 figs. 15.5 × 23.5 cm. Price, $3.75.

In presenting the 1931 model, the fifth edition, of this well-known textbook, Dr. Daniels has made excellent contribution to the literature of physical chemistry designed for the use of students, both young and old, in this rapidly changing field of knowledge.

In general the arrangement is similar to the older editions. The chapters on Elementary Thermodynamics, Kinetics, Photochemistry and Atomic Structure have been rewritten and chapters on Chemical Thermodynamics, using the notation of G. N. Lewis, and Introduction to Quantum Theory have been added.

The method of presentation is particularly fortunate, in that the language is non-technical in so far as possible. Models, mechanisms and analogies with common phenomena and concrete examples are freely employed in explaining the mathematically expressed physical laws, which in their written form are all too frequently but hieroglyphics to the student with a non-mathematical mind. The logical presentation and frequent references to earlier passages in the book add much to its instructive value and its readability. A suggestion from a prejudiced critic would call for the further revision of the chapter on gases, introducing a few paragraphs dealing with the great mass of recently acquired knowledge of high pressure gas phenomena, and the uses and limitations of equations of state.

The authors and the publishers are to be congratulated for the production of this attractive and valuable book.

EDWARD P. BARTLETT

Leitfähigkeit und Überführungszahlen in flüssigen und festen Elektrolyten. (Conductivity and Transference Numbers in Liquid and Solid Electrolytes.) Vol. XII of the "Handbuch der Experimental Physik," "Electrochemistry," Edited by K. FAJANS. Part 1, by Dr. L. EBERT and Dr. C. TUBANDT. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany, 1932. xvi + 495 pp. 138 figs. 17.5 × 25 cm. Price, M. 43; bound, M. 45.

This book is the first half of a new treatise on electrochemistry by several authors under the editorial supervision of Fajans. It forms a part of the "Handbuch der Experimentalphysik." The volume at hand covers Conductivity in Liquid Electrolytes, Transference Numbers in Liquid Electrolytes (by L. Ebert) and Conductivity and Transference Numbers in Solid Electrolytes (by C. Tubandt). Another volume dealing with other branches of electrochemistry by other authors is promised in the near future.

To write a really modern treatise on electrochemistry at the present time is a difficult task because the great bulk of the literature was written from the point of view of the Arrhenius theory. Although the main emphasis

is properly placed on the experimental methods, facts and laws, rather than on theories, Ebert has shown extraordinary skill in selecting the portions of the older literature of permanent value and reinterpreting them from the point of view of the Debye–Hückel theory. The detailed mathematics of this theory is generally omitted but the fundamental premises are clearly stated, and the final equations given and discussed. The book should be helpful to many chemical students who find the mathematical style of the original literature a serious obstacle.

The portion of the book by Tubandt dealing with solid electrolytes describes clearly and interestingly a field which has been unduly neglected by American electrochemists.

Although the authors have purposely avoided giving a complete bibliographic guide to the literature of electrochemistry, there are numerous citations of the original articles which have been selected with good judgment. The book is written with Teutonic thoroughness and system and is clearly the best and most up-to-date treatise on the portions of the science which it covers.

GRINNELL JONES

An Introduction to Organic Chemistry. By ALEXANDER LOWY, Ph.D., Professor of Organic Chemistry, University of Pittsburgh, and BENJAMIN HARROW, Ph.D., Assistant Professor of Chemistry, College of the City of New York. Third edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. xiv + 412 pp. 15.5 × 23.5 cm. Price, $3.00.

The arrangement, the order of presentation and the type of the material in the third edition of this text follow closely that of the first edition, a more extended review of which was published in THIS JOURNAL, **47**, 900 (1925). The authors have succeeded in bringing the book up to date by the inclusion of many of the recent advances made in organic chemistry, as, for instance, in ethylene chemistry, products from vinylacetylene, sugar structures, etc.

The text has been edited well, and it is relatively free from errors. The reviewer doubts, however, if the production of oxalic acid from sawdust would be considered a present-day commercial process (p. 92). The formula for muscarine (p. 110) as the aldehyde of betaine is, without doubt, wrong. It would seem, too, that if the cleansing action of soap is discussed at all, a more adequate explanation should be given. The authors have retained the section on the Electron Conception of Valence that appeared in the first edition. Since this is based on the speculation of the period of 1910 to 1916, it is fortunate that no attempt has been made to apply the ideas in the presentation of the material.

The clear statement of fact and the generous use of structural formulas give a good basis for the popularity of this text.

R. R. RENSHAW

Quantitative analytische Mikromethoden der organischen Chemie in vergleichender Darstellung. (Quantitative Analytical Micro Methods in Organic Chemistry. A Comparative Review.) By C. WEYGAND, Professor of Chemistry at the University of Leipzig. Akademische Verlagsgesellschaft m. b. H., Schlossgasse 9, Leipzig C 1, Germany, 1931. xi + 279 pp. 79 figs. 16 × 23.5 cm. Price, M. 16; bound, M. 18.

This book is a valuable contribution to the literature of micro-analytical methods of organic chemistry. In addition to the elegant micro methods which have resulted from the brilliant work of Professor Pregl and his associates at Graz, a number of less familiar micro and semi-micro methods are included.

As would be expected, the major portion of the book is devoted to Pregl's micro methods. In spite of the fact that Professor Pregl's book describing these methods is exceedingly well written, it is perhaps desirable to incorporate into these methods the experience of still another laboratory. This portion of the book will be particularly appreciated by those who do not have the opportunity to learn these methods from someone already familiar with them.

The book has been carefully edited, but perhaps it should be noted that the use of sodium hydroxide for the absorption of carbon dioxide in the semi-micro method described on page 130 is not in agreement with the directions published in the reference cited.

W. M. LAUER

Die hochmolekularen organischen Verbindungen—Kautschuk und Cellulose. (High Molecular Organic Compounds—Rubber and Cellulose.) By HERMANN STAUDINGER, Dr. Phil., Professor and Director of the Chemical Laboratories of the University of Freiburg. Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany, 1932. xv + 540 pp. 113 figs. 17.5 × 26 cm. Price, RM. 49.60; bound, RM. 52.

It has for some time been increasingly evident that current scientific journals were becoming inadequate to satisfy Professor Staudinger's copiousness as an expositor of his own researches and speculations. The problem thus raised is solved by the book under review where, untrammeled by editorial restrictions, the author succeeds in bringing the record of his views and experimental accomplishments up to date.

In his preface Professor Staudinger states that the plan was initially to reprint all of his previous publications in this field together with numerous new researches, but the circumstances of the times prevented the realization of this plan; and so in the present work we have the 63rd, 64th, 65th, 66th 67th, 68th and 69th numbered communications on high polymers, and the 38th and 39th in the series labeled isoprene and rubber. All of these are based largely on new experimental material and they bring further information concerning polystyrene, polyoxymethylene, polyethylene oxide,

polyacrylic acid, rubber and balata, and cellulose. Besides this the 11th communication on isoprene and rubber is reprinted (from *Kautschuk*, 1925) for its historical value together with fresh and renovated footnotes.

The first 156 pages of the book will be of most value to the general reader since they contain a general exposition of the properties and structure of high polymers. Unfortunately, this exposition is not as concise or as well-proportioned and organized as it might be. It is in parts unnecessarily repetitious. Abandoned views of erstwhile opponents are again set forth and again re-demolished; but aside from this the contributions of other investigators are, by comparison, rather inadequately recognized. The author is inclined to be dogmatic concerning certain speculative points of interpretation where, in fact, only slender and dubious evidence is available (*e. g.*, on pp. 73 and 293 in the interpretation of the viscosity behavior of polyethylene oxides, and on p. 115 concerning the structure of balata).

It is to be hoped, however, that these comparatively minor defects and the rather excessive profusion and prolixity of Staudinger's writings will not conceal from the reader the genuine importance of Staudinger's contributions to the knowledge of macromolecular materials. There are doubtless some points on which his views will prove to be wrong, but in the main he has been consistently right even during the great revival of speculative confusion from 1924–1929 when many European writers abandoned the fundamental ideas of orthodox organic chemistry in their attempts to deal with rubber, polysaccharides and proteins. By synthetic reactions of polymerization Staudinger provided giant molecules of relatively simple structure; he demonstrated the general structural plan of these molecules and furnished the first actual experimental material on the relation between properties and structure of linear macromolecules. The extent to which the subject of molecular colloids was clarified by Staudinger on the basis of this material is perhaps not yet generally appreciated; but there is no question that his contributions have been very important factors in the progress lately made on the structure of rubber and cellulose. They are likely to be equally significant in connection with future developments in proteins.

The most important new material in the book under review is concerned with measurements of viscosities. Staudinger's attempts to estimate molecular weights by this method have been greeted with much skepticism. He now presents a great mass of data all tending to demonstrate, in so far as it is possible to infer from the mere fact of self-consistency, that there is a simple and direct relation between the molecular weight of linear molecules and their "specific viscosities" in sufficiently dilute solutions. More astonishing is the fact that, within certain limits, the viscosity at a given concentration is determined only by the length of the polymeric chain and is practically unaffected by the presence of substituent groups or by the

presence of unsaturations or other atoms than carbon in the chain (but *ad hoc* assumptions are required to bring some materials in line with this conclusion). The author states repeatedly and emphatically (*e. g.*, pp. 79, 80, 83 and 244) that linear molecules in solution are rigidly extended, but on page 130 he admits that they may bend. He no longer considers that long molecules bear free valences at the ends, or that they are rings. They are open chains with terminal groups.

The chemistry of macromolecular materials is still in its infancy and although its growth during the past few years has been exceedingly rapid, some time must elapse before its theories are firmly enough grounded to permit the writing of a generally satisfactory textbook. Meanwhile everyone interested in this field must have access to Professor Staudinger's book. Chemists generally who seek new, fresh, and spacious fields will find it a rich source of provoking suggestions for thought and investigation.

The book is beautifully printed. At the end there is a bibliography of Staudinger's papers and a subject index.

WALLACE H. CAROTHERS

Die Vitamine nebst einer Einleitung über chemische Dynamik biologischer Vorgänge. (The Vitamins, with an Introduction to the Chemical Dynamics of Biological Processes.) By ADOLF JOLLES. Verlagsbuchhandlung Franz Deuticke, Wien, Austria, 1932. 157 pp. Price, M. 10.

As the preface of this monograph states, this review of the vitamins aims to present a general picture of the subject rather than to discuss it from the standpoint of the special investigator in this field of nutrition. The author has succeeded in his object and has shown a good grasp of the subject as well as a knowledge of the voluminous literature. The first fifty pages are concerned with a consideration of the ferments and at the end the various hormones of the endocrines as well as the value of a vegetarian diet are discussed. The pamphlet is one of a series dealing with the scientific basis of nutrition.

ALFRED F. HESS

BOOKS RECEIVED

September 15, 1932–October 15, 1932

IRA S. ALLISON. "The Geology and Water Resources of Northwestern Minnesota." Bulletin 22, Minnesota Geological Survey. The University of Minnesota Press, Minneapolis, Minn. 245 pp. $1.00.

EARL C. H. DAVIES. "Fundamentals of Physical Chemistry." P. Blakiston's Son and Co., Inc., 1012 Walnut St., Philadelphia, Pa. 370 pp.

P. DEBYE. "The Structure of Molecules." Authorized translation by Winifred M. Deans. Blackie and Son, Ltd., 50 Old Bailey, London E. C. 4, England. 190 pp. 15/–.

J. ALLEN HARRIS AND WILLIAM URE. "Experimental Chemistry for Colleges." McGraw-Hill Book Company, Inc., 330 West 42d St., New York. 192 pp. $1.25.

OLIVER KAMM. "Qualitative Organic Analysis." Second edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York. 311 pp. $2.75.

FRANK B. KENRICK. "An Introduction to Chemistry." The University of Toronto Press, Toronto, Canada. 434 pp. $3.00.

I. E. KNAGGS AND B. KARLIK. "Tables of Cubic Crystal Structure of Elements and Compounds." With a Section on Alloys by C. F. Elam. Published by Adam Hilger, Ltd., 98 Kings Road, London N. W. 1, England. 90 pp. 11/6d, net.

W. KUHN AND K. FREUDENBERG. "Drehung der Polarisationsebene des Lichts." Band 8, Abschnitt III, "Hand- und Jahrbuch der chemischen Physik," herausgegeben von A. Eucken und K. L. Wolf. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 142 pp. RM. 12.80.

MAURICE LECAT. "L'Azéotropisme. La Tension de Vapeur des Mélanges de Liquides. Bibliographie." Maurice Lamertin, Éditeur, Rue Coudenberg 58–62, Bruxelles, Belgium. 134 pp. 15 belgas.

J. F. LIVERSEEGE. "Adulteration and Analysis of Foods and Drugs. Birmingham Methods and Analyses of Samples. Review of British Prosecutions during Half a Century." D. Van Nostrand Co., 250 Fourth Ave., New York. 599 pp.

DOROTHY MOYLE NEEDHAM. "The Biochemistry of Muscle." E. P. Dutton and Co., 286–302 Fourth Ave., New York. 166 pp. 5s, net.

MICHAEL POLANYI. "Atomic Reactions." Williams and Norgate, Ltd., 28–30 Little Russell St., London W. C. 1, England. 64 pp. 6/– net.

J. H. REEDY. "Elementary Qualitative Analysis for College Students." Second edition. McGraw-Hill Book Co., Inc., 330 West 42d St., New York. 163 pp. $1.50.

E. WERTHEIM. "A Manual of Elementary Organic Chemistry." Second edition, revised. Mimeographed by Brumfield and Brumfield, Ann Arbor, Mich. 519 pp. $4.50.

"Book of Chemical Labels, as Recommended by the Committee on Labels, The Division of Chemical Education of the American Chemical Society." Printed by Robert Haag, 38 Murray St., New York. 56 pages of labels. $1.00, singly.

"Current Science." Published by the Indian Institute of Science. K. S. Varadachar, Secretary, Indian Institute of Science, Hebbal P. O., Bangalore, India. Annual subscription, Rs. 6.

The Journal of the American Chemical Society

VOL. 54 DECEMBER, 1932 No. 12

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

PROPERTIES OF ACTIVE CHARCOAL REACTIVATED IN OXYGEN AT 400°

BY I. M. KOLTHOFF

RECEIVED JANUARY 20, 1932 PUBLISHED DECEMBER 13, 1932

Charcoal activated at high temperatures does not adsorb alkali hydroxide from aqueous solutions. This fact first stated by F. E. Bartell and E. J. Miller[1] has been confirmed later by various investigators. H. R. Kruyt and G. S. de Kadt[2] noticed that active charcoal heated for some time in the presence of oxygen at 400° acquired acid properties and adsorbed sodium hydroxide. Since the adsorbent and catalytic properties of charcoal seem to depend very much upon its method of preparation and since little is known of the form in which oxygen is present at the surface of the carbon, a more detailed study was made of the properties of active charcoal, the surface of which showed an acid character.

Experimental

Three kinds of charcoal were used in this work. Active sugar charcoal was prepared from ash-free sugar in a way similar to that of Bartell and Miller.[1] Another product was "Carbo medicinalis Neu Merck" made ash free according to the directions of Miller,[3] the adsorbent properties of which have been described in a previous paper.[4] A third product was Nuchar, obtained from the Eastman Kodak Company. After extraction with hydrochloric acid and hydrofluoric acid and reactivation at 950°, the ash content was 0.1%. None of these products adsorbed sodium hydroxide from 0.01 *N* solution after activation at 900 to 950°, whereas all three adsorbed inorganic acids from their aqueous solutions.

Formation of "Acid Substance" on the Surface of Charcoal by Heating in Oxygen.—Samples of the various kinds of charcoal activated at 950°

[1] Bartell and Miller, THIS JOURNAL, **44**, 1866 (1922); **45**, 1107 (1923); *J. Phys. Chem.*, **28**, 992 (1924); Miller, THIS JOURNAL, **46**, 1150 (1924); **47**, 1270 (1925); Bull. No. 73, Agricultural Experiment Station, Michigan State College, 1925.

[2] Kruyt and de Kadt, *Kolloid Z.*, **47**, 44 (1929); *Kolloid Beih.*, **32**, 249 (1931); G. S. de Kadt, Thesis, Utrecht, 1929.

[3] E. J. Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

[4] I. M. Kolthoff and E. van der Goot, *Rec. trav. chim.*, **48**, 265 (1929).

were heated at various temperatures in an alundum boat in an electrically heated Pyrex or quartz tube in a slow stream of dry and moist oxygen, respectively. After the indicated time of heating, the loss in weight and the adsorbent properties toward 0.01 *N* sodium hydroxide were determined. The reproducibility of the experiments depends upon the amount of charcoal heated; the formation of the acid substance is to be attributed to a surface reaction. If two boats were placed one after the other, the charcoal in the first invariably contained much more of the acid substance than the sample in the second.

It may be mentioned that at temperatures between 100 and 200° the combustion of the charcoal took place very slowly. After a prolonged time of heating at 200°, the charcoal increased in weight slightly (0.5 to 2%) in spite of the slight losses by combustion. This indicates that part of the oxygen is fixed on the surface; it is not removed after prolonged heating in a vacuum at 200°. This fixed oxygen has no acid properties. No change in the properties of charcoal was noticed if samples outgassed at 900–1000° were heated in oxygen-free nitrogen between 100 and 600°.

Experiments with Sugar Charcoal: 1-1.5-g. Samples.—In the adsorption experiment 0.5 g. was shaken with 50 cc. of 0.01 *N* sodium hydroxide and the alkalinity determined in 25 cc. of filtrate. The results are given in Table I.

TABLE I

SUGAR CHARCOAL HEATED IN DRY OXYGEN

Temp., °C.	Time of heating in hours	Loss in weight of C in %	Milliequiv. NaOH ads. by 1 g. of carbon
200	6	−0.2	0.03
250	6	− .3	.04
300	6	.2	.16
350	6	2.5	.4
400	6	2.5	.7

In Table II some results are given of experiments with Merck charcoal. With Eastman's charcoal practically the same results were obtained.

From the results it may be inferred that the best way of preparing charcoal, whose surface is practically saturated with the acid substance, is by heating small samples of the activated products (about 1 g.) for six hours in a slow current of dry oxygen at about 400°.

It seems that the initial formation of this acid takes place slowly, but when once started it progresses rapidly. Water vapor seems to promote the oxidation and the formation of the acid substance. In the following experiments Merck charcoal (freshly heated for six hours to 950°) was treated with purified oxygen, which had been saturated with water vapor at 25° by passing through three wash bottles containing water.

Acid is also formed at lower temperatures in the presence of water. Half-gram samples of Merck charcoal (freshly heated to 950°) were heated

TABLE II

MERCK CHARCOAL HEATED IN DRY OXYGEN

Temp., °C.	Time of heating in hours	Loss in weight of carbon in %	Grams of carbon shaken with 50 cc. of 0.01 *N* NaOH	Milliequiv. NaOH ads. by 1 g. of carbon
200	6.5	−2	0.5	0.032
250	6	−2	.5	.06
300	6	3	.5	.20
300	6.5	0.5	.5	.08
350	3	4	.5	.47
350	6	20	.25	1.04
380	6	28	.25	1.00
400	6	20	.25	0.96
450	3	2	.25	.10
450	6	50	.25	1.36
450	6	45	.25	1.12
500	3	2	.5	0.2
500	6	90		
550	3	98		

TABLE III

MERCK CHARCOAL HEATED IN MOIST OXYGEN

Temp., °C.	Time of heating in hours	Loss in weight of carbon in %	Grams of carbon shaken with 50 cc. of 0.01 *N* NaOH	Milliequiv. NaOH ads. by 1 g. of carbon
200	6	32	0.5	0.54
250	6	37	.5	.64
300	6	60	.5	.84
350	6	85	.1	3.6

in a Pyrex flask with conductivity water, purified air being passed through the boiling suspension.

After two days the charcoal was collected, filtered and shaken with 0.01 *N* sodium hydroxide; 0.088 milliequivalent of the latter was adsorbed by 1 g. of charcoal. If the suspension was boiled for a week this figure increased to 0.2 milliequivalent. Formation of acid even took place at room temperature if the charcoal was left in not too dry an atmosphere.

Samples of Merck charcoal (freshly heated to 950°) were kept in desiccators over water, deliquescent sodium bromide and concentrated sulfuric acid, respectively, for six months. The sample kept over sulfuric acid did not adsorb any sodium hydroxide, that kept over sodium bromide 0.08 milliequivalent per 1 g. of carbon, and the one kept over water 0.075 milliequivalent.

In agreement with the statement of Kruyt and de Kadt[2] it was noticed that charcoal heated in oxygen at 400° is wetted much more easily by water than after activation at 900°. It seems that the acid formed changes the hydrophobic character of the charcoal into a hydrophilic one.

The difference in hygroscopic character between charcoal activated at 950° and samples reheated for six hours in dry oxygen at 400° is shown by

the following experiments.[5] Freshly heated samples were placed in desiccators of various humidities at room temperature. The increases in weight are given in Table IV.

TABLE IV

HYGROSCOPIC CHARACTER OF C950 AND C400

Relative water vapor tension	Time of standing in days	Water content in % C950	Water content in % C400
100 (water)	18	38.4	53
100	28	40.0	53
60	18	12.5	29.2
60	28	12.4	30.5
0 (H_2SO_4)	18	0.0	0.0
0	28	0.0	0.0

Stability of the Acid on the Surface.—Weighed samples of C400 were heated at various temperatures in a high vacuum, cooled, saturated with dry air and weighed in a closed weighing bottle. 0.25-g. samples were shaken with 50 cc. of 0.01 *N* sodium hydroxide in order to determine whether the acid content of the C400 had decreased during the heating. It appeared that the acid on the charcoal was quite stable in a vacuum at temperatures below 500°. Even after heating for thirty hours at this temperature the adsorbed amount of base was the same as that adsorbed by the original C400. After heating for twenty-four hours at 575° a slight decrease in weight was noticed and the adsorption of sodium hydroxide showed a marked decrease. The original sample adsorbed 1.04 milliequivalents of base per 1 g., whereas after twenty-four hours of heating at 575° this amount decreased to 0.4 milliequivalent. After heating for twenty-four hours at 600°, 0.03 to 0.12 milliequivalent was adsorbed by 1 g. of charcoal.

From these experiments it may be inferred that the acid or acid oxide present on the C400 decomposes slowly at temperatures between 575 and 600°. At higher temperatures this decomposition takes place much more rapidly.

Properties of the "Acid Charcoal."—In many respects the properties of the charcoal the surface of which has an acid nature (C400) are quite different from those of carbon activated at 900 to 1000° (C950). C400 adsorbs strong bases; C950 does not, and may even give a negative adsorption. A suspension of C400 in water is negatively, a similar suspension of C950 is positively, charged.[3,6]

Hydrolytic Adsorption by C400.—If C950 is shaken with an inorganic salt solution a hydrolytic adsorption of the acid takes place and the filtrate

[5] In the following work ash-free Nuchar was used. Samples freshly heated for six hours at 950° will be designated as C950; those treated afterward for six hours in oxygen at 400° as C400.

[6] S. Roychoudhury, *J. Ind. Chem. Soc.*, **8**, 433 (1931).

has an alkaline reaction (Bartell and Miller[1]). If C400 is shaken with an inorganic salt solution, the filtrate has an acid reaction. 1.5 g. of C400 was shaken with 50 cc. of 0.01 *N* sodium chloride.

The filtrate had a P_H of 3.5, 25 cc. taking about 8.2 cc. of 0.01 *N* barium hydroxide with phenolphthalein as an indicator. The color change was very vague, although the filtrate had been freed from carbon dioxide; near the end-point the appearance of a slight brownish turbidity was noticed. The small hydrogen-ion concentration and the high titration acidity together with the vague color change of the indicator show the presence of a very weak acid in the filtrate. The acid reaction found in the filtrate therefore cannot be attributed to a hydrolytic adsorption of the base by C400, liberating an equivalent amount of hydrochloric acid. By a chloride titration of the filtrate it was shown that only a slight trace of the anion was adsorbed by the charcoal (0.02 milliequivalent Cl by 1 g.). The experiments show conclusively that part of the acid substance present on the surface of C400 is removed by shaking with a salt solution. It is of interest to note that even the extract of C400 in pure water had an acid reaction: 1 g. of C400 was shaken with 50 cc. of conductivity water, the filtrate had a P_H of 4.3 (the original water of 5.8); 25 cc. took 1 cc. of 0.01 *N* sodium hydroxide with phenolphthalein as an indicator (vague color change). From these and other experiments it is inferred that there is a definite chemical compound with acid properties present at the surface of C400. Attempts to identify the nature of this acid have failed so far; larger quantities of material are required for this purpose.

Adsorbent Properties of C400 as Compared with those of C950 toward Acids.—The results of a few adsorption experiments are given in Table V. A more detailed report of the adsorption of organic acids by C400 and C950 with regard to the applicability of Traube's rule will be given in a later communication.

TABLE V

ADSORPTION OF ACIDS BY C400 AND C950

Amount of charcoal used, g.	Solution used in adsorption experiment	Milliequivalents of acid adsorbed by 1 g. C400	C950
0.25	50 cc. 0.01 *N* hydrochloric acid	0.00	0.41
.5	50 cc. 0.01 *N* hydrochloric acid	− .01	.36
.25	50 cc. 0.01 *N* sulfuric acid	− .08	.57
.25	50 cc. 0.01 *N* molar phosphoric acid	− .02	.30 (m. mols.)
.25	50 cc. 0.01 *N* acetic acid	− .04	.81

The apparent slight negative adsorption of the acids by C400 has to be attributed to the extraction of some of the acid from the surface of the charcoal. By a chloride determination in the filtrate it was shown that no hydrochloric acid was adsorbed by C400. By heating the latter product for twenty-four hours in a vacuum at 620°, it assumed the properties of

C950. The acid had been removed from the surface and it adsorbed inorganic and organic acids almost to the same extent as C950.

The adsorbent properties of C400 and C950 toward iodine were also determined. The adsorption by the former was distinctly less than that by the latter, but the difference was of a quite different order than that of the acids.

Peroxide in C950 and C400.—A. B. Lamb and L. W. Elder, Jr.,[7] found that the extract obtained by shaking dilute sulfuric acid with activated coconut charcoal contained a trace of peroxide. The filtrate obtained by us after shaking C950 and C400 with *N* sulfuric acid also contained a trace of peroxide, as shown by the potassium iodide–starch test; the reaction in the filtrate of C400 being distinctly less intense than that in the filtrate of C950. The same results were obtained in the filtrates obtained by successive extractions, but the difference in behavior between both types of charcoal was very small.

Catalytic Effect of Charcoal on Oxidation by Oxygen.—It is well known that charcoal promotes oxidation. A. Kutzelnigg[8] showed that "carbo medicinalis Merck" (ash 2.53%) favors the air oxidation of potassium ferrocyanide. The experiments with this reagent can be conducted in a simple way; it appeared, however, that the results are very much dependent upon the P_H of the solution. In preliminary experiments 0.25 g. of C400 and of C950, respectively, were shaken for fifteen minutes with 50 cc. of a freshly prepared 0.05 molar ferrocyanide solution in conductivity water. In 25 cc. of filtrate the ferrocyanide content was determined iodimetrically. The blank after the same time of shaking required 1.75 cc. 0.01 *N* thiosulfate, the filtrate of C950 0.83 cc., that of C400 4.03 cc. of 0.01 *N* reagent. The conclusion that C400 promotes the air oxidation of ferrocyanide more than C950 is not warranted, as is shown below. The difference in the behavior between the two kinds of charcoal is explained by the fact that a hydrolytic adsorption takes place on shaking the ferrocyanide with C950, whereby the solution becomes alkaline, whereas the C400 gives the solution a distinct acid reaction. In order to get a comparable result, 0.25 g. of charcoal with 50 cc. of the solution was first shaken for thirty minutes, then transferred into glass cells through which purified oxygen gas was bubbled with a velocity sufficient to keep the charcoal in suspension for one hour. In order to have the same conditions, the suspension of C400, that of C950 and the blank were placed in series one after the other. The results are given in Table VI.

The speed of oxidation of ferrocyanide by oxygen increases with decreasing P_H; charcoal activated at 900–1000° promotes this oxidation, whereas C400 hardly has any effect. The acid adsorbed on the surface of

[7] Lamb and Elder, Jr., THIS JOURNAL, **53**, 157 (1931).

[8] A. Kutzelnigg, *Ber.*, **63B**, 1753 (1930).

the latter therefore either spoils its oxygen electrode function or decreases the adsorption of free oxygen.

If the C400 was heated for ten hours at 620° in vacuum it acquired the same promoting effect as C950. The properties of the latter did not change on heating for ten hours at 600° in a vacuum.

TABLE VI

PROMOTING ACTION OF C950 AND C400 ON OXIDATION OF FERROCYANIDE BY OXYGEN

Composition of solution containing 0.025 molar ferrocyanide	*P*H of mixture	Cc. of 0.01 *N* thiosulfate by 25 cc. of filtrate C400	C950	Blank
0.05 *N* HCl	Appr. 1.5	16.90	67.90	10.32
0.1 *N* acetic acid	Appr. 3.0	15.23	63.91	16.31
Phthalate buffer	3.0	12.50	55.60	13.03
Phthalate buffer	4.0	10.00	46.72	9.95
Phthalate buffer	5.0		23.40	5.27
Phthalate buffer	5.0	6.00	26.97	6.25
Phthalate buffer	6.0	...	30.65	4.40
Phosphate buffer	6.0	...	26.97	6.25
Phosphate buffer	6.0	...	27.91	3.00
Phosphate buffer	7.0	...	16.20	1.45
Phosphate buffer	8.0	...	5.53	1.37

Decomposition of Sodium Thiosulfate in the Presence of C400 and C950.—It has been noticed by I. M. Kolthoff[9] that charcoal activated at high temperatures (900°) promotes the decomposition of thiosulfate in its aqueous solutions. A 0.01 *N* sodium thiosulfate solution in a buffer with a *P*H of 6 is stable for a long time; if shaken for twenty-four hours with active charcoal (C900) no thiosulfate is present in the filtrate as indicated by the titration with iodine. Thiosulfuric acid is removed from the solution by hydrolytic adsorption, the acid decomposes at the surface of the charcoal and another fraction of the thiosulfate will be hydrolytically adsorbed. It was of interest to compare the influence of C950 and C400 on the decomposition of thiosulfate.

The surface of C400 is covered with an acid and for this reason it may accelerate the decomposition of thiosulfate; on the other hand, this charcoal no longer shows any hydrolytic adsorption of the acid of the salt; 0.25 g. of charcoal was shaken with 50 cc. of 0.01 *N* sodium thiosulfate in

TABLE VII

INFLUENCE OF C400 AND C950 UPON DECOMPOSITION OF SODIUM THIOSULFATE

Composition of 0.01 *N* $Na_2S_2O_3$ solution	Time of shaking in hours	Cc. of 0.01 *N* iodine required by 25 cc. of filtrate C400	C950
Water	3	20.00	21.20
Water	24	13.00	6.75
Phosphate buffer *P*H 6.0	3	14.10	2.40
Phosphate buffer *P*H 6.0	24	0.25	0.00

[9] I. M. Kolthoff, *Rec. trav. chim.*, **48**, 298 (1929).

water or in a phosphate buffer with a P_H of 6.0. The blanks without charcoal did not change their strengths during the course of the experiments. A few results are given in Table VII.

In spite of the presence of the acid substance at the surface of the C400 the latter has less promoting effect upon the decomposition of thiosulfate than C900 has.

Summary

Charcoal activated at 900 to 1000° and heated thereafter in oxygen at 300 to 500° forms at its surface a definite chemical compound with acid character. The optimum temperature for preparing this "acid charcoal" is 400°. The acid on the surface is stable in a vacuum at temperatures as high as 500–550°. The "acid charcoal" is much more hygroscopic than the product activated at 950°.

The adsorbent and catalytic properties of the "acid charcoal" are quite different from those of carbon activated at 900–1000°.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN UNI-UNIVALENT CHLORIDE SOLUTIONS AT CONSTANT TOTAL MOLALITY

BY J. ERSKINE HAWKINS

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In this investigation the electromotive force of cells of the following types was measured

(A) $H_2/HCl(m_1)/AgCl/Ag$ and

(B) $H_2/HCl(m_1), MCl(m_2)/AgCl/Ag$

M represents either lithium, sodium or potassium and the total molality $m_1 + m_2 = 4.0$, 5.0 and 6.0.

Harned[1] has measured cells of the same type, using calomel electrodes instead of the silver–silver chloride electrodes and where $m_1 + m_2 = 0.1$, 1.0 and 3.0. All calculations at these concentrations are based on his measurements. Recalculations were carried out, due to a slight error which Harned[2] pointed out.

A few investigators[3] have measured cells of the type (A) containing pure hydrochloric acid at a concentration above three molal. However, no previous determinations have been made with cells of type (B), wherein $m_1 + m_2$ is greater than three molal.

[1] Harned, THIS JOURNAL, **48**, 326 (1926).

[2] Harned, *Trans. Am. Electrochem. Soc.*, **51**, 571 (1927).

[3] Ellis, THIS JOURNAL, **38**, 737 (1916); Linhart, *ibid.*, **39**, 2601 (1917); Randall and Young, *ibid.*, **50**, 989 (1928).

This investigation was carried out with the following purposes: (1) to test the linear variation of log γ of hydrochloric acid with concentration, at total electrolyte concentration above three molal; (2) to determine, over the wide range from 0.1 to 6.0 molal, how closely the measured values of the activity coefficients of hydrochloric acid in these solutions agree with those calculated by Hückel's theory.[4]

Experimental

The hydrogen electrodes were prepared by platinizing platinum foil in a solution of chloroplatinic acid containing 0.5 g. of platinum per 100 cc. of solution until a black deposit of platinum was obtained. Freshly prepared electrodes were used in every case.

The silver–silver chloride electrodes were prepared by baking two coatings of carefully prepared silver oxide paste on platinum spirals for three hours each, at a temperature of about 450°, followed by the electrolytic formation of the chloride in a three-fourths molal solution of hydrochloric acid. A current of two to three milliamperes was passed for two hours.

Reproducibility was obtained in almost every case within 0.2 millivolt and in many within 0.1 millivolt. The maximum variation was less than 0.5 millivolt, and this in only a few cases. Equilibrium was reached within from two to five hours.

The difficulty encountered in obtaining closer reproducibility was at first thought to be due to a solubility effect of the silver chloride electrodes. However, variations in the procedure failed to reveal this as the cause. For instance, the hydrogen electrode was permitted to come to equilibrium before the silver chloride electrode was inserted in the cell. The silver chloride electrode in question was thoroughly rinsed in a solution of the same composition as that in the cell just before it was introduced. Equilibrium was reached in a few minutes and no further change in the electromotive force of the cell was perceptible even after thoroughly shaking the cell. In other cases the solution to be used was made up and electrolytically deposited silver chloride was placed in the solution and allowed to stand for several days. During this period the mixture was shaken frequently, and then placed in the cell. These procedures gave entirely satisfactory check results on the same solution. Another point in favor of the absence of a large solubility effect is the fact that a comparison of the activity coefficients of hydrochloric acid at a concentration as high as 8.0 molal, determined by this method and by the vapor pressure method, shows a difference of only 0.25%, corresponding to a difference in electromotive force of less than 0.2 millivolt. This is an excellent agreement at such high concentration for two methods.

Any effect on the silver chloride electrode due to diffusion of hydrogen through the solution was found to be negligible. Many of the measurements were made in cells having a stopcock between the two compartments and these were kept closed except when making the readings. Values by this method checked those obtained when the stopcocks were left open during the entire experiment. Had there been any diffusion of hydrogen into the silver electrode compartment, the electromotive force would have been altered due to the reaction $AgCl + {}^1/_2 H_2 = Ag + H^+ + Cl^-$.

All measurements were made at 25 ± 0.02°.

Calculations and Discussion

1. After careful consideration of the data available the electromotive force of the cell H_2 (1 atm.) / HCl (0.1) / AgCl / Ag was taken to be

[4] Hückel, *Z. physik. Chem.*, **26**, 93 (1925).

0.35265 volt at 25°. The activity coefficient γ of hydrochloric acid was calculated from the observed electromotive force by the equation

$$\log \gamma = \frac{0.35265 - E}{0.1183} + (8.8976 - 10) - 1/2 \log m_1(m_1 + m_2) \qquad (1)$$

E is the observed electromotive force corrected to a hydrogen pressure of one atmosphere. The activity coefficient of 0.1 molal hydrochloric acid was taken to be 0.79. The values of E and γ calculated by this equation are given in Table I, columns 2 and 3, respectively.

TABLE I

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN ALKALI CHLORIDE MIXTURES AT CONSTANT TOTAL MOLALITY

Part 1. HCl–LiCl

(1) m_1	(2) E, volts	(3) γ obs.	(4) γ, Hückel	(5) γ
		$m_1 + m_2 = 0.1$		
0.01	...	0.786	0.781	0.790
.05	...	.788	.781	.789
		$m_1 + m_2 = 1.0$		
0.01	...	0.803	0.790	0.822
.10	...	.802	.789	.821
		$m_1 + m_2 = 3.0$		
0.01	...	1.302	1.310	1.409
.10	...	1.298	1.360	1.403
		$m_1 + m_2 = 4.0$		
0.10	0.2147	1.830	1.827	1.871
.50	.1735	1.824	1.824	1.874
1.00	.1578	1.823	1.821	1.863
2.00	.1390	1.827	1.810	1.860
3.00	.1289	1.777	1.802	1.846
		$m_1 + m_2 = 6.0$		
0.10	.1697	3.592	3.265	3.270
.50	.1285	3.582	3.258	3.270
1.00	.1113	3.536	3.255	3.265
2.00	.0945	3.469	3.230	3.244
3.00	.0856	3.365	3.210	3.228
4.00	.0793	3.325	3.197	3.210
5.00	.0742	3.259	3.182	3.190

Part 2. HCl–NaCl

		$m_1 + m_2 = 0.1$		
0.01	...	0.785	0.775	0.784
.05	...	.786	.777	.786
		$m_1 + m_2 = 1.0$		
0.01	...	0.765	0.725	0.757
.10	...	.766	.730	.762
.50	...	.782	.754	.786

TABLE I (*Continued*)

(1) m_1	(2) E, volts	(3) γ, obs.	(4) γ, Hückel	(5) γ
		$m_1 + m_2 = 3.0$		
0.01	...	1.085	1.060	1.114
.10	...	1.084	1.068	1.123
.50	...	1.106	1.102	1.156
1.00	...	1.135	1.146	1.200
2.00	...	1.224	1.238	1.290
		$m_1 + m_2 = 4.0$		
0.10	0.2311	1.330	1.324	1.390
.50	.1884	1.367	1.363	1.424
1.00	.1686	1.416	1.418	1.480
2.00	.1472	1.521	1.532	1.588
3.00	.1337	1.624	1.652	1.704
		$m_1 + m_2 = 5.0$		
0.10	.2133	1.683	1.652	1.720
.50	.1708	1.724	1.705	1.769
1.00	.1513	1.778	1.769	1.830
2.00	.1299	1.908	1.904	1.903
3.00	.1159	2.046	2.052	2.105
4.00	.1048	2.199	2.213	2.254
		$m_1 + m_2 = 6.0$		
0.10	.1962	2.145	2.064	2.138
0.50	.1536	2.197	2.120	2.190
1.00	.1342	2.263	2.210	2.266
2.00	.1127	2.435	2.368	2.423
3.00	.0989	2.599	2.550	2.590
4.00	.0877	2.799	2.738	2.778
5.00	.0785	2.998	2.944	2.978
6.00	.0703	3.207	3.170	3.190
		Part 3. HCl-KCl		
		$m_1 + m_2 = 0.1$		
0.01	...	0.778	0.769	0.777
.05	...	.782	.774	.781
.10	...	.790	.781	.788
		$m_1 + m_2 = 1.0$		
0.01	...	0.712	0.666	0.693
.10	...	.712	.676	.703
.50	...	.752	.723	.749
1.00	...	.806	.785	.816
		$m_1 + m_2 = 3.0$		
0.01	...	0.859	0.873	0.855
.10	...	.861	.835	.866
.50	...	.909	.888	.922
1.00	...	.963	.960	.994
2.00	...	1.123	1.123	1.180
3.00	...	1.311	1.340	1.382

TABLE I (*Concluded*)

(1) m_1	(2) E, volts	(3) γ, obs.	(4) γ, Hückel	(5) γ
		$m_1 + m_2 = 4.0$		
0.10	0.2474	0.969	0.978	1.005
.50	.2043	1.002	1.040	1.070
1.00	.1816	1.102	1.123	1.154
2.00	.1566	1.270	1.307	1.343
3.00	.1382	1.483	1.531	1.568
4.00	.1222	1.753	1.784	1.834
		$m_1 + m_2 = 5.0$		
1.00	.1709	1.213	1.293	1.318
2.00	.1450	1.422	1.504	1.530
3.00	.1266	1.660	1.750	1.778
4.00	.1096	2.005	2.038	2.070
5.00	.0955	2.358	2.378	2.420

In Fig. 1 the values of log γ are plotted against m_1. This definitely shows that the principle of the linear variation of log γ with concentration

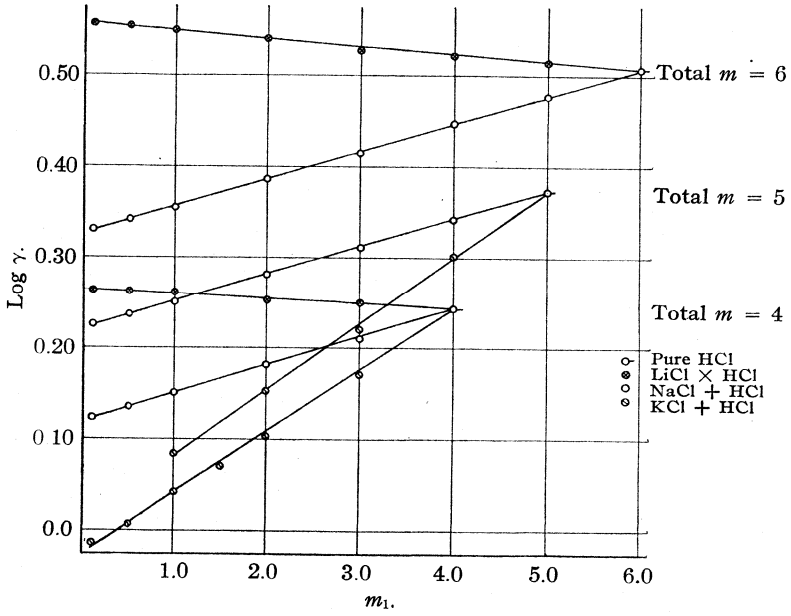

Fig. 1.—The linear variation of the log γ of hydrochloric acid with the concentration of hydrochloric acid at very high constant total molality.

of the hydrochloric acid, in mixtures with uni-univalent chlorides at constant total molality, holds at very high concentration as predicted by Harned. In addition, this plot distinctly shows that, above a total concentration of three molal, the activity coefficient of hydrochloric acid in

lithium chloride is greater than that of the pure acid at the same concentration. Although Hückel[4] discusses this case on page 141 of his article, no satisfactory explanation for this behavior is available. It is believed that a correct application of Scatchard's[5] treatment of the Debye theory will not predict this result. The author is convinced that it is illogical to assume that the activity of the lithium ion becomes greater with increase in salt concentration and decrease in acid concentration than it is in a pure salt solution. This would necessitate a greater activity for lithium chloride than for hydrochloric acid at the same concentration and such has not been shown to be the case.

2. Hückel's theoretical treatment[4] of concentrated solutions was tested. This procedure is briefly as follows. The activity coefficient of the acid was calculated by the equation

$$\log \gamma = \frac{-0.354\sqrt{2C_T}}{1 + A\sqrt{2C_T}} + B(2C_1) + B'(2C_T - 2C_1) - \log(1 + 0.002\, wm_T) \quad (2)$$

in which A, B and B' are constants. The points of measurements chosen for the determination of A corresponded to 0.1, 1.0 and 6.0 molal hydrochloric acid. The following are the values obtained for these constants: $A = 0.607$, $B = 0.091$, $B' = 0.055$, 0.073 and 0.091 for potassium, sodium and lithium chlorides, respectively. These values are somewhat different from those obtained by Harned[1] and by Scatchard.[6] This is of course due mainly to the fact that their values were derived from data covering a narrower range of concentration, and from an equation which is an approximation and cannot be expected to be exactly valid from 0.0 to 6.0 molal. C_T is the total molar concentration of the solution and C_1 is the molar concentration of the acid present. The values of C_T for the total concentrations from 0.1 to 3.0 molal were taken as published by Harned and Åkerlöf,[7] those for C_T of pure acid above 3.0 molal were calculated from the density data published in the "International Critical Tables,"[8] and for mixtures above 3.0 molal the densities were determined by use of a Mohr–Westphal balance at 25 ± 0.2° and C_T then calculated; w is the formula weight of water and m_T is the total molal concentration.

The values of γ determined by equation (2) are given in column 4 of Table I. A comparison with the experimental values (column 3) shows that about 75% of the observed values and those calculated by the Hückel equation agree within 3%. The greatest deviation (less than 10%) occurs in the lithium chloride–acid mixtures at a total concentration of 6.0 molal.

3. Another method was used to determine the constants of the Hückel equation, (2). The resulting values of γ are given in column 5 of Table I.

[5] Private communication 1925: *Physik. Z.*, **33**, 22 (1932).

[6] Scatchard, THIS JOURNAL, **47**, 2098 (1925).

[7] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[8] Vol. III, 1928, p. 54.

These values agree with the observed values almost as well as those calculated by the Hückel method, which are given in column 4.

It was assumed (1) that the actual volume occupied by a mole of water remained constant at each concentration of solution, (2) that the diameter of all ions was the same, (3) that there exists a physically homogeneous distribution of all ions, (4) that the shape of the ions is spherical, or that the effect of variation in shape is eliminated by assuming a solution in which the ions are spherical and have properties equivalent to those in the solution under consideration. The constants obtained from consideration of pure hydrochloric acid solutions were applied to the solutions containing the alkali chlorides.

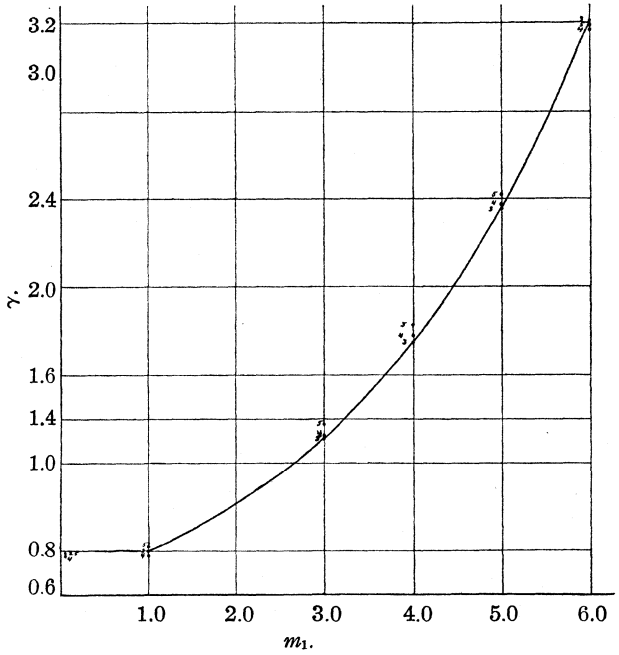

Fig. 2.—The activity coefficients of pure hydrochloric acid determined by various methods. The numbers correspond to the columns of Table I from which the data are taken.

The term "nearest distance of approach" of the ions is taken to mean the shortest distance between the centers of the nuclei of two ions of unlike charge. From consideration of the densities of solutions of hydrochloric acid it was found that the volume increase per mole of acid becomes constant with increase in concentration. This constant is 21.0 cc. per mole of hydrochloric acid. Dividing by $2 \times 6.06 \times 10^{23}$ gives 17.4×10^{-24} (approx.). From this the nearest distance of approach or apparent ionic

diameter, a, is found to be 3.22×10^{-8}, and the constant $A = a\sqrt{4\pi\epsilon^2 4N/D_0kT\ 1000}$, is 0.747 at 25°. The other constants of equation (2) were evaluated by the same procedure as in part 2. The values thus obtained are: $B = 0.0864$ and $B' = 0.0503$, 0.0698 and 0.0875 for potassium, sodium and lithium chlorides, respectively.

In Fig. 2 the activity coefficients of pure acid, determined by the various methods, are plotted against molality.

Summary

1. The electromotive force of hydrochloric acid–alkali chloride cells at constant total molality has been measured.

2. Various methods of calculating the activity coefficients of hydrochloric acid in alkali chloride mixtures have been used and a comparison of the results has been given.

3. It has been shown that the linear variation of log γ with concentration is valid at the high concentrations used.

4. An approximate simplified method for the determination of the constants of the Hückel equation has been used with satisfactory results.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE ACCURATE DETERMINATION OF CYANIDE BY DISTILLATION FROM SULFURIC ACID SOLUTION

BY H. ARMIN PAGEL AND WARNER CARLSON

RECEIVED APRIL 28, 1932 PUBLISHED DECEMBER 13, 1932

In a certain investigation in this Laboratory it became necessary to determine accurately alkali cyanide in the presence of relatively large amounts of chloride, bromide, nitrate or sulfate by distillation from moderately strong sulfuric acid solution. A large number of methods in use for industrial, agricultural and biological analysis involve the isolation of cyanide by distillation from sulfuric acid solution. In such cases, however, the highest degree of accuracy is rarely demanded. Roe[1] discourages the practice of distilling from strong acid solution, stating that (1) at higher temperatures there is a loss of hydrocyanic acid due to hydrolysis to ammonium formate; (2) the hydrocyanic acid is evolved too rapidly to be quantitatively absorbed in the alkaline absorbing solution.

No contradiction to Roe's statement, or data on either the maximum obtainable accuracy or the possible interference of large amounts of salts could be found, hence this investigation was carried out.

Materials and Apparatus.—All salts used in this work were reagent grade. Arbitrary strength (approx. 0.19 N) solutions of potassium cyanide

[1] J. H. Roe, THIS JOURNAL, **45**, 1878–1883 (1923).

were standardized daily against 0.2000 *N* silver nitrate, by the well-known Liebig–Denigès method as modified by Kolthoff.[2]

In order to duplicate conditions, the volume prior to titration was adjusted to 450 cc., both in standardization and in the analysis of the distillates. Conductivity water was used throughout. Distillation was carried out in a 500-cc. Pyrex distilling flask which was fitted with a two-holed rubber stopper carrying a thermometer and a glass tube drawn to a fine capillary extending to the bottom of the flask. A very gentle flow of air through the latter prevented any bumping or back suction during distillation. The hydrocyanic acid was absorbed in a relatively simple absorption apparatus. A wide-mouthed bottle, 5.5 cm. in diameter and 20 cm. in height, was fitted with a two-holed rubber stopper carrying a small (2.5 cm. diameter) inverted, long-stem funnel, so adjusted that the mouth of the funnel was fixed about 2 cm. from the bottom of the bottle. An auxiliary absorption tube consisting of a U-shaped three-bulb calcium chloride tube (Péligot type) was fitted to the other stopper hole. The funnel stem was fitted to a 16-cm. all-glass condenser, which was in turn connected to the side tube of the distilling flask. The rubber connections were of heavy-walled suction tubing, tightly wrapped with adhesive tape to ensure a very snug fit.

The alkaline absorption solution was prepared by diluting 15 cc. of 6 *N* sodium hydroxide to approximately 200 cc. A 100-cc. pressure operated pipet (with a highly constricted tip to assure uniform delivery) was used in measuring the cyanide portions.

Procedure.—The cyanide solution was pipetted directly into the distilling flask. The absorption apparatus and condenser were then connected to the flask and weighed amounts of the salts introduced, followed by water and 6 *N* sulfuric acid in rapid succession. (Total volume about 250 cc.) The stopper was immediately inserted and the flask thoroughly agitated until the salt had dissolved. The air flow through the ebullition tube was then started and the solution distilled at a moderate rate for a period of thirteen to fifteen minutes, after boiling had commenced. (From 60 to 80 cc. of solution distilled over during this time.)

Discussion

Series (A) and (B) show that very accurate and consistent results are obtained when the rate of heating up to the distillation temperature is rapid (five minutes). When heated about one-half as rapidly (Series (C)), the results in general are from 0.1 to 0.3% low. The conditions under which low results were obtained (Series (D)) would obviously be unwarranted in an actual determination by this method. Yet the results

[2] Kolthoff and Furman, "Volumetric Analysis (Practical Volumetric Analysis)," John Wiley and Sons, Inc., New York, 1929, Vol. II, p. 239.

RESULTS OBTAINED UNDER VARIOUS CONDITIONS

Salts added, g.	Error, %	Salts added, g.	Error, %	Salts added, g.	Error, %
(Series A)		(Series B)		8 NaCl	−0.30
6 NaCl	−0.02	6 NaCl	−0.11	8 NaCl	− .04
6 NaCl	.00	8 NaCl	− .02	8 NH_4Cl	− .19
6 NH_4Cl	− .02	8 NH_4Cl	+ .02	8 $(NH_4)_2SO_4$	− .08
6 KBr	.00	8 KBr	+ .02	8 $(NH_4)_2SO_4$	− .17
6 KBr	− .02	8 KBr	− .08	(Series D)	
10 $(NH_4)_2SO_4$	− .06	8 $(NH_4)_2SO_4$	.00	9 KBr	− .42
10 $(NH_4)_2SO_4$	− .15	8 NH_4NO_3	− .02	8 NaCl	− .59
7 NH_4NO_3	− .13	8 NH_4NO_3	+ .02	8 NaCl	− .51
7 NH_4NO_3	.00	(Series C)		8 $(NH_4)_2SO_4$	− .51
		8 NH_4NO_3	− .08		
		8 NH_4NO_3	− .17		

Series (A) and (B): 0.35 and 0.60 *N* excess H_2SO_4, respectively, heated to boiling in about five minutes. Series (C): 0.60 *N* excess H_2SO_4, heated to boiling in about eleven minutes. Series (D): 0.60 *N* excess H_2SO_4, heated very slowly to 95° and maintained at this temperature thirteen to fifteen minutes before distilling.

indicate that the loss due to hydrolysis should be negligible when the hydrocyanic acid is removed from solution in relatively much shorter time, as was done in Series (A) and (B).

A number of determinations were made in which the auxiliary absorbing tube was left off. In this case the inverted funnel was merely placed as usual in the open bottle. Losses ranging from 0.1 to 0.3% resulted.

Summary

1. Alkali cyanide in presence of large amounts of chloride, bromide, nitrate, or sulfate, may be determined accurately by distillation from moderately strong sulfuric acid solution, without loss due to hydrolysis or mechanical loss of hydrocyanic acid vapor.

2. The description of materials and apparatus used, procedure, and tabulated data, showing the effect of salts and of physical conditions, have been included.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 95]

THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE. AN APPLICATION OF THE EXTENDED DEBYE–HÜCKEL THEORY TO INTERPRETATION OF FREEZING POINT MEASUREMENTS

BY HUGH M. SPENCER

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Introduction

The importance of activity coefficients of potassium chloride solutions to questions of electrode potentials has made desirable a reinterpretation of the values hitherto available. The more recent values are by Scatchard[1] (1925, based (1) on e. m. f. measurements of MacInnes and Parker 1925, and of Beattie 1920, (2) on freezing point measurements, not corrected for heats of dilution, (3) on vapor pressure measurements of Lovelace, Frazer and Sease at 20°), Randall and White (1926, based on vapor pressure measurements of Lovelace, Frazer and Sease interpreted with the help of freezing point measurements), Jones and Bury (1927, based on their freezing point measurements, corrected for the heats of dilution)[2] and Harned (1929, based on e. m. f. measurements of concentration cells with intermediate amalgam electrodes).

Though the Hückel equation

$$\log \gamma = -\frac{0.356\sqrt{2c}}{1 + A\sqrt{2c}} + 2Bc - \log(1 + 0.036m) \qquad (1)$$

certainly seems to serve admirably as an empirical expression for representation of activity coefficients as a function of concentration for solutions of moderate and high concentration, the assumptions upon which the equation was derived are no longer valid at these concentrations, and in fact at lower concentrations where the assumptions are probably valid[3] the extended Debye–Hückel theory for symmetrical valence type salts leads to another form[4]

[1] (a) G. Scatchard, THIS JOURNAL, **47**, 648 (1925); (b) M. Randall and A. McL. White, *ibid.*, **48**, 2514 (1926); (c) E. R. Jones and C. R. Bury, *Phil. Mag.*, [7] **3**, 1032 (1927); (d) H. S. Harned, THIS JOURNAL, **51**, 416 (1929).

[2] Some gross error was introduced in correcting for the heat of dilution, resulting in too large corrections.

[3] T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

[4] The first terms of Equations 1 and 2 are the same. Harned found for potassium chloride $A = 0.76$, $B = 0.0204$ and hence $a = 3.26$ Å. (This differs from the value selected in the present paper.) For 0.01 M KCl, by Equation 1, $\log \gamma = 0.04528 + 0.00041 - 0.00016 = -0.04503$; $\gamma = 0.9015$ and by Equation 2, $\log \gamma = -0.04528 - 0.00057 - 0.00003 = -0.04588$; $\gamma = 0.8997$. Thus the terms added by the complete expansion of the Debye–Hückel equation have the same sign as the limiting effect term whereas the net value of the added terms of the Hückel equation has opposite sign.

$$-\log \gamma = 1.53636 \left(\frac{z^2}{10^8 a}\right) \frac{x}{1+x} - 0.15382 \left(\frac{z^2}{10^8 a}\right)^3 10^3 \left[\frac{1}{2} X_3(x) - 2Y_3(x)\right] - 0.0770 \left(\frac{z^2}{10^8 a}\right)^5 10^5 \left[\frac{1}{2} X_5(x) - 4Y_5(x)\right] \quad (2)$$

These factors as well as the uncertainty that the cell reactions in the amalgam cells were purely the postulated ones made it appear unwise to accept the determination made by use of Equation 1. No satisfactory calculations of the activity coefficients from freezing point measurements with corrections for the heats of dilution have been made. The partial molal heats of dilution and the partial molal heat capacities necessary for such calculations have been determined by Lange and Monheim, Wüst and Lange and by Randall and Rossini, respectively.[5] The freezing point determinations used include the recent ones of Karagunis, Hawkinson and Damköhler.[6]

These data have been treated according to the methods of Lewis and Randall and of Randall and White[7] with an added feature. Since the uncertainty in measurements of $j/m^{1/2}$ rapidly becomes very large as the dilution is increased as does that of j/m for non-electrolytes,[8] some guiding principle besides the theoretical limit at $m = 0$, was sought and found in theoretical values of j calculated by Gronwall, La Mer and Sandved's[3] extension of the Debye–Hückel theory.

Theoretical $j/zm^{1/2}$ and Experimental $j/m^{1/2}$ for Potassium Chloride.—Values of $j/m^{1/2}$ were calculated[9] for each set of experimental data and plotted as ordinate *versus* $m^{1/2}$ as abscissas. The values from the work of Jones and Bury, Karagunis, Hawkinson and Damköhler, Adams, Hovorka and Rodebush and Menzel fall on a smooth curve mostly within the limits of error caused by the form of the function. Even though the limiting value of $j/m^{1/2}$ be used, an undesirable amount of uncertainty remains in the course of the curve between the point where the form of the function makes its experimental value too uncertain, and infinite dilution.

[5] E. Lange and J. Monheim, *Z. Elektrochem.*, **35,** 29 (1929), and *Z. physik. Chem.*, [A] **150,** 349 (1930); Wüst and E. Lange, *ibid.*, **116,** 161 (1925); M. Randall and F. D. Rossini, THIS JOURNAL, **51,** 323 (1929). See also F. D. Rossini, *Bur. Standards J. Research*, **7,** 54 (1931).

[6] (a) L. H. Adams, THIS JOURNAL, **37,** 481 (1915); (b) F. Flügel, *Z. physik. Chem.*, **79,** 585 (1912); (c) F. Hovorka and W. H. Rodebush, THIS JOURNAL, **47,** 1614 (1925); (d) H. Jahn, *Z. physik. Chem.*, **50,** 144 (1904); **59,** 35 (1907); (e) E. R. Jones and C. R. Bury, *Phil. Mag.*, [7] **3,** 1032 (1927), Ref. 1c; (f) G. Karagunis, A. Hawkinson and G. Damköhler, *Z. physik. Chem.*, [A] **150,** 433 (1930); (g) H. Menzel, *Z. Elektrochem.*, **33,** 68 (1927); (h) A. D. C. Rivett, *Z. physik. Chem.*, **80,** 543 (1912); (i) W. H. Rodebush, THIS JOURNAL, **40,** 1204 (1918).

[7] (a) G. N. Lewis and M. Randall, "Thermodynamics," The McGraw-Hill Book Co., New York, 1923, p. 348; (b) M. Randall and A. McL. White, THIS JOURNAL, **48,** 2514 (1926).

[8] W. D. Harkins and R. W. Wampler, THIS JOURNAL, **53,** 850 (1931).

[9] $j = 1 - \vartheta/2 \cdot 1.858m$.

Theoretical values of j, using round values of "a" for various values of $x(=\kappa a)$, and thence $j/zm^{1/2}$ as a function of $zm^{1/2}$ for round values of "a," have been calculated from Equation 113 and Tables II, III and IV of Gronwall, La Mer and Sandved. The coefficients of the terms of the equation are different from those given by Gronwall, La Mer and Sandved, due to the use of Birge's[10] values of $k = 1.3709 \times 10^{-16}$, 0°C. = 273.18°K., $\epsilon = 4.770 \times 10^{-10}$ and the average of Drude's and Wyman's[11] determinations of the dielectric constant. The change of temperature and consequently of dielectric constant is allowed for by use of three sets of coefficients shown in Table I.

TABLE I

COEFFICIENTS OF TERMS

Range of $zm^{1/2}$	1	2	3
0 to 0.16	3.4480	0.16397	0.07798
0.16 to 0.41	3.4469	.16381	.07785
0.41 to 1.00	3.4451	.16355	.07765

For the most dilute concentrations, then

$$= 3.4480 \frac{z^2}{10^8 a}\left[\frac{2}{x} - \frac{1}{1+x} + \frac{2}{x^2}\ln(1+x)\right] - 0.16397\left(\frac{z^2}{10^8 a}\right)^3 10^3\,[X_3(x) - 6Y_3(x)] - 0.07798\left(\frac{z^2}{10^8 a}\right)^5 10^5\,[X_5(x) - 10Y_5(x)] \quad (3)$$

The first bracket term reduces to $2Y_1(x)$-$X_1(x)$, where $X_1(x) = 1/(1+x)$. Values of the bracket terms were calculated, the first, from a reciprocal table and Table II, Gronwall, La Mer and Sandved, the second and third, from Tables III and IV of the same paper, respectively, for round values of "a" at various values of x.

Table II contains the values of j, $j/zm^{1/2}$ and $zm^{1/2}$ resulting from Equation 3. The values of $j/zm^{1/2}$ were plotted as ordinates against $zm^{1/2}$ as abscissas, as in Fig. 1, with the same scales as used in plotting measured $j/m^{1/2}$ *vs.* $m^{1/2}$ for potassium chloride solutions. By superimposition of the family of the theoretical curves over the measured one, it was estimated that the parameter "a" = 3.6 Å. would coincide with the curve of measured values in the region of lowest concentrations for which the function $j/m^{1/2}$ can be obtained with reasonable accuracy. Values of j, $j/zm^{1/2}$ and $zm^{1/2}$ were calculated for this value of "a" and added to the curve of measured values. These values along with the limiting value of $j/zm^{1/2} = 0.3726$ were used in extrapolating to infinite dilution.

The provisional values of activity coefficients, γ', were determined by the method of Randall[12] by which

[10] R. T. Birge, *Rev. Modern Physics*, **1**, 1 (1929).

[11] (a) P. K. L. Drude, *Ann. Physik*, **59**, 61 (1896); $D = 88.23 - 0.4044t + 0.001035t^2$; (b) J. Wyman, *Phys. Rev.*, **35**, 613 (1930); $D = 78.54[1 - 0.0046(t-25) + 0.000008(t-25)^2]$.

[12] M. Randall, THIS JOURNAL, **48**, 2512 (1926).

TABLE II

THEORETICAL VALUES OF j, $j/zm^{1/2}$ AND $zm^{1/2}$

	a in Å.	1	2	3	4	5	6	7	8	3.6
$x = 0.01$	j	0.0121932	0.0057351	0.0037919	0.0028365	0.0022665	0.0018875	0.0016172	0.0014147	0.0031537
	$j/zm^{1/2}$	.3952	.3718	.3687	.3677	.3673	.3670	.3669	3668	.3680
	$zm^{1/2}$	.03086	.01543	.01029	.00771	.00617	.00514	.00441	.00386	.00857
$x = 0.02$	j	.025345	.011381	.007512	.005608	.004477	.003727	003193	.002792	.006238
	$j/zm^{1/2}$	.4107	.3689	.3652	.3635	.3628	.3624	.3622	.3619	.3639
	$zm^{1/2}$	.06171	.03086	.02057	.01543	.01234	.01029	.00882	.00771	.01764
$x = 0.03$	j	.038966	.017042	.011149	.008311	.006630	.005517	.004725	.004132	.009244
	$j/zm^{1/2}$	.4210	.3687	.3613	.3591	.3581	.3576	.3573	.3571	.3595
	$zm^{1/2}$	.09256	.04628	.03086	.02314	.01851	.01543	.01322	.01157	.02571
$x = 0.04$	j	.052622	.022512	.014672	.010924	.008711	.007246	.006204	.005425	.012159
	$j/zm^{1/2}$	.4264	.3648	.3566	.3541	3529	.3523	.3519	.3517	.3547
	$zm^{1/2}$	.12342	.06171	.04114	.03086	.02468	.02057	.01763	.01543	.03428
$x = 0.05$	j	.065298	.027847	.018117	.013478	.010743	.008935	.007649	.006688	.015013
	$j/zm^{1/2}$	.4226	.3610	.3523	.3495	.3482	.3475	.3471	.3468	.3504
	$zm^{1/2}$	.15427	.07714	.05142	.03857	.03086	.02571	.02204	.01928	.04285
$x = 0.1$	j	.127538	.052545	.033963	.025210	.020074	.016686	.014280	.012482	.028097
	$j/zm^{1/2}$	.4134	.3406	.3302	.3268	.3253	.3245	.3240	.3236	.3278
	$zm^{1/2}$	.3085	.1543	.1029	.0771	.0617	.0514	.0441	.0386	.0857
$x = 0.15$	j	.174541	.073551	.047609	.035343	.028141	.023393	.020018	.017498	.039392
	$j/zm^{1/2}$	.3771	.3178	.3086	.3055	.3040	.3033	.3028	.3025	.3064
	$zm^{1/2}$	.4268	.2314	.1543	.1157	.09256	.0771	.0661	.0579	.1286
$x = 0.2$	j	.208936	.091403	.059368	.044132	.035155	.029227	.025016	021869	.049172
	$j/zm^{1/2}$	.3386	.2962	.2886	.2861	.2848	.2842	.2838	.2835	.2869
	$zm^{1/2}$	.6171	.3086	.2057	.1543	.1234	.1029	.0882	.0771	.1714
$x = 0.3$	j	.253181	.119348	.078275	.058332	.046524	.038717	.033151	.028988	.064958
	$j/zm^{1/2}$	.2735	.2579	.2537	.2521	.2513	.2510	.2507	.2505	.2526
	$zm^{1/2}$	.9256	.4628	.3086	.2314	.1851	.1543	.1322	.1157	.2571
$x = 0.4$	j	.281187	.139955	.092479	.069138	.055209	.045961	.039370	.034436	.076935
	$j/zm^{1/2}$	.2278	.2268	.2248	.2241	.2237	.2234	.2233	.2232	.2244
	$zm^{1/2}$	1.2342	.6171	.4117	.3086	.2468	.2057	.1763	.1543	.3428
$x = 0.5$	j	0.301863	.155393	.103317	.077408	.061877	.051544	.044165	.038637	.086080
	$j/zm^{1/2}$	.1958	.2015	.2009	.2007	.2005	.2005	2004	.2004	.2009
	$zm^{1/2}$	1.5427	.7714	.5142	.3857	3086	.2571	.2204	.1928	.4285
$x = 0.6$	j	0.318760	.167132	.111627	.083732	.067019	.055848	.047868	.041883	.093034
	$j/zm^{1/2}$	.1722	.1805	.1809	.1809	.1810	.1810	.1810	.1810	.1809
	$zm^{1/2}$	1.8513	.9256	.6171	.4628	.3703	.3086	.2645	.2314	.5142

$$\log \gamma' = -j/2.3026 - \frac{2}{2.3026}\int_0^m j/m^{1/2}\, dm^{1/2} + 0.000125\int_0^m \frac{\vartheta}{m}\, d\vartheta \qquad (4)$$

Values of ϑ/m were plotted against ϑ and values of the function $0.000125\int_0^m \vartheta/m\, d\vartheta$ were determined graphically for round values of concentration. These are given in Table III, along with the values of $-\frac{j}{2.3026} - \frac{2}{2.3026}\int_0^m \frac{j}{m^{1/2}}\, dm^{1/2}$, $\log \gamma'$ and γ' at round values of concentration.

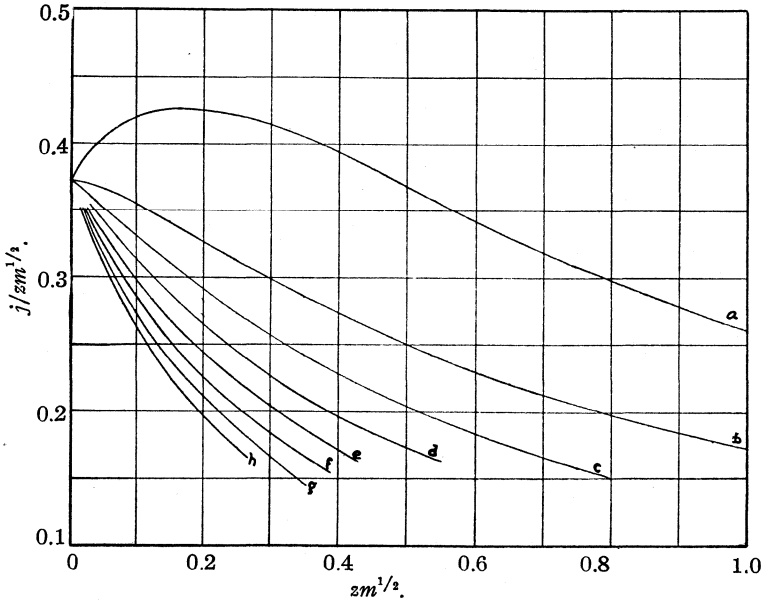


Fig. 1.—Theoretical $j/zm^{1/2}$ *vs.* $zm^{1/2}$ curves: a, 1 Å.; b, 2; c, 3; d, 4; e, 5; f, 6; g, 7; h, 8 Å.

Table IV contains the values used in the determination of the corrections due to the heat of dilution.

$$\log \gamma = \log \gamma' - 27.754\int_0^m \frac{1}{m}\, dx$$

where $x = -\overline{L}_{1(298)}y + (\overline{C}_{p_1} - \overline{C}_{p_1^0})z$, y and z being temperature functions defined by Lewis and Randall.[7a] (Note other use of x and z.) The values of $\overline{L}_1$, the partial molal heat content of water in potassium chloride solutions at 25°, are by Lange and Monheim, those of the partial molal heat capacity for the solvent less that of pure water are by Randall and Rossini.[5] The values of the function $-27.754\int_0^m (1/m)\, dx$ were determined graphically and are included in Table IV along with the corrected values of $-\log \gamma$ and γ.

TABLE III

PROVISIONAL VALUES OF ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTIONS

m	$m^{1/2}$	$-\frac{j}{2.3026}$	$-\frac{2}{2.3026}\int_0^m j/m^{1/2}\,dm^{1/2}$	$1.25\times10^{-4}\int_0^m \vartheta/m\,d\vartheta$	$\log\gamma'$	γ'
0	0	0	0		0	1
0.001	0.0316	−0.00489	−0.01000		−0.01489	0.9663
.002	.0447	− .00678	− .01402		− .02080	.9532
.005	.0707	− .01031	− .02174	0.00001	− .03204	.9289
.01	.1000	− .01392	− .03020	.00002	− .04410	.9034
.02	.1414	− .01848	− .04129	.00003	− .05974	.8715
.05	.2236	− .02586	− .06153	.00008	− .08731	.8179
.1	.3162	− .03203	− .08096	.00015	− .11284	.7712
.2	.4472	− .03836	− .10517	.00029	− .14324	.7358
.35	.5916	− .04376	− .12815	.00057	− .17134	.6740
.5	.7071	− .04720	− .14436	.00071	− .19085	.6444
.75	.8660	− .05089	− .16424	.00103	− .21410	.6108
1.0	1.0000	− .05346	− .17917	.00137	− .23126	.5871
1.25	1.1180	− .05496	− .19127	.00169	− .24454	.5695
1.5	1.2247	− .05569	− .20138	.00201	− .25506	.5559

Discussion of Results

Gronwall, La Mer and Sandved probably had a network plot of j as a function of x for the two sets of parameters "a" and $z\kappa$ for the solution of their Equation 113. Their treatment would undoubtedly lead to satisfactory values of $\vartheta_{(obs.)} - \vartheta_{(calcd.)}$, and thus of "$a$," if applied in the range for which the experimental data and the assumptions underlying the theory are sufficiently accurate, and one could calculate log γ in the very dilute range by Equation 2. However, if one were using the freezing point data for the determination of activity coefficients, the experimental data would be cast into the $j/zm^{1/2}$ *vs.* $m^{1/2}$ form for the range above which the assumptions of the theory are not expected to be valid, so this should prove the simpler method. The theoretical $j/zm^{1/2}$ *vs.* $zm^{1/2}$ curve can of course be used for any symmetrical valence type salt.

A plot of the function $-27.754\int_0^m (1/m)\,dx$ against molality shows that the correction for the heat of dilution lowers the activity coefficient at concentrations below about 0.12 M for potassium chloride.

The data of Harned for the cell

Ag, AgCl(s), KCl(m), K_xHg, KCl(0.1 M), AgCl(s)Ag

on which his values of the activity coefficient were based have been put into the form[13]

$$\log\gamma + \text{const.} = -\frac{E}{0.11831} - \log m \pm$$

[13] M. Randall, *Trans. Faraday Soc.*, **23**, 502 (1927).

TABLE IV

CORRECTIONS DUE TO HEATS OF DILUTION AND FINAL VALUES OF THE ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°

m	ϑ	$\bar{L}_1$	$\bar{C}_{p_1} - \bar{C}_{p_1}^0$	$-y\bar{L}_1$	$+z(\bar{C}_{p_1} - \bar{C}_{p_1}^0)$	x	$\frac{1}{m}$	$-27.754\int_0^m \frac{1}{m}\,dx$	$-\log \gamma'$	$-\log \gamma$	γ
0.001									0.01489		0.9663
.002									.02080		.9532
.005									.03204		.9289
.01	0.037	−0.0027	−0.0002	+0.00000018	−0.00000017	+0.00000001	100	−0.00006	.04410	0.04416	.9033
.02	.071	− .0061	− .0004	+ .00000041	− .00000034	+ .00000007	50	− .00017	.05974	.05991	.8711
.05	.171	− .0161	− .0009	+ .00000109	− .00000077	+ .00000032	20	− .00044	.08731	.08775	8171
.1	.342	− .0223	− .0019	+ .00000152	− .00000169	− .00000017	10	− .00026	.11284	.11310	7707
.2	.677	+ .0110	− .009	− .00000076	− .00000819	− .00000895	5	+ .00148	.14324	.14176	.7383
.35	1.330	+ .27	− .020	− .0000192	− .0000194	− .0000386	2.86	+ .00454	.17134	.16680	.6811
.5	1.655	+ .76	− .034	− .0000547	− .0000336	− .0000883	2	+ .00780	19085	.18305	.6561
.75	2.464	+2.23	− .063	− .0001658	− .0000668	− .0002326	1.33	+ .01262	.21410	.20148	.6288
1.	3.265	+3.95	− .099	− .0003031	− .0001109	− .0004140	1	+ .01845	.23126	.21281	.6126
1 25	4.066	+5.95	− .141	− .000471	− .0001677	− .000639	0.8	+ .02407	.24454	.22047	.6019
1.5	4.866	+8.22	− .187	− .000671	− .0002340	− .000905	.667	+ .02948	.25506	.22558	.5949

and plotted as abscissas against $m^{1/2}$ as ordinate, and compared with a plot of log γ *vs.* $m^{1/2}$ from freezing point measurements. It is scarcely possible to superimpose as much of the first curve as that between two concentrations on the second curve. In view of the forthright thermodynamic character of the freezing point method involving, besides inaccuracy of data, only the assumption[14] of constancy of $\overline{C}_{p_1}$-$\overline{C}_{p_1}^0$ it appears that the cell reaction is not purely the one postulated. If temperature coefficients of the cell reaction were available, a test of the purity of reaction could be made by comparison of the ΔH's with thermochemical values.

Summary

1. The activity coefficients of potassium chloride in aqueous solutions at 25° have been determined from freezing point measurements including the recent ones by Jones and Bury and by Karagunis, Hawkinson and Damköhler. Corrections for the heats of dilution have been made.

2. Theoretical values of j, $j/zm^{1/2}$ and $zm^{1/2}$ for symmetrical valence type salts have been calculated from the extension of the Debye–Hückel theory by Gronwall, La Mer and Sandved and offer a satisfactory guide for extrapolating from the region where the function $j/zm^{1/2}$ becomes difficult or impossible to measure accurately, to infinite dilution.

UNIVERSITY, VIRGINIA

[14] Undoubtedly this assumption is not strictly valid. From the data assembled by Awbery ["International Critical Tables," Vol. V, p. 115] and Rossini's approximate equations for $\overline{C}_{p_1} - \overline{C}_{p_1}^0$ (Ref. 5), one finds for 0.5551 *M* KCl $-(\overline{C}_{p_1} - C_{p_1}^0)$ at 18, 21.5 and 25° equal to 0.076, 0.065 and 0.065, for 1.110 *M* KCl, 0.155, 0.155 and 0.167, and for 1.665 *M* KCl, 0.203, 0.203 and 215 cal. mole^{-1} deg.$^{-1}$, respectively. Thus over this smaller range of temperature $\overline{C}_{p_1} - \overline{C}_{p_1}^0$ is practically independent of the temperature, though the values at 25° do not agree with those derived without using equations by Randall and Rossini. The value of the correction is believed not to be seriously affected by this uncertainty.

Since this paper was written Saxton and Smith [THIS JOURNAL, **54**, 2626 (1932)] have reported the results of their accurate measurements of the boiling points of potassium chloride solutions. They use the same values of $\overline{C}_{p_1} - \overline{C}_{p_1}^0$ at 25° and slightly different values of L_1 in correcting their activity coefficients to 100°. It is interesting to note that by assuming that $\overline{C}_{p_2} - \overline{C}_{p_2}^0$ is also independent of temperature, they find the activity coefficients at 25° by Harned[1d] lead to values at 100° in good agreement with their values from boiling point measurements.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

REDUCTION OF PALLADIUM OXIDE BY CARBON MONOXIDE[1]

BY PAUL V. MCKINNEY

RECEIVED JUNE 11, 1932 PUBLISHED DECEMBER 13, 1932

In a previous article Taylor and McKinney[2] reported their observation that a sample of palladium oxide was not noticeably reduced by carbon monoxide at temperatures below 100°. Since oxide from the same preparation was reduced readily by hydrogen at 25° this fact appeared to be an exception to the generalization of Wright and Luff[3] and the experiments of Fay, Seeker, Lane and Ferguson.[4] A review of the data of these authors shows that in general carbon monoxide reduction starts at lower temperatures than the reduction with hydrogen in accordance with the heat of formation of water, and of carbon dioxide from the monoxide and oxygen.

In agreement with the conclusions of Langmuir[5] concerning reactions producing heterogeneous solid phases,[6] the reductions of copper oxide by hydrogen and by carbon monoxide have been classified as reactions at an interface.[7] In contrast Benton and Emmett[8] find that the reduction of ferric oxide by hydrogen has the characteristic properties of Langmuir's heterogeneous reactions resulting in the formation of solid solutions. In the former type the amount of reduction increases to a maximum while with the latter the rate decreases continuously with time. In the temperature range from 100 to 138° the reduction of palladium oxide starts rapidly but in the course of two hours falls off to negligible rates. Above 156° the reaction proceeds to completion. The effects of carbon dioxide and of oxygen on the reduction have been studied. In the case of copper oxide oxygen retarded the reduction, whereas at all temperatures it was found to increase the amount of palladium oxide reduced. Metallic copper is a catalyst for the combination of carbon monoxide and oxygen while palladium is not active toward this reaction.

Experimental Method

Purified carbon monoxide was passed at the rate of 22.8 cc. (0° and 760 mm.) per minute over a charge of 2.3 g. of palladium oxide and any carbon dioxide in the exit gas

[1] Acknowledgment is made to the Faculty of the Department of Chemistry of Princeton University for their courtesy in permitting the author the use of the facilities of the Frick Chemical Laboratory during the preliminary part of this investigation.

[2] Taylor and McKinney, THIS JOURNAL, **53**, 3604 (1931).

[3] Wright and Luff, *J. Chem. Soc.*, **33**, 1, 504 (1878).

[4] Fay, Seeker, Lane and Ferguson, *Polytechnic Engineer*, **10**, 72 (1910).

[5] Langmuir, THIS JOURNAL, **38**, 2263 (1916).

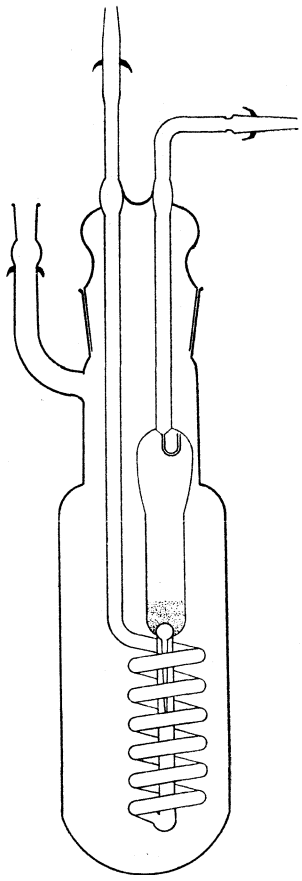
[6] Pease and Taylor, *ibid.*, **43**, 2179 (1921).

[7] Jones and Taylor, *J. Phys. Chem.*, **27**, 623 (1923).

[8] Benton and Emmett, THIS JOURNAL, **46**, 2728 (1924); Emmett, *Trans. Am. Electrochem. Soc.*, **51**, 207 (1927).

was determined. Palladium oxide was prepared from the chloride by the method of Shriner and Adams.[9] Unless otherwise stated the entire apparatus and sample were flushed with nitrogen for two to five hours before each determination, the nitrogen being purified from traces of oxygen. Carbon monoxide was prepared by dropping formic acid on hot sulfuric acid, and was stored over water in a forty liter carboy from which it was forced by water pressure as desired. Any oxygen introduced by the water was removed by a copper furnace, the carbon dioxide absorbed by askarite and the gas dried by phosphorus pentoxide. An electrolytic generator was used to introduce oxygen into the gas stream. When carbon dioxide was desired the mixed gases were passed over heated copper.

Analysis.—The extent of reduction was followed in each case by analysis for carbon dioxide in the exit gas by one of the following methods. In the early experiments the carbon dioxide was absorbed in barium hydroxide in a special bottle with a Jena glass filter plate and spiral. The excess alkali was then titrated by standard hydrochloric acid. To eliminate the back pressure on the flowmeter due to the absorption bubbler the following *physical method* of analysis was devised. A trap of known volume was constructed and attached to a constant volume manometer. The exit gases from the reaction vessel were passed for a definite time through the trap cooled in liquid air. The carbon monoxide was quickly pumped off and the liquid air removed, allowing the pressure of the carbon dioxide in the known volume to be determined at room temperature. When this method proved too slow to follow the course of the reduction during the first fifteen minutes a *flow method* was arranged. The gas from the reaction vessel was passed through a large liquid air trap to remove carbon dioxide, then through a coil to warm it again to room temperature and through a second calibrated flowmeter. By this means the reduction was followed for each minute. The only difficulty experienced by condensing the carbon monoxide occurred when fresh liquid air was used inadvertently, *i. e.*, hour old liquid air from a compressor which had been running for several hours.



Apparatus.—The apparatus was completely glass sealed except for the rubber stoppers sealed with picein wax on the carboy and carbon monoxide and oxygen generators, and two ground-glass seals as noted below. In order to determine the possible effect of vapors from the vacuum stopcock grease or the paraffin oil used in the flowmeter one experiment at 100° was performed with liquid air surrounding a safety trap placed just before the reaction vessel. Since the results were identical with other runs at 100° this precaution was not subsequently observed. The fineness of the palladium oxide as a powder caused great difficulty in any method of supporting it on glass wool, asbestos or constrictions in the tube. The reaction vessel was then constructed as shown in the diagram using no other material than Pyrex glass. If there was a sudden surge of the gas when nitrogen or carbon mon-

[9] Shriner and Adams, THIS JOURNAL, **46**, 1683 (1924).

oxide was turned on or in changing from one analysis vessel or method to another, the wider expansion chamber above the charge allowed the powder to lift and release the pressure around itself. The fine jet at the top cut down the velocity of the gas flow in these sudden spurts, preventing the powder from being blown from the reaction vessel. The present design has several advantages over one recently described[10] to overcome the same difficulties in that the unknown volume of gas in the region of the temperature fluctuations is less, the inert volume of the vessel is much less, ensuring more immediate removal of reaction products from the reaction vessel, and finally the reacting gas is preheated and except for channeling flows up around the entire charge. In addition interchangeable ground-glass seals were provided to connect the reaction vessel and also allow the introduction of the copper furnace between it and the flowmeter when carbon dioxide was desired.

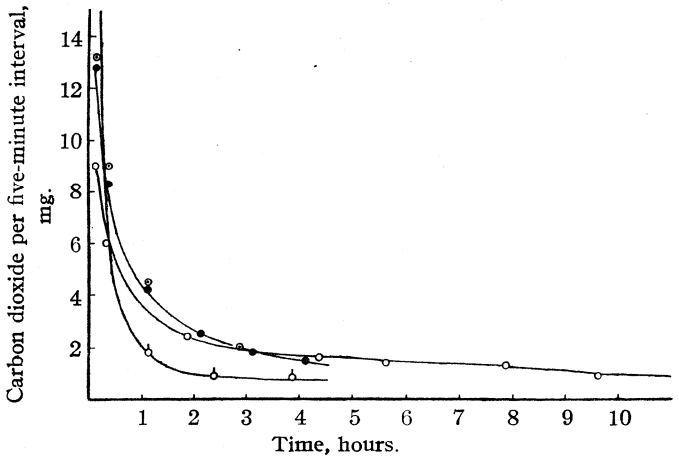


Fig. 1.—Reduction of palladium oxide at low temperatures; ○, 100°; ●, 110°; ⊙, 124°; ◌̣, 138°.

Temperature of Reduction.—The direct reduction of palladium oxide at low temperatures where the reaction does not proceed to completion is given in Fig. 1. After the first period the reaction decreases very rapidly to negligible amounts. At 138° the charge was only half reduced after four hours. If this partially reduced material is heated to a higher temperature, the reduction increases but only becomes complete around 218°. The data for a sample first reduced at 100° are given in Table I. In the second column the time elapsed since the start of the reduction is given in hours, while in column three the duration of the individual measurement is stated. When the reduction is begun at 156° it proceeds to completion, the entire amount of carbon monoxide introduced reacting. Figure 2 shows the course of the reaction during the first fifteen minutes at this temperature.

In the present work nitrogen was used to sweep air from the apparatus in order to prevent a possible effect due to the catalytic reaction of carbon monoxide with oxygen on the surface of the oxide to be reduced. Since previous workers do not record having removed air from their apparatus before the passage of carbon monoxide, a sample of palladium oxide was examined in that manner. In order to detect the slightest reduction the absorption of carbon dioxide was continued thirty to forty-five minutes. This

[10] Samuel Yuster, *J. Phys. Chem.*, **36**, 1056 (1932).

TABLE I

Temp., °C.	Time Elapsed, hours	Of expt.	CO_2, cc.	Cc./min.	Analysis method
	0 hrs.	15 min.	13.8	0.92	Chem.
	0.2	10	6.1	.61	Phys.
	0.5	35	15.7	.45	Chem.
	1.0	45	11.7	.26	Chem.
	1.7	15	3.8	.25	Phys.
100	2.0	(2.2 hrs.)	20.3		Chem.
	4.2	15	2.4	.16	Phys.
	5.5	15	2.1	.14	Phys.
	7.7	15	2.0	.13	Phys.
	9.5	15	1.3	.09	Phys.
	10.0	15	18.9	1.27	Phys.
	10.2	15	13.8	0.92	Chem.
156	11.0	15	6.5	.43	Phys.
	12.2	15	4.2	.28	Phys.
	13.0	4	102.0	25.0	Phys.
218	13.1	10	70.0	7.0	Chem.
	13.2	30	10.0	0.33	Chem.

sample produced carbon dioxide equivalent to 5.8 mg. per five-minute interval at 23°. When the apparatus was flushed with nitrogen for two hours prior to the determination, 4.5 mg. of carbon dioxide per five-minute interval was obtained. Reduction or carbon dioxide formation in each of these cases fell to negligible amounts after the second hour. Finally a sample of the oxide was heated with a stream of nitrogen passing over it for two hours at 156°. Carbon monoxide was then passed for two hours at 23° and no carbon dioxide could be detected. When this sample was heated to 56°, reduction could just be detected in one hour. At 76° it proceeded in measurable amounts. Although the reaction at 23° when the air is not first removed is probably due to adsorbed oxygen, there is also evidence for simultaneous reduction of the oxide since the color of the palladium oxide changes from chocolate-brown to black. In the last case above this did not occur until after the sample had been reducing for fifteen minutes at 76°.

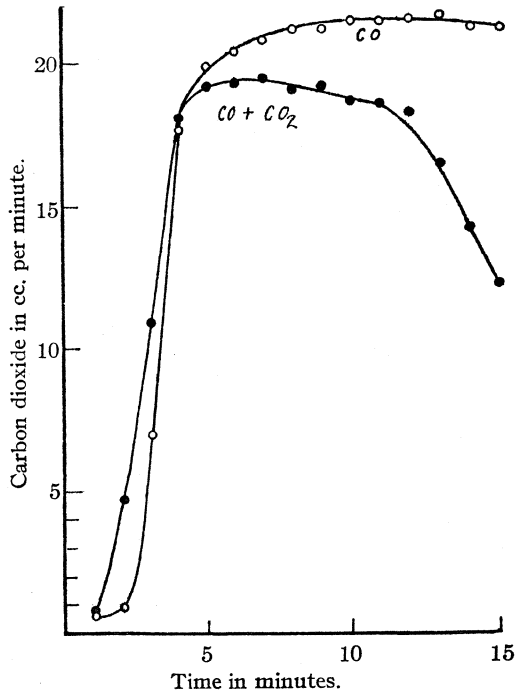


Fig. 2.—Effect of carbon dioxide on reduction at 156°.

Effect of Carbon Dioxide.—The rapid decrease in the rate of reduction below 156° suggested that a product of the reaction might be re-

tarding the further reaction; 2.8 cc. per minute of carbon dioxide was introduced into the stream of carbon monoxide by means of the electrolytic generator and copper furnace. Figure 2 presents the results, the small amount of carbon dioxide entirely inhibiting the reduction at 100°, no reaction being observed over a period of three hours. The reduction begins as usual at 156° in the presence of this amount of carbon dioxide but is retarded somewhat in the latter stages and as in the case of those reductions started at lower temperature does not appear to proceed to completion. This is quite similar to the result found for copper oxide and carbon monoxide by Jones and Taylor. Although not mentioned explicitly by them, the area under Curve V of their Fig. 3 is much less than that under Curve III for the unretarded reduction. These authors attribute the action of carbon dioxide to its absorption by the unreduced copper oxide. The adsorptions on palladium oxide have not been determined.

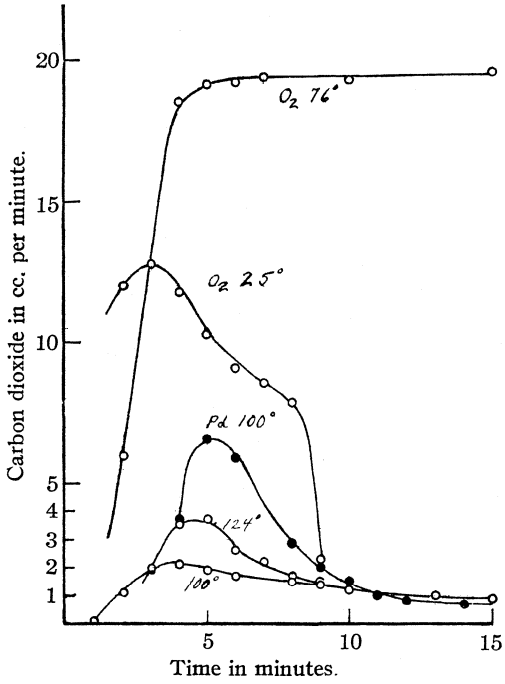


Fig. 3.

Effect of Reduced Palladium.—The charge of completely reduced palladium was mixed with a fresh sample of the oxide and reduced at 100°. The reaction began slightly more rapidly but fell off in the same manner as normally, Fig. 3. This slight increase in the initial reduction may be an autocatalytic effect or it may equally be the effect of oxygen adsorbed on the palladium and not removed by the stream of nitrogen before beginning the reduction. Oxygen is strongly adsorbed on palladium; carbon dioxide is not.[11] In the reduction of NiO, Benton and Emmett found that the addition of freshly reduced nickel to a sample of nickel oxide did not appreciably affect the rate of reduction, although the reaction is autocatalytic. In the reduction of copper oxide the freshly reduced metal increased the reaction rate. The exact time at which the maximum reduction occurs cannot be significant because it was impossible to heat the charge instantly to the desired temperature. The watch was started at the moment the boiling bath was brought up about the reaction vessel.

Effect of Oxygen.—Oxygen was passed with the carbon monoxide at 100°. The rate of reduction increased immediately to the entire amount of carbon monoxide passing and continued to the complete reduction of the palladium oxide. This was surprising and a second sample was reduced at 76° in the same manner with oxygen present, Fig. 3; 1.4 cc. of oxygen was introduced and the carbon dioxide equivalent 2.8 cc. was subtracted in each case from the analysis data. There is also an increased reduction of the palladium oxide at 25° but it is not complete, soon falling off to negligible amounts.

Palladium oxide appears to catalyze the reaction of carbon monoxide with oxygen and the heat developed by this reaction is effective in causing the reduction of palladium

[11] Burns and Taylor, THIS JOURNAL, **43**, 1274 (1921).

oxide. However carbon dioxide, or carbon monoxide itself, retards the reaction and the partially reduced Pd–PdO mixture is no longer effective to cause the combination of carbon monoxide and oxygen. The lowest temperature at which the combination of carbon monoxide and oxygen was observed over the completely reduced palladium was 218°.

Conclusion

The present results indicate that the reduction of palladium oxide occurs as an interfacial reaction. The very fineness of the palladium oxide as a powder is sufficient reason for the absence of an induction period. However, some process is strongly retarding the reaction at the interface since at the lower temperatures (100–124°) only 20% of the oxide is reduced before the reaction rate has decreased to negligible amounts. Probably carbon dioxide, the reaction product, is strongly adsorbed. This retarding action of carbon dioxide must necessarily occur from adsorption at the interface or on palladium oxide, since palladium was not found to adsorb it appreciably. Oxides in general adsorb carbon dioxide and water more than the metals. The adsorption of carbon monoxide is very strong on palladium, desorption increasing rapidly above 110°.

In order to show that the adsorption of carbon dioxide actually occurred, a sample of palladium oxide, 54% reduced, was flushed with nitrogen at room temperature. On raising the temperature, 3.8 cc. of carbon dioxide was evolved at 110° and 19.7 cc. at 218°. When carbon monoxide was passed over this sample at 110°, less than 1 cc. of carbon dioxide was evolved in thirty minutes but when flushed with nitrogen and again heated 12.6 cc. was evolved at 218°. These two cases represent an adsorption of approximately 60 and 40 volumes, respectively, per volume of palladium to be compared with an adsorption by completely reduced palladium, as measured by Taylor and Burns, of 14.4 volumes of carbon monoxide, 11.5 volumes of oxygen and 0.05 volume of carbon dioxide.

The action of oxygen in accelerating the reduction is difficult to explain, for although it is as strongly adsorbed on palladium as carbon monoxide, the two gases do not react on the metal at these temperatures. It is noteworthy that in all cases a large excess of carbon monoxide was present in the gas stream, and that if a partially reduced sample was allowed to remain open to the air for some time it then showed a preliminary increased evolution of carbon dioxide. The adsorptions on palladium oxide will be investigated.

Summary

1. A slight initial reduction of palladium oxide by carbon monoxide has been observed at 23°. If adsorbed oxygen is removed the reduction does not occur below 76°. Samples of the oxide have been reduced at 100, 110, 124, 138 and 156°. Below 156° the reduction does not proceed to completion but decreases in rate with time.

2. The presence of carbon dioxide in the stream of carbon monoxide

inhibits the reduction of palladium oxide at 100° and retards the completion of the reduction at 156°.

3. Oxygen in small amounts has been found to accelerate the reaction, causing complete reduction at 76°.

4. Palladium previously reduced from the oxide is only slightly autocatalytic toward the reduction. However, it is possible to consider that the reaction occurs at the interface and is retarded by strong adsorption of the product carbon dioxide on the oxide.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 97]

THE FREE ENERGIES AND HEATS OF FORMATION OF TETRAHYDRATE AND ANHYDROUS FORMS OF CADMIUM BROMIDE AND THEIR TRANSITION TEMPERATURES

BY HUGH M. SPENCER AND ROBERT F. SELDEN[1]

RECEIVED JUNE 20, 1932 PUBLISHED DECEMBER 13, 1932

Introduction

In order that thermodynamic quantities may be fixed with the greatest possible exactness, it is necessary that they be determined by as many independent methods as are available. Spencer and Randall[2] in their theoretical treatment of cells involving the halides of silver, mercury, lead and cadmium tested the consistency of the various combinations involved by expressing the standard electromotive force of formation of the cadmium halides as determined through measurements of the electromotive force of formation of each of the other metallic salts of the same halogen and the metathetical relation of the halide and the corresponding cadmium halide. The standard electromotive force of formation[3] is that of the reaction by which the compound is formed from the elements and water in their standard states.

The standard electromotive force of formation of cadmium bromide may be calculated through those of mercurous and silver bromides. At the time when the experimental work of the present paper was completed there existed the measurements of Oeholm[4] on the cell

[1] Du Pont Fellow in Chemistry 1929–1930.

[2] H. M. Spencer and M. Randall, unpublished.

[3] The use of this quantity rather than the electromotive force of formation from the elements in their standard states and water in the saturated solution is open to the objection that with the data available interpolations or extrapolations are required for obtaining the free energy of transfer of water from the standard state to the saturated solution in question, and uncertain quantities subject to revision are inserted. However, the same quantity is introduced in all summations for a given halide.

[4] L. W. Oeholm, *Acta Soc. Sci. Fennicae*, **41**, 1 (1913).

$$Cd(\text{in het. amalg.}),\ CdBr_2{\cdot}4H_2O(s),\ \text{satd. } CdBr_2{\cdot}4H_2O + HgBr,\ HgBr(s),\ Hg(l) \quad (1)$$

for which $E = 0.55916 - 0.000366\ (t\text{-}18) - 0.0000046(t\text{-}18)^2$, or $E_{298.1} = 0.55637$ v. Ishikawa and Ueda[5] have since found for the same cell, $E = 0.55614 - 0.0004237(t - 25) - 0.00000589(t - 25)^2$ or $E_{298.1} = 0.55614$ v. From a reinterpretation of the bromine electrode and measurements of Gerke and Geddes[6a] and of Ishikawa and Ueda[6b] on the hydrogen–mercurous bromide cell, Spencer and Randall[7] find the electromotive force of formation of mercurous bromide to be 0.9259_2 (through Ishikawa and Ueda) or 0.92620 v. (through Gerke and Geddes). They accept $E_{298.1} = 0.0505$ v. as the best value of the electromotive force for the reaction

$$Cd(s) = Cd(\text{in het. amalg.}) \quad (2)$$

Ishikawa and Ueda[5] have shown that for

$$4H_2O(l) = 4H_2O(\text{in satd. } CdBr_2.4H_2O);\ \Delta F_{298.1} = -276 \text{ cal.} \quad (3)$$

Thus the standard electromotive force of formation of the tetrahydrate of cadmium bromide is 1.53854 v. using the results of Ishikawa and Ueda, or 1.53906 v. through the results of Oeholm and of Gerke and Geddes.

Obata[8] studied the cell

$$Cd(\text{in het. amalg.}),\ CdBr_2{\cdot}4H_2O(s),\ \text{satd. } CdBr_2{\cdot}4H_2O + PbBr_2,\ PbBr_2(s),\ Pb(\text{in het. amalg.}) \quad (4)$$

and found $E = 0.14505 - 0.00037(t - 20) - 0.000005(t - 20)^2$ or $E_{298.1} = 0.14307$. Spencer and Randall have taken $E_{298.1}$ for the cells

$$Pb(s) = Pb(\text{in het. amalg.}) \quad (5)$$

$$Pb(s) + Br_2(l) = PbBr_2(s) \quad (6)$$

to be 0.00586 and 1.34560 (through the results of Ishikawa and Ueda or 1.3458 as best average of results). Combining the reaction of Cell 4 with Reactions 2, 3, 5 and 6, the standard electromotive force of formation of the tetrahydrate of cadmium bromide is 1.53929 or 1.53949 v., respectively. The difference is thus 0.2–1.0 m. v., too great to be attributed to experimental error.

This paper presents the measurements on the cells

$$Cd(\text{in het. amalg.}),\ CdBr_2{\cdot}4H_2O(s),\ \text{satd. } CdBr_2{\cdot}4H_2O + AgBr,\ AgBr(s),\ Ag(s) \quad (7)$$

and

$$Cd(\text{in het. amalg.}),\ CdBr_2(s),\ \text{satd. } CdBr_2 + AgBr,\ AgBr(s),\ Ag(s) \quad (8)$$

through the ranges 25–35° and 35–45°, respectively. Cell 7, along with the standard electromotive force of formation of silver bromide, and Reactions 2 and 3, permits a determination of the standard electromotive

[5] F. Ishikawa and Y. Ueda, *J. Chem. Soc. Japan*, **51**, 634 (1930), translated by Dr. K. Kitsuta.

[6] (a) R. H. Gerke and J. R. Geddes, *J. Phys. Chem.*, **31**, 886 (1927); (b) F. Ishikawa and Y. Ueda, *J. Chem. Soc. Japan*, **51**, 59 (1930).

[7] The present value differs from their value in the "International Critical Tables," McGraw-Hill Book Co., New York, 1930, Vol. VII, p. 260.

[8] J. Obata, *Proc. Phys. Math. Soc. Japan*, [3] **3**, 64, 136 (1921).

force of formation of the tetrahydrate of cadmium bromide partially independent (*i. e.*, except that Reactions 2 and 3 are involved) of the two mentioned above. Measurements were made over a range of temperatures and Cell 8 was investigated in order that the heats of reaction and transition temperature might be obtained.

Preparation of Materials

Mercury after the usual washing with mercurous nitrate was distilled three times at low pressure, the last in a stream of oxygen-free nitrogen. This last distillate was caught in a receiving vessel, illustrated in Fig. 1, in the following manner. The tip of the exit tube from the mercury still was placed within the tube (T) of the receiving vessel. The vessel was continuously swept out with dry oxygen-free electrolytic hydrogen during the entire distillation process. Hydrogen was admitted through the stopcock (S) and escaped through the tube (T). The flow of hydrogen was continued throughout the interim between cessation of distillation and the closing of the mercury trap (D) by cap (C). The mercury was stored under hydrogen in the receiving vessel.

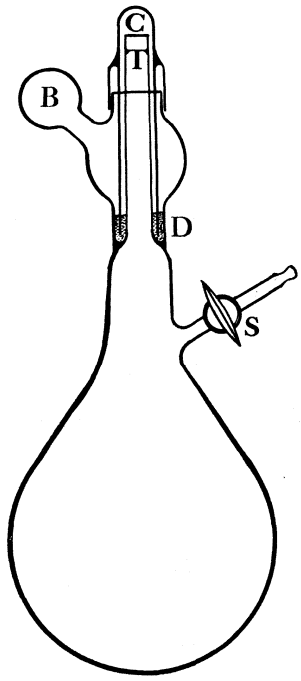


Fig. 1.

Conductivity water was used in the preparation of the cell solutions and in recrystallizations (except in the first steps of some purifications).

Cadmium bromide (Baker's C. P.) was thrice recrystallized by vacuum desiccation at temperatures below its transition point of 35.8°. The crystallizing dish containing the solution with its cover glass in place was placed within a glass cylinder (made from a bottle) and both rested on a large watch glass. The glass cylinder was covered with another large watch glass and the whole rested upon the plate of the desiccator. This arrangement prevented contamination due to evolution of bromine gas which would have resulted from the solution bumping and coming into contact with the sulfuric acid desiccating solution.

Cadmium sulfate and potassium bromide were twice recrystallized.

Silver nitrate was recrystallized twice from conductivity water in the dark room. Neither the final crystals nor the solutions made from them were ever exposed to other than red light for any period of time.

The cadmium bromide solution intended for use in the cells was saturated with respect to cadmium bromide and silver bromide. It was protected at all times from actinic light. The silver bromide was prepared in the dark room by adding very slowly about 200 cc. of 0.05 *M* silver nitrate to 285 cc. of 0.006 *M* potassium bromide kept at 80°. To facilitate rapid settling of the finely divided silver bromide, about 1.0 cc. of concentrated perchloric acid was added. After twelve washings by decantation the silver bromide was added to the cadmium bromide solution.

Silver oxide was prepared by adding slowly through a separatory funnel a silver nitrate solution (20 g. in 350 cc. of water) to a dilute solution of barium hydroxide (excess) at 50°. The barium hydroxide solution was made by adding about 400 cc. of a

saturated stock solution to about 1150 cc. of boiling distilled water through a siphon loosely inserted in the stopper of the flask holding the water. The separatory funnel containing the silver nitrate solution was fitted into this stopper just as the boiling was stopped so that precipitation was effected in the absence of carbon dioxide. The first few of the many washings of the precipitate were made with hot boiled conductivity water.

Preparation of Electrodes

Carmody[9] has shown that silver deposited from a $KAg(CN)_2$ solution must be washed free of cyanide with extreme care if reproducible electrodes are to be had. The necessity of this was avoided in the present investigation by using as the base a spiral of pure silver, instead of silver-plated platinum. From this point the silver–silver bromide electrodes were prepared in the same manner as Noyes and Ellis'[10] silver–silver chloride electrodes. The silver bromide was deposited from 0.5 *M* potassium bromide solution with a current of 4 milliamperes for five hours. These were never exposed to actinic light.

Two-phase cadmium amalgams of 10 to 14 weight per cent. cadmium were used. Amalgams of these compositions remain heterogeneous over the range 25–45°. Moesveld and de Meester[11] have shown that below 13.5% Cd equilibrium is attained at 25° at least within a few hours. The amalgams were prepared by electrolyzing a solution containing the desired amount of cadmium sulfate with a platinum anode and a given amount of mercury as cathode. The amalgam was thus obtained with an acid solution above it which prevented oxide formation on the surface of the amalgam. When once freed from the acid solution, oxidation of the liquid amalgam occurred so rapidly that a special procedure had to be developed whereby the amalgam was not only washed in but kept in an inert atmosphere until needed. This procedure will be described in some detail, because an amalgam free from all oxide contamination was an essential component of the cells to be described.

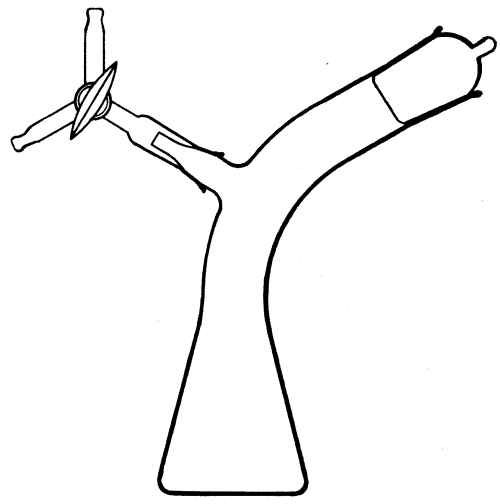


Fig. 2.

The amalgam was melted if it had been allowed to cool and transferred along with some of the sulfuric acid solution to the container shown in Fig. 2. This apparatus was a modification of one used by Carmody, details of which were obtained by private communication. It was clamped loosely with its bottom resting on a wire gauze. The gauze was strongly heated while the solution above the amalgam was periodically poured off through the side arm by tilting the vessel, and replaced by boiling distilled water. By repetition of this process the amalgam was not only washed free of all acid but the air in the container was displaced by escaping steam as well. When washing was complete, the cap to the side arm

[9] W. R. Carmody, THIS JOURNAL, **51**, 2901 (1929).

[10] A. A. Noyes and J. H. Ellis, *ibid.*, **39**, 2532 (1917).

[11] A. L. Th. Moesveld and W. A. T. de Meester, *Z. physik. Chem.*, **130**, 146 (1927).

and the stopper were put into place and the container removed from the heat immediately. Because of the high temperature involved, a very stiff stopcock grease was necessary on both ground glass joints. The amalgam was then cooled in an ice box until it was completely solid. The water remaining in the vessel was then drawn off through the stopcock attached to the cap on the side arm. To prevent any slow oxidation of the solid amalgam the vessel was repeatedly evacuated and filled with an inert gas, *i. e.*, nitrogen.

Preparation of Cells and Experimental Method.—Most of the measurements were made with cells containing two electrodes of each kind, shown in Fig. 3, a modification of the H-cell with an upper cross arm and outlet and side arms for convenience in assembling the cell with the exclusion of oxygen. The silver bromide electrodes were supported in ground-glass stoppers closing the main arms. In these cells four combinations of the two kinds of electrodes were measured. Later single cells each containing one electrode of each kind were made up and measured in sets of six. In these cells the silver bromide electrode was supported by a tube which closed a mercury seal over the main tube. The earliest measurements, which proved to be valueless, were made in double cells in which the silver bromide electrodes were supported by cork stoppers coated with cement, and the side arms were closed by screw-clamps on rubber tubes rather than by stopcocks.

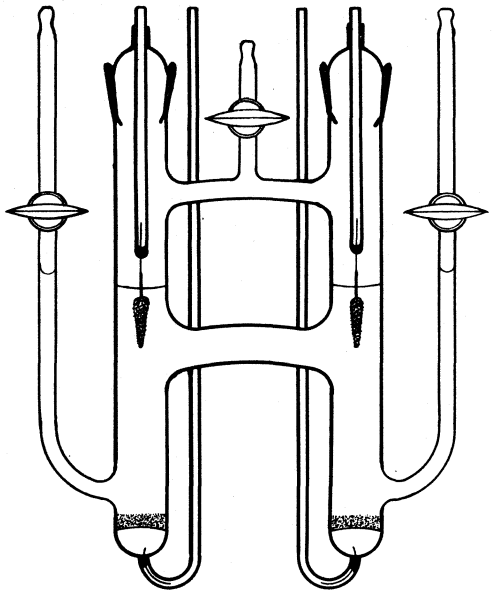


Fig. 3.

The cells were rendered opaque with a thick black paint made by mixing carbon black with varnish. Preparation of the cells was carried out in the presence of red light and as far as possible the cell was swept out continuously with nitrogen while all the components were being put in place. The proper amount of cadmium bromide solution, removed by a pipet from the supernatant stock solutions, was added to the cell and at the same time filtered to remove any silver bromide which might be suspended in it. After nitrogen had been bubbled through for several minutes, molten cadmium amalgam and finally the tetrahydrate or anhydrous form of cadmium bromide in amount sufficient to ensure presence of crystals at the highest temperature used were added through funnels made of glass tubing. Finally the silver bromide electrodes were put into place and nitrogen was bubbled alternately through first one limb and then the other of the cell for twenty to thirty minutes.

An oil thermostat with a temperature regulator capable of keeping temperature constant within plus or minus 0.015° of any desired temperature over the range 25 to 45° was used. The temperatures were obtained with a thermometer which had been compared with another thermometer certified by the Bureau of Standards. Temperature intervals were also obtained with a Beckmann thermometer. Measurements of potential were made with a Leeds and Northrup Type K potentiometer and Type R (2500-C) galvanometer. The potentiometer, galvanometer, standard cell and the

switch box through which electrical corrections were completed with the cells in the thermostat, were all placed on interconnected metal plates. The shield system was not grounded.[12]

Though there were instances where the cells gave values which proved to be constant with an hour of immersion and also when twelve hours were necessary, five or six hours were generally sufficient, though possibly not requisite, as it was often convenient to leave the experiment for that period after adjustment of temperature. Except in cases where the solid phase underwent a change of form, adjustment of potential to a new temperature was generally complete within that time and frequently by the time the thermostat had been adjusted. Readings were taken at intervals of two to four hours until constancy was proved. As a rule, the bath temperature was successively fixed at 25, 30, 35, 37.5, 40 and 45°, and then lowered to 25° again. After this it was fixed at any value that was of immediate interest. In some cases the results obtained upon lowering the temperature appeared to represent better equilibrium values than those obtained initially. Measurements were made at every temperature after both lowering and raising the temperature but not in each series of measurements.

In spite of all precautions to make the cell function properly, some of the cells "aged" before the whole series of measurements were complete, in which case the results obtained after this phenomenon made its appearance have been omitted from the tables. This "aging" made itself evident by a gradual but steadily increasing deviation between the various pairs of electrodes. All cells, given sufficient time, showed this phenomenon.

Results and Discussion

Tables I and II summarize the average potentials for the cells in which the tetrahydrate and the anhydrous form, respectively, of cadmium bromide were the saturating solids. The values marked with one asterisk were made after measurements at lower and higher temperatures. Those marked with two asterisks were approached twice in one direction. The values for Cells 5 to 10 represent the average of the four combinations of two electrodes except in a few cases where real divergences appear. In Cell 5 the silver electrodes had become different when measurements at 37.50° were made the third time and ones at 40° for the second time. Here one pair of values coincided with all four of an earlier set. In Cell 7 one cadmium amalgam electrode appeared to be sluggish in response to changes of temperature. The temperatures indicate the true values with an uncertainty of 0.02°.

What appears to be an equilibrium value of the electromotive force for a metastable condition was obtained with Cell 6 by lowering the temperature from 37.5 to 35°. In Cell 3, though all the values appeared to be too low, there existed the same difference in readings at 37.5 and 35°. The metastable condition persisted at 35° for six hours. The thermostat was then allowed to cool to 28.3° for several hours and on readjustment to 35° the cells gave values different from the earlier ones by approximately the same amount as for the stable and metastable conditions in Cell 6.

The values of Tables I and II have been plotted and the data obtained from these curves are tabulated in Table III. The slopes of these curves.

[12] W. P. White, THIS JOURNAL, **36**, 2011 (1914).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Cd(in het. amalg.), $CdBr_2 \cdot 4H_2O$(s), satd. $CdBr_2 \cdot 4H_2O$ + AgBr, AgBr(s), Ag(s)

Cell no.	E 25°	E 27°	E 30°	E 33°	E 35°
2	0.48833*				
5	.48837**		0.48415		0.47889*
6	.48838		.48366		.47840
7	.48839		.48347		.47846
8	.48814		.48333		.47805*
9	.48819		.48337		.47831
12–1			.48436*	0.48149	
12–2			.48408*	.48147	[a]
12–4			.48431	.48174	
12–6			.4844[b]	.48180	
13–1		0.48686	.48439		
13–2		.48685	.48445		
13–3		.48685	.48409		
13–4		.48685	.48446		
13–5		.48685	.48429		
13–6		.48684	.48422		
13–1[c]	.48821	.48661		.48144	
13–2	.48824	.48666		.48141	
13–3	.48832	.48682		.48130	
13–4	.48833	.48685		.48194	
13–5	.48829	.48679		.48147	
13–6	.48828	.48676		.48156	

[a] At 35° Cells 12–1, –2, –4 and –6 were divergent and higher than was expected, indicating that they were not saturated.

[b] Cell 12–6 became insensitive in the middle of the run and later recovered.

[c] The order of temperature changes for Cell 13 was 27, 30, 35 (for a period insufficient for attainment of constancy), 27, 25 and 33°.

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS

Cd(in het. amalg.), $CdBr_2$(s), satd. $CdBr_2$ + AgBr, AgBr(s), Ag(s)

Cell no.	35° (metastable)	37.5°	40°	45°
5		0.47807*	0.47797**	0.47774
6	0.47772	.47759*	.47749*	.47720
8		.47758		
9		.47766	.47760	
10		.47734	.47730	

i. e., $\partial E/\partial T$, at 25° are given in the second column, the slopes at the transition point for the tetrahydrate of cadmium bromide cells in the third column, and for the anhydrous form at this temperature in the fourth column. The transition temperatures in the fifth column were obtained from the intersections of the curves.

Ishikawa and Ueda[5] have shown that, contrary to facts hitherto accepted, the tetrahydrate of cadmium bromide changes at a temperature

TABLE III

TEMPERATURE COEFFICIENTS OF ELECTROMOTIVE FORCE AND THE TRANSITION TEMPERATURE

Cell no.	$-(\partial E/\partial T) \times 10^6$ 25°	$-(\partial E/\partial T) \times 10^6$	$-(\partial E/\partial T) \times 10^6$	E at transition temp.	Transition temp.
5	787	1168	32	0.47814	35.63 °C.
6	882	1118	42	.47770	35.64
7	980	1036			
8	898	1100			
9	896	1032	26	.47770	35.61
Mean	890	1091	33		

near 36° to the anhydrous form rather than to $CdBr_2 \cdot H_2O$ (or $CdBr_2 \cdot 1.5$-H_2O).[13] With the Bremer-Frowein tensimeter they determined the vapor pressures of the systems (a) $CdBr_2 \cdot 4H_2O$(s)–saturated solution, (b) $CdBr_2 \cdot 2.6H_2O$, *i. e.*, $CdBr_2 \cdot 4H_2O$(s)–$CdBr_2$(s), and found for the range 20–35°

$$\text{(a) } \log p_{(\text{mm.})} = 1.32491 - 2095.4(1/T - 1/298.1); \quad (p \pm 0.07 \text{ mm.}) \qquad (9)$$

$$\text{(b) } \log p_{(\text{mm.})} = 1.24102 - 2731.1(1/T - 1/298.1); \quad (p \pm 0.06 \text{ mm.}) \qquad (10)$$

For 37.5, 40 and 42.5° they found p in Series (a), 40.43 ± 0.10, 46.26 ± 0.06 and 52.68 ± 0.05, in Series (b), 40.23 ± 0.06, 46.03 ± 0.12 and 52.7 ± 0.05 mm., respectively. Moreover, measurements were made at 20 and 42.5° on a mixture of the tetrahydrate and anhydrous form corresponding to a solid of composition $CdBr_2 \cdot 0.348H_2O$ and the values checked Series (b).

The direct determination of the water of crystallization of the solid prepared above the transition point, as given, is unconvincing. Their dehydration and hydration experiments at 25° with 34.3% and 24.8% sulfuric acid, the vapor pressures of which (16 and 19.6 mm.) are, respectively, lower and higher than 17.35 mm., the dissociation pressure, as measured are very interesting. The first solution changes mixtures of the tetrahydrate and water, of compositions, $CdBr_2 \cdot 4H_2O + 0.69H_2O$ and $CdBr_2 \cdot 4H_2O + 0.79H_2O$ to $CdBr_2$ in two to four hundred hours without any discontinuity in the water content–time curves and leaves the higher temperature form unchanged while the second solution takes the higher temperature form and the tetrahydrate plus 0.97 mole of water to the tetrahydrate also without any discontinuity. We have repeated the experiments in which an attempt was made to obtain an intermediate degree of hydration from the form prepared in the ordinary way slightly above the transition point, and have found from the analysis for bromide ion that the salt is anhydrous.

Whereas the transition temperature determined from our cells is 35.63° and that determined from the cadmium bromide–mercurous bromide cells is 36.0°, it seemed expedient to investigate the transition point by the usual

[13] (a) R. Dietz, *Z. anorg. Chem.*, **20**, 240 (1899); (b) M. Étard, *Ann. chim. phys.*, [7] **2**, 503 (1894).

thermal methods. This leads to 35.82°, assuming the same deviation of the thermometer (*i. e.*, −0.02°) at this temperature as at 32.38°, the transition point for decahydrate–anhydrous forms of sodium sulfate.

The mean value of the potential at 25°, $E_{298.1} = 0.48829$ or 0.4883 v. from Table I, represents the tendency for the reaction

$$\text{Cd(in het. amalg.)} + 2\text{AgBr(s)} + 4\text{H}_2\text{O(in satd. CdBr}_2\cdot 4\text{H}_2\text{O)} = 2\text{Ag(s)} + \text{CdBr}_2\cdot 4\text{H}_2\text{O(s)}$$

to occur. This represents in an abbreviated form the complete cell reaction

$$\frac{n_1}{n_1 - n_1'}(\text{Cd}\cdot n_1'\text{Hg}) + 2\text{AgBr(s)} + \frac{4}{A-4}(\text{CdBr}_2\cdot A\text{H}_2\text{O}) = 2\text{Ag(s)} + \frac{4}{A-4}\text{CdBr}_2\cdot 4\text{H}_2\text{O(s)} + \frac{n_1'}{n_1 - n_1'}(\text{Cd}\cdot n_1\text{Hg});$$

$$E_{298.1} = 0.4883 \text{ v.}, \left(\frac{\partial E}{\partial T}\right)_{298.1} = -8.9 \times 10^{-4}$$

$$\Delta H_{298.1} = -34{,}777 \text{ cal.}, E_{308.73} = 0.4777 \text{ v.}, \left(\frac{\partial E}{\partial T}\right)_{308.73} = -1.091 \times 10^{-3}, \Delta H_{308.73} = -37{,}589 \text{ cal.} \quad (7')$$

where n_1 and n_1' are, respectively, the moles of mercury per mole of cadmium in the liquidus and solidus and A is the number of moles of water per mole of cadmium bromide in the saturated solution. Combining with Reaction 2 or rather 2′

$$\text{Cd(s)} + \frac{n_1'}{n_1 - n_1'}(\text{Cd}\cdot n_1\text{Hg}) = \frac{n_1}{n_1 - n_1'}(\text{Cd}\cdot n_1'\text{Hg}); \quad E_{298.1} = 0.0505 \text{ v.}, \quad \Delta H_{298.1} = -5682 \text{ cal.} \quad (2')$$

and that for the formation of silver bromide from its elements

$$2\text{Ag(s)} + \text{Br}_2\text{(l)} = 2\text{AgBr(s)}; \quad E_{298.1} = 0.9937 \text{ v.}^{14} \quad (11)$$

we have for the formation from the elements and the saturated solution

$$\text{Cd} + \text{Br}_2\text{(l)} + \frac{4}{A-4}(\text{CdBr}_2\cdot A\text{H}_2\text{O}) = \frac{A}{A-4}\text{CdBr}_2\cdot 4\text{H}_2\text{O(s)}; \quad E_{298.1} = 1.5325 \text{ v.} \quad (12')$$

and since for

$$\frac{4}{A-4}\text{CdBr}_2\text{(in satd. CdBr}_2\cdot 4\text{H}_2\text{O)} + \frac{16}{A-4}\text{H}_2\text{O(in satd. CdBr}_2\cdot 4\text{H}_2\text{O)} = \frac{4}{A-4}\text{CdBr}_2\cdot 4\text{H}_2\text{O(s)}; \quad \Delta F = 0 \text{ and } E = 0; \quad (13)$$

$$\text{Cd} + \text{Br}_2\text{(l)} + 4\text{H}_2\text{O(in satd. CdBr}_2\cdot 4\text{H}_2\text{O)} = \text{CdBr}_2\cdot 4\text{H}_2\text{O(s)}; \quad E_{298.1} = 1.5325 \text{ v.}, \Delta F_{298.1} = -70{,}722 \text{ cal.} \quad (12)$$

Equation 3 follows from Ishikawa and Ueda's measurement[5] of the vapor pressure of the saturated solution of the tetrahydrate at 25°, $p = 21.15$ mm. (Equation 9), and hence, adding Equations 3 and 12, we find for the standard free energy and electromotive force of formation of the tetrahydrate of cadmium bromide

$$\text{Cd(s)} + \text{Br}_2\text{(l)} + 4\text{H}_2\text{O(l)} = \text{CdBr}_2\cdot 4\text{H}_2\text{O(s)}; \quad \Delta F^\circ_{298.1} = -70{,}722 \text{ cal.}, E^\circ_{298.1} = 1.5385 \text{ v.} \quad (14)$$

[14] Though this value of the electromotive force of formation of silver bromide was derived primarily for this paper, it has seemed best to present the basis for it in another paper by one of the authors and Professor Randall.[2]

From Ishikawa and Ueda's measurement of the vapor pressure of the system $CdBr_2 \cdot 4H_2O(s)$–$CdBr_2(s)$, $p = 17.35$ mm. (Equation 10), at 25°

$$CdBr_2 \cdot 4H_2O(s) = CdBr_2(s) + 4H_2O(l); \quad \Delta F^\circ_{298.1} = 745 \text{ cal.} \qquad (15)$$

and thence for

$$Cd(s) + Br_2(l) = CdBr_2(s); \quad \Delta F^\circ_{298.1} = -70{,}253 \text{ cal.}, \; E^\circ_{298.1} = 1.5223 \text{ v.} \qquad (16)$$

These values are in excellent agreement with the values determined through mercurous bromide by Ishikawa and Ueda.[15] We shall see that the heats of reactions calculated from the two sets of data do not agree satisfactorily.

The heat effect of the reaction

$$\frac{A}{A-4} CdBr_2 \cdot 4H_2O(s) = CdBr_2(s) + \frac{4}{A-4} (CdBr_2 \cdot AH_2O) \qquad (17)$$

is required in the calculation of the heat of formation of cadmium bromide from the electromotive force measurements. It may be split into three parts, for each of which Ishikawa and Ueda[5] have determined calorimetrically the heat effects at 25°, where $A = 13.454$

$$CdBr_2(s) + 400H_2O = CdBr_2 \cdot 400H_2O; \quad \Delta H_{298.1} = -762 \text{ cal.}, \qquad (18)$$

$$\frac{4}{13.454-4} (CdBr_2 \cdot 13.454H_2O) + \frac{4}{13.454-4} 386.546 \, H_2O = \frac{4}{13.454-4} (CdBr_2 \cdot 400H_2O); \quad \Delta H_{298.1} = \frac{4}{13.454-4} (44) = 19 \text{ cal.} \qquad (19)$$

$$\frac{13.454}{13.454-4} (CdBr_2 \cdot 400H_2O) = \frac{13.454}{13.454-4} CdBr_2 \cdot 4H_2O(s) + \frac{13.454}{13.454-4} 396 \, H_2O; \quad \Delta H_{298.1} = \frac{13.454}{13.454-4} (-7139) = -10{,}160 \text{ cal.} \qquad (20)$$

$$\frac{13.454}{9.454} CdBr_2 \cdot 4H_2O(s) = CdBr_2(s) + \frac{4}{9.454} (CdBr_2 \cdot 13.454H_2O); \quad \Delta H_{298.1} = -10{,}903 \text{ cal.} \qquad (17)$$

By addition of Reactions 7′, 2′, 17 and that for the formation of two moles of silver bromide,[16] for which $\Delta H = -47{,}620$, the ΔH of formation of cadmium bromide (Reaction 16) is $-77{,}176$ cal. From Ishikawa and Ueda's cells involving mercurous bromide, $\Delta H_{298.1}$ for the reaction corresponding to 7′ is $-31{,}494$ cal. Addition of this reaction to Reactions 2′, 17 and that for the formation of two moles of mercurous bromide, $-50{,}940$ (Thomsen), $-49{,}000$ (Nernst), $-49{,}100$ (Varet) or $-49{,}240$ cal. ("I. C. T."), gives for the ΔH of formation of cadmium bromide $-77{,}213$, $-75{,}273$, $-75{,}373$ or $-75{,}513$ cal., respectively. Oeholm's mercurous bromide

[15] In Ishikawa and Ueda's paper the free energies and potentials are referred to α-cadmium. The heat capacity data used in their calorimetric measurements are not very satisfactory. The results nominally given in 18° calories can probably be considered approximately correct.

[16] T. J. Webb, *J. Phys. Chem.*, **29**, 816 (1925).

cells yield −31,590 cal., for the reaction corresponding to 7′. Similar treatment of Obata's cells involving lead bromide, for which $\Delta H_{298.1} = -12{,}380$ cal., along with ΔH for Reactions 5 and 6, −82 and −66,350 cal., respectively, the latter by Braune and Koref, and Reactions 2′ and 17 gives for the ΔH of formation of cadmium bromide −73,427 cal.

Bichowsky[17] has recalculated the calorimetric value of the heat of formation of solid cadmium bromide and found −75,790 cal. This is based primarily on the values of Thomsen and of Nernst, −75,640 and −76,300, for the formation in solution. Thomsen's value results from the combination of four equations. Nernst[18] measured directly the heat effect of formation in solution (often quoted as heat of formation of the solid) in the presence of a small excess of bromine and found −76,400 ± 600 cal. (actual average of his data) which when corrected by reason of his use of 112.1 as the atomic weight of cadmium, yields −76,610 cal. This magnitude should be further increased to express the result in 15° calories. Ishikawa and Ueda's measurement of the heat of solution of cadmium bromide, $\Delta H = -762$ cal. now supersedes −440 by Thomsen so that the −75,790 given by Bichowsky would now be changed to −75,570 cal.

Thus while the values derived from the silver and mercurous bromide cells do not agree well, the calorimetric values to which they are to be compared are in the same range and of the same order of variability.

Comparison of the silver and mercurous bromide cells is disappointing in another respect, though the method is very sensitive to experimental error. Addition of Reaction 7′ and the reverse of the reaction in cells with anhydrous cadmium bromide as the solid phase

$$2\mathrm{Ag(s)} + \mathrm{CdBr_2(s)} + \frac{n_1'}{n_1 - n_1}(\mathrm{Cd}\cdot n_1\mathrm{Hg}) = \frac{n_1}{n_1 - n_1}(\mathrm{Cd}\cdot n_1'\mathrm{Hg}) + 2\mathrm{AgBr(s)},\ E_{308.73} = -0.4777\ \mathrm{v.}$$
$$(\partial E/\partial T)_{308.73} = 3.3 \times 10^{-5} \qquad (21)$$

yields Reaction 17, $\Delta H_{308.73} = 15{,}074$ cal. The corresponding reactions in the mercurous bromide cells give $\Delta H_{308.73} = 12{,}094$ cal. The difference of these values from the calorimetric one at 25°, 10,903 cal., is not surprising when one considers that not only the ratio A but also the heat effects of the three individual reactions are different at the higher temperature.

Summary

1. The electromotive forces of the following cells

Cd(in het. amalg.), $CdBr_2\cdot 4H_2O$(s), satd. $CdBr_2\cdot 4H_2O$ + AgBr, AgBr(s), Ag(s),
Cd(in het. amalg.), $CdBr_2$(s), satd. $CdBr_2$ + AgBr, AgBr(s), Ag(s)

[17] F. R. Bichowsky, "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. V, p. 185.

[18] W. Nernst, *Z. physik. Chem.*, **2**, 23 (1888).

prepared in the absence of oxygen have been measured over the ranges 25–35 and 35–45° respectively.

2. The transition temperature, $CdBr_2 \cdot 4H_2O(s)$–$CdBr_2(s)$–saturated solution, was found to be 35.63° by the cell measurements and 35.82 by the usual thermal method, and the hydration of the stable solid phases has been discussed.

3. The standard electromotive force and free energy of formation of cadmium bromide have been found to check those through mercurous bromide and not those through lead bromide. The heats of formation have been compared with the calorimetric values.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 23]

SOME REACTIONS OF COMPLEX CHLORIDES OF TRIVALENT AND PENTAVALENT TUNGSTEN

BY RALPH C. YOUNG

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When tripotassium ditungsti-chloride, $K_3W_2Cl_9$, prepared by the method of Olsson[1] was treated with a solution of potassium hydroxide at 5°, a vigorous evolution of hydrogen occurred as simultaneously a precipitate of an hydroxide or hydrous oxide formed. These same phenomena occurred also when $K_3W_2Cl_9$ was heated with water. An oxide of trivalent tungsten is not stable even at low temperatures when prepared in aqueous solutions. It is therefore to be expected that, if the mechanism of complex cyanide formation in the case of tungsten is similar to that of molybdenum,[2] with the intermediate formation of an hydroxide, a complex cyanide of tetravalent tungsten would form when $K_3W_2Cl_9$ is treated with potassium cyanide solution in an atmosphere of nitrogen. Such has proved to be the result even when the reaction is carried out at low temperatures. Hydrogen is not evolved in this reaction in which oxidation of the tungsten occurs but if the contents of the solution after reaction are made acid, the Schiff test for aldehyde is obtained. Hydrogen cyanide and ammonia are present in the solution, resulting from the hydrolysis of the potassium cyanide, and it is known that hydrogen cyanide is reduced in neutral solutions to formaldehyde and ammonia. These compounds are able to form certain condensation products, which may be the reason for not obtaining the test for aldehyde until the solution was made acid.

It seemed of interest to determine to what extent the tungsten in $K_3W_2Cl_9$ would be oxidized in an atmosphere of nitrogen by water alone, and by

[1] Olsson, *Z. anorg. allgem. Chem.*, **88**, 49 (1914).

[2] Young, THIS JOURNAL, **54**, 1402 (1932).

alkali of different concentrations. It was planned to determine this oxidation by measuring the hydrogen evolved in one set of experiments and by titration of the tungsten reaction product with standard potassium permanganate in another set of experiments.

By means of an apparatus consisting of a reaction vessel of 100-cc. capacity connected with a gas buret adapted to collect the hydrogen evolved over mercury, a study was made of the extent of the oxidation of the tungsten when potassium tungsti-chloride reacted in the presence of nitrogen with water, 6 *N* potassium hydroxide solution and a 50% solution of potassium hydroxide, respectively. To hasten the reaction the solution was occasionally heated for a short time to the boiling point, and the reaction was allowed to continue until there was no more evidence of the evolution of hydrogen. All volumes were reduced to standard conditions of temperature and pressure on a dry gas basis and the increase in each case measured the hydrogen evolved.

In Table I are given the results of several experiments. Complete solution occurred only when a 50% solution of potassium hydroxide was used, a black precipitate was formed in the experiments with water and a dark colloidal mass with 6 *N* potassium hydroxide.

TABLE I

$K_3W_2Cl_9$, g.	$K_3W_2Br_9$, g.	Solution used, cc.	H_2 evolved at S. T. P., cc.	H_2 equivalent to oxidation of W from valence 3 to 4, cc.	W oxidized from valence 3 to 4, %
2.2126		35 H_2O	35.2	61.1	57.6
1.9066		35 H_2O	31.8	53.1	59.8
1.8290		35 6 *N* KOH	42.3	50.9	83.0
1.7511		35 6 *N* KOH	39.1	48.7	80.3
1.3369		35 50% KOH	35.9	37.2	96.5
1.3247		35 50% KOH	36.0	36.8	97.8
	1.6503	35 50% KOH	29.7	30.7	96.7

The insoluble product formed in the reaction of $K_3W_2Cl_9$ with water was obtained in an apparatus designed for carrying out the reaction and the subsequent filtration and washing with water, alcohol and ether, all in an atmosphere of nitrogen. A determination of total chlorine and hydrochloric acid in the water showed that hydrolysis had been complete. A weighed sample of the vacuum-dried product was ignited in a stream of oxygen which passed over hot copper oxide and then into a weighed Marchand tube with calcium chloride to collect the water. The hot copper oxide served to oxidize any hydrogen that might be formed by the reaction of the lower valence oxide with the water held as hydrous water. From the final weight of the tungstic oxide, WO_3, 0.6084 g., the weight of the water, 0.0858 g., and the original sample, 0.6441 g., there was calculated the composition of the anhydrous product. Other determinations checked these results.

Anal. Calcd. for W_6O_9: O, 13.53; W, 86.48. Found: O, 13.55, 13.73; W, 86.42, 86.28.

The above composition corresponds to three molecules of WO_2 and one of W_2O_3: that is, three atoms of tetravalent tungsten, and two of trivalent tungsten. This is in accord with the fact that 60% of the tungsten in $K_3W_2Cl_9$ was oxidized to valence four

by heating with water, as measured by the hydrogen evolved. The hydrolysis of $K_3W_2Cl_9$ and subsequent oxidation of the tungsten by the water is expressed by the equation

$$5W_2Cl_9^{=} + 18H_2O \longrightarrow 45Cl^- + 30H^+ + 2W_5O_9 + 3H_2$$

On dilution and subsequent acidification of the 50% potassium hydroxide solution there was obtained a brown precipitate which was washed with water, alcohol and ether and pumped dry. It was ignited as described previously. From 0.3654 g. of the hydrous oxide there was obtained 0.0377 g. of water and 0.3505 g. of the tungstic acid. The initial anhydrous product corresponds to the following composition, which was checked by other determinations.

Anal. Calcd. for WO_2: W, 85.19; O, 14.81. Found: W, 84.82; O, 15.19.

From the above facts it is apparent that tungsten dioxide does not react with solutions of potassium hydroxide to evolve hydrogen, a result which is not in agreement with a statement by Riche,[3] which has been included in many reference books on chemistry.

To test more thoroughly the question of the ability of the tungsten to be oxidized beyond the tetravalent stage by a potassium hydroxide solution, experiments were carried out in a flask fitted with side tubes through which nitrogen was continuously passed, while the solution was boiled. At the end of a two-hour period of heating, the solution was cooled, acidified with hydrochloric acid, and the precipitated tungsten dioxide was titrated with standard potassium permanganate, the whole process being carried out in an atmosphere of nitrogen. The results are shown in Table II. The results accord very well with those obtained by measuring the oxidation of the tungsten by the amount of hydrogen evolved.

TABLE II

$K_3W_2Cl_9$, g.	Solution used, cc.	Cc. of 0.1265 *N* $KMnO_4$ calcd. to oxidize the W from valence 3 to 6	Cc. of 0.1265 *N* $KMnO_4$ calcd. to oxidize the W from valence 4 to 6	0.1265 *N* $KMnO_4$ used, cc.	W oxidized from valence 3 to 4 by solution, %	W oxidized to valence 5 by solution, %
0.3250	20 50% KOH	19.15	12.77	12.83	99.0	0.0
.2938	20 50% KOH	17.31	11.54	11.67	97.7	.0
.3520	20 6 *N* KOH	20.74	13.83	15.12	81.3	.0
.3218	20 6 *N* KOH	18.97	12.65	13.96	79.2	.0
.3076	20 H_2O	18.13	12.09	14.34	62.7	.0
.2831	20 H_2O	16.68	11.12	13.30	60.7	.0
.3075	20 50% KOH presence of air	18.12	12.08	10.10	100.0	32.7
.2760	20 50% KOH presence of air	16.26	10.84	7.00	100.0	70.8

Preparation and Properties of Tripotassium Ditungsti-Bromide, $K_3W_2Br_9$.—The tripotassium ditungsti-bromide used in one of the experiments was prepared by the reduction with tin of tungstic acid dissolved in concentrated hydrobromic acid, by a procedure similar to that by which Olsson[4] made the chloride. Under the microscope, the compound appeared as brown transparent hexagonal plates which analysis showed to be practically pure $K_3W_2Br_9$. The tungsten was determined as WO_3, the potassium as potassium sulfate and the bromine as silver bromide.

Anal. Calcd. for $K_3W_2Br_9$: K, 9.74; W, 30.55; Br, 59.71. Found: K, 9.79, 9.76; W, 30.75, 30.86; Br, 59.88, 59.62.

[3] Riche, *Ann. chim. phys.*, **50**, 30 (1857).

[4] Olsson, *Z. anorg. allgem. Chem.*, **88**, 49 (1914).

In an atmosphere of carbon dioxide, a sample weighing 0.3607 g. required 14 cc. of 0.1265 *N* $KMnO_4$ to oxidize the tungsten to the hexavalent condition, corresponding to 1.771 milliequivalents of the oxidizing agent, the theoretical being 1.796 milliequivalents. Subsequent determinations checked these results.

Tripotassium ditungsti-bromide gives in the absence of oxygen a brown solution when concentrated, which on dilution becomes orange, then pink. It reacts with hot water and alkalies in the presence of air with the formation of hydrogen as simultaneously a black product is formed, which finally changes to brown tungsten dioxide. With Ag^+, a brown solid was obtained, and with Cd^{++}, a dark gray solid. Cu^{++} was reduced to Cu^+ and Hg^{++} to Hg_2^{++} by the complex tungsti-bromide.

Reaction of $(NH_4)_2WOCl_5$ with Potassium Cyanide.—Complex salts of pentavalent tungsten react with potassium cyanide solution to form a complex cyanide of tetravalent tungsten, $K_4W(CN)_8$. Pentavalent salts of molybdenum also give a tetravalent molybdenum cyanide, $K_4Mo(CN)_8$, with potassium cyanide. Bucknall and Wardlaw[5] in giving a mechanism for the latter reaction propose as one of the steps the evolution of oxygen. To test this hypothesis for tungsten, diammonium tungsten oxypentachloride was prepared according to the method of Collenberg[6] and in the apparatus mentioned above 1.1470 g. of the pentavalent tungsten salt was allowed to react with a solution of 2 g. of potassium cyanide in 10 cc. of water. On the addition of the cyanide solution, a blue color developed at the surface of the solid oxychloride. The salt then on heating dissolved in the cyanide solution with a yellow color. No oxygen was evolved.

It seems more logical to explain the reaction of the pentavalent tungsten salt to give the tetravalent cyanide as due to the fact that the initial action of the potassium cyanide due to hydrolysis is to form the so-called blue oxide, a compound of tungsten dioxide and tungsten trioxide. Subsequently the potassium cyanide would dissolve the dioxide and trioxide to form, with the dioxide, $K_4W(CN)_8$, and with the trioxide, a tungstate, both of which reactions have been found to take place.[7] To test the above hypothesis, 2.00 g. of the ammonium tungsten oxypentachloride was treated with 5 g. of potassium cyanide in 20 cc. of water and the solution was heated to near the boiling point for five minutes and allowed to cool slowly to room temperature; 0.03 g. of a brown solid, which proved to be tungsten dioxide, remained undissolved. The orange-yellow solution was acidified with hydrochloric acid; a precipitate formed which was separated from the solution by decantation. It was washed with dilute hydrochloric acid and the washings were added to the yellow solution. By the addition of cadmium chloride to this solution there was precipitated the yellow dicadmium tungsten octacyanide octahydrate, $Cd_2W(CN)_8 \cdot 8H_2O$, which after drying *in vacuo* weighed 1.2 g. The weight of the cadmium salt calculated to be formed, on the assumption that the pentavalent salt reacts to give both a tungstate and the complex octacyanide, is 1.7 g.

The precipitate was completely dissolved in dilute ammonium hydroxide, thus showing the absence of the dioxide of tungsten, and after the solution had been made acid with hydrochloric acid, benzidine hydrochloride was added to completely precipitate a benzidine hydrochloride tungstic acid complex. This complex was filtered, washed, dried, and ignited; 0.50 g. of tungstic oxide was obtained, while according to the hypothesis outlined above, 0.55 g. would have been formed. The recovery of 70% of the theoretical quantity of cadmium tungsten octacyanide, which was not greater on account of incomplete reaction of the tungsten dioxide with potassium cyanide, and on account of the appreciable solubility of the cadmium salt, and the recovery of 90% of

[5] Bucknall and Wardlaw, *J. Chem. Soc.*, 2988 (1927).

[6] Collenberg, *Z. anorg. allgem. Chem.*, **102**, 247 (1918).

[7] In a recent paper, Jakob and Turkiewicz [*Roczniki Chem.*, **11**, 569 (1931)] have proposed a similar mechanism for the reaction of $(NH_4)_2MoCl_5$ with KCN.

the theoretical quantity of tungstic oxide, indicate that the reaction of a pentavalent salt of tungsten with potassium cyanide follows the mechanism as outlined above, as expressed by the following equations

$$2WOCl_5^{=} + 6OH^- \longrightarrow W_2O_5 + 10Cl^- + 3H_2O$$
$$W_2O_5 + H_2O + 8CN^- \longrightarrow W(CN)_8^{=\,=} + WO_4^{=} + 2OH^-$$

Summary

The behavior of the compound $K_3W_2Cl_9$ with water in an atmosphere of nitrogen, and with solutions of potassium hydroxide of various concentrations was studied; the extent of oxidation of the tungsten was obtained in one series of experiments by measurement of the volume of hydrogen evolved and in another series by titration of the resulting tungsten oxide with standard potassium permanganate solution. It was found that with water alone 60% of the tungsten was oxidized to valence four, and there was recovered an oxide of tungsten of composition $3WO_2 \cdot W_2O_3$ or W_5O_9. With a solution of 6 *N* potassium hydroxide, 80% of the tungsten was oxidized to valence four while with a 50% solution of potassium hydroxide, oxidation of the tungsten proceeded completely to valence four, and there was recovered the oxide, WO_2. Only in the presence of air was the tungsten oxidized beyond this valence.

Potassium cyanide solution reacts with salts of trivalent tungsten and also with those of pentavalent tungsten to produce $K_4W(CN)_8$. In the former case, the oxidation of the tungsten takes place even in a nitrogen atmosphere and at room temperature because of the intermediate formation of an unstable oxide due to the alkaline character of the potassium cyanide solution. When $(NH_4)_2WOCl_5$ was treated with potassium cyanide solution, a blue oxide of tungsten was first formed, which is produced when there is present tetravalent and hexavalent tungsten. Further action of the potassium cyanide caused complete solution to take place with the formation of $K_4W(CN)_8$ and K_2WO_4.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

EQUILIBRIUM IN BINARY SYSTEMS UNDER PRESSURE. III. THE INFLUENCE OF PRESSURE ON THE SOLUBILITY OF AMMONIUM NITRATE IN WATER AT 25°

BY L. H. ADAMS AND R. E. GIBSON

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It has been shown[1] that it is possible to calculate without any approximate assumptions the influence of high pressure on the solubilities of the pure solid components in a binary system, if the requisite simple thermodynamic data at all pressures are available. Furthermore, methods were described in detail whereby the data peculiar to changes under pressure might be obtained with a high degree of precision. The application of these principles and methods to the influence of pressure on two-phase equilibria in the system, NH_4NO_3–H_2O, at 25° has brought to light results of considerable interest. The solubility of ammonium nitrate is very greatly altered by the application of hydrostatic pressure; indeed, we have found that one hundred grams of water which dissolves 208.9 grams of ammonium nitrate at atmospheric pressure will only dissolve 42.25 grams of the salt when the pressure on the system is 10 kilobars.[2] The impression is still prevalent that hydrostatic pressure has but little effect on equilibria in condensed systems. We quote from Rothmund[3] the following passage which has in different versions been repeated from time to time: "Die nicht sehr zahlreichen Beobachtungen, welche über den Einfluss des Druckes auf die Löslichkeit vorliegen, bestätigen, dass dieser Einfluss ein sehr geringer ist, was ja auch von vornherein erwartet werden kann, da das Volumen und die sonstigen Eigenschaften bei festen und flüssigen Stoffen sich mit dem Drucke nur wenig ändern." (The few observations that have been made on the influence of pressure on solubility indicate strongly that this influence is a very small one, a conclusion that might certainly have been expected, as the volume and other properties of solid and liquid substances vary only slightly with pressure.) Since this statement was written, Cohen[4] and his school have brought forward several examples of systems where large changes of solubility have resulted from relatively small changes of pressure, and, in fact, as each new system is investigated, it becomes more and more apparent that any general statements about the effect of pressure on condensed systems are rather apt to be misleading. The data are still inadequate to support a generalization.

[1] L. H. Adams, THIS JOURNAL, (a) **53**, 3769 (1931); (b) **54**, 2229 (1932).

[2] 1 kilobar = 1000 bars or approx. 1000 atm.

[3] V. Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung," Leipzig, 1907, p. 81.

[4] See especially E. Cohen and A. L. Th. Moesveld, *Z. physik. Chem.*, **93**, 385 (1919); E. Cohen, W. de Meester, and A. L. Th. Moesveld, *ibid.*, **114**, 321 (1924).

In this paper we shall present the experimental data and the calculations necessary for the determination of the solubility curves of NH_4NO_3 **IV**[5] and ice_{VI} under pressure at 25°, and thence construct the pressure–concentration diagram, which we shall check at certain points by direct measurements of phase changes under pressure.

Experimental

Specific Volumes of Ammonium Nitrate Solutions at Atmospheric Pressure.—Of all the thermodynamic data necessary for our calculations none are more important than the partial volumes of the components in the solutions at atmospheric pressure. These are derived directly from the specific volumes of solutions of different concentrations. The values of the densities or specific volumes of solutions of ammonium nitrate which are summarized in the "International Critical Tables"[6] were hardly of sufficient accuracy for our work, so a series of determinations at 25° was made with the apparatus and procedure which have already been frequently used and described.[7] The experimental results are recorded in Table I, the temperature of the thermostat being 25 ± 0.003° and the volume of the pycnometer being taken as 55.0368 ml. The values at even concentrations, obtained by interpolation from a plot of the first differences against the concentration,

TABLE I

SPECIFIC VOLUMES OF SOLUTIONS OF AMMONIUM NITRATE AS DETERMINED EXPERIMENTALLY AT 25°

Corrected weight Salt	Corrected weight Solution	Weight fraction of salt, x_2	Weight of soln. in pycnometer	Specific volume ml./g., v
0	0	0		1.002932
0.9983	99.8842	0.009995	55.0981	0.998887
4.9477	99.0136	.049970	55.9886	.983000
7.9591	80.2827	.099138	57.1017	.963838
11.9318	79.4705	.150141	58.2849	.944272
17.9221	89.5478	.200140	59.4743	.925388
21.8358	87.3707	.249921	60.6916	.906828
22.7062	90.8086	.250045	60.6941	.906790
31.9456	91.2455	.350106	63.2391	.870297
43.7932	97.9445	.447123	65.8417	.835896
49.3806	89.8086	.549843	68.7554	.800472
60.2629	100.4476	.599944	70.2415	.783537
58.1451	89.5440	.649347	71.7538	.767023
64.8719	99.5058	.651941	71.8341	.766163
66.6345	98.3358	.677622	72.6417	.757647

[5] NH_4NO_3 **IV** is the orthorhombic form of solid ammonium nitrate which is stable at atmospheric pressure between −18 and 32.3°. The effect of pressure is to increase in both directions the temperature range over which the modification **IV** is stable.

[6] "I. C. T.," Vol. III, p. 59.

[7] R. E. Hall, *J. Wash. Acad. Sci.*, **14**, 167 (1924); R. E. Gibson, *J. Phys. Chem.*, **31**, 496 (1927); *ibid.*, **55**, 690 (1931).

are given in Table II. In each case the interpolation interval was so small that no appreciable error was introduced.

TABLE II

THE SPECIFIC VOLUMES OF AMMONIUM NITRATE SOLUTIONS, THE APPARENT VOLUME OF THE SALT, AND THE PARTIAL VOLUMES OF THE SALT AND WATER AT EVEN INTERVALS OF CONCENTRATION

x_2	v	ϕ	$\phi_{obs.} - \phi_{calcd.} \times 10^5$	$\bar{v}_2$	$\bar{v}_1$
0	1.002932	(0.5932)		0.5932	1.002932
.01	0.99888$_5$	.5981	−38	.6005	1.00291
.05	.98298$_9$	.60404	− 2	.6090	1.00267
.10	.96351$_3$	.60872	22	.6157	1.00216
.15	.94432$_6$	.61222	9	.6207	1.00145
.20	.92544$_0$	.615465	9	.6252	1.00050
.25	.906807	.618404	0	.6293	0.99930
	.906799				
.30	(.88843)	(.62127)	(− 1)	.6332	.99782
.35	.870335	.624080	2	.6367	.99608
.375	(.86138)	(.62546)	(3)	.6383	.99523
.40	(.85249)	(.62682)	(4)	.6398	.99428
.45	.834890	.629502	5	.6426	.99222
.50	(.81753)	(.63212)	(4)	.6451	.98995
.525	(.80893)	(.63341)	(2)	.6463	.98868
.55	.800404	.634698	0	.6474	.98741
.60	.783519	.637242	(− 6)	.6491	.98515
.65	.766808	.639662	(−23)	.6504	.98299
	.766806				
.68	.756860	.641060	(−38)	.6510	....
.6763	....	....	....	.6509	....

The partial or fictive volumes of the salt ($\bar{v}_2$) and of the water ($\bar{v}_1$) in the solutions were calculated with the help of the intermediate quantity ϕ, the "apparent volume" of one gram of ammonium nitrate in a solution, which is defined by the equation

$$v = x_2\phi + x_1 v_w \qquad (1)$$

where v_w is the specific volume of pure water. Several investigators[8] have recently confirmed the opinion that ϕ, or its analog the apparent molal volume, is a linear function of the square root of the volume concentration over a considerable range which appears to extend down to infinitely dilute solutions. We found that a slightly different form of equation, namely

$$\phi = 0.59318 + 0.049161 x_2^{1/2} \qquad (2)$$

fitted our results from 1 to 15% within the experimental error, even though the concentration was expressed as the weight fraction. This equation was used in the estimation of ϕ at zero concentration and in the calculation of the fictive volumes in solutions containing from zero to 10% of ammonium nitrate. A second equation

[8] See Adams, Ref. 1b, Footnote on p. 2233.

$$\phi = 0.594118 + 0.043431x_2^{1/2} + 0.020524x_2^{3/2} \quad (3)$$

represented the data moderately well above 10%, as will be seen in column 4 of Table II which gives the difference between the values of ϕ as observed and as calculated by equation (3). It might be remarked that equation (3) fitted the results even better than a four constant power series in $(x_2/x_1)^{1/2}$. The interpolated values of v, enclosed in parentheses in Table II, were obtained from values of ϕ calculated by equation (3) and corrected from a deviation curve. In this way a table of x_2 at even intervals of 0.05 and of ϕ was constructed. The first divided differences, $\Delta\phi/\Delta x_2$, which were taken as giving the mean values of $d\phi/dx_2$ at the intermediate concentrations, were plotted against x_2. From this curve were read the mean values of $d\phi/dx_2$ corresponding to the concentrations listed in Table II. By this simple procedure all the data necessary for computing the partial volumes of the salt, $\bar{v}_2$, were made available and substituted in the formula

$$\bar{v}_2 = x_1x_2\frac{d\phi}{dx_2} + \phi \quad (4)$$

The resulting values of $\bar{v}_2$ are given in the fifth column of Table II. These figures were carefully compared with values of $\bar{v}_2$ as calculated directly from equation (3) together with the slopes of the deviation curve. The agreement was excellent at all concentrations above $x_2 = 0.10$, showing that the method of tabular differences was very satisfactory. The relation

$$v = x_1\bar{v}_1 + x_2\bar{v}_2 \quad (5)$$

was used to calculate $\bar{v}_1$, the fictive volumes of the water in the various solutions.

Changes in the Total and Partial Volumes under Pressure.—By the piston-displacement method[9] the *compressions* of the solutions produced by a rise of pressure from 2 to P kilobars were compared directly with the *compressions* of pure water produced by the same increase of pressure. To remind the reader of our nomenclature we may add that k represents the total *compression* or relative volume change per cc. at 1 atm., when the pressure is raised a definite amount from atmospheric pressure, and that k' stands for the same quantity when the upper limit of the pressure is fixed at 2 kilobars. Thus directly from the experimental observations we obtain the difference between $(k - k')$ for water and $(k - k')$ for the solution. This quantity we call $(\Delta k - \Delta k')$. The glass piezometer method[10] was used in the determination of k', which, together with the known values of the compressions of water,[11] led to an estimate of the compressions k of the various solutions. The product of k and the specific volume of the solution at 1 bar gave $\Delta_P v$, the increase in the specific volume of the solution pro-

[9] Adams, Ref. 1a, pp. 3773–3780.

[10] Adams, Ref. 1a, p. 3773.

[11] Summarized by Adams, Ref. 1a, Table II.

duced by the corresponding increase of pressure. Now it will readily be seen that equations (1), (4) and (5) may be written in the forms[12]

$$\Delta_P v = x_2 \Delta_P \phi + x_1 \Delta_P v_w \qquad (1')$$

$$\Delta_P \bar{v}_2 = x_1 x_2 \frac{d}{dx_2} \Delta_P \phi + \Delta_P \phi \qquad (4')$$

$$\Delta_P v = x_1 \Delta_P \bar{v}_1 + x_2 \Delta_P \bar{v}_2 \qquad (5')$$

The change in the apparent volume of the salt $\Delta_P \phi$ was computed by equation (1'), and the values obtained were found, within the scope of our measurements, to be linear functions of x_2. The constant slopes, $\frac{d}{dx_2} \Delta_P \phi$, at the different pressures are given in the last column of Table V. Tables III, IV and V record, respectively, the values of k, $\Delta_P v$ and $\Delta_P \phi$ at different pressures in solutions of different concentrations. The values of $\Delta_P \bar{v}_2$ recorded in Table VI represent a weighted mean of the values calculated from $\Delta_P \phi$ by equation (4'), and of a series computed directly from the slopes of $(\Delta k - \Delta k')$ with respect to x_2, taken as smoothed func-

TABLE III

EXPERIMENTAL VALUES OF $10^4 k$ FOR AMMONIUM NITRATE SOLUTIONS AT HIGH PRESSURES

P in kilobars	x_2....0	0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0	0
1.0	393	351	309	289	270	250
2.0	699	626	556	524	490	467
3.0	945	850	762	719	677	667
4.0	1152	1039	935	891	840	
5.0	1330	1205	1087	1039	1001	
6.0	1485	1349	1222	1174	1151	
7.0	1622	1478	1344	1300		
8.0	1746	1592	1451			
9.0	1858	1701	1553			
10.0	1964	1802	1650			

TABLE IV

VALUES OF $10^4 \Delta_P v$ FOR AMMONIUM NITRATE SOLUTIONS AT HIGH PRESSURES

P	x_2....0	0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0	0
1.0	− 394	− 332	− 275	− 249	−225	−202
2.0	− 701	− 591	− 494	− 452	−409	−378
3.0	− 948	− 803	− 677	− 620	−565	−540
4.0	−1155	− 981	− 831	− 768	−701	
5.0	−1334	−1138	− 966	− 895	−836	
6.0	−1489	−1274	−1086	−1012		
7.0	−1627	−1396	−1194	−1120		
8.0	−1751	−1503	−1290			
9.0	−1863	−1606	−1380			
10.0	−1970	−1702	−1466			

[12] The operator Δ_P indicates the finite change in the particular quantity produced by a finite change of pressure, the other variables, T and x, being kept constant.

TABLE V

VALUES OF $10^4\Delta_P\phi$ FOR SOLUTIONS OF AMMONIUM NITRATE AT DIFFERENT PRESSURES AND VALUES OF $\frac{d}{dx_2}\Delta_P\phi$

P	x_2....0.15	0.30	0.375	0.45	0.525	$\frac{d}{dx_2}\Delta_P\phi \times 10^3$
0.001	0	0	0	0	0	
1.0	20	3	− 8	− 18	− 29	−13
2.0	33	− 10	− 37	− 51	− 86	−29
3.0	20	− 43	− 72	− 98	−171	−39
4.0	6	− 80	−123	−147		−52
5.0	− 27	−107	−163	−227		−60
6.0	− 53	−147	−216	−316		−63
7.0	− 87	−183	−275			−64
8.0	−100	−213				−75
9.0	−153	−253				−68
10.0	−180	−290				−73

TABLE VI

CHANGES IN THE PARTIAL VOLUMES OF AMMONIUM NITRATE IN VARIOUS SOLUTIONS UNDER PRESSURE. WEIGHTED MEAN OF $10^3\Delta_P\bar{v}_2$

P	x_2....0	0.15	0.30	0.375	0.45	0.525
0.001		0	0	0	0	0
1.0		0.6	− 2.6	− 4	− 5	− 6
2.0		− 0.5	− 6.9	−10	−12	−15
3.0		− 3.1	−11.6	−15	−19	−24
4.0		− 6.0	−17.0	−21	−24	
5.0		−10.0	−21.4	−26		
6.0		−13.2	−25.8	−31		
7.0		−16.7	−29.8	−35		
8.0		−19.8	−34.5			
9.0		−23.6	−37.6			
10.0		−27.1	−42.0			

TABLE VII

CHANGES IN THE PARTIAL VOLUMES OF WATER IN SOLUTIONS OF AMMONIUM NITRATE UNDER PRESSURE. $10^3\Delta_P\bar{v}_1$

P	x_2....0	0.15	0.30	0.375	0.45	0.525
0.001		0	0	0	0	0
1.0		− 39.1	− 38.1	− 37.4	− 36.4	−35.8
2.0		− 69.4	− 67.3	− 66.2	− 64.7	−62.9
3.0		− 93.9	− 91.7	− 90.2	− 88.0	−87.1
4.0		−114.3	−111.4	−110.2	−107.5	
5.0		−132.1	−128.9	−127.5		
6.0		−147.5	−144.3	−143.4		
7.0		−161.3	−157.9	−158.2		
8.0		−173.3	−169.4			
9.0		−184.8	−181.0			
10.0		−195.4	−191.4			

tions of the pressure. Equation (5′) was used to calculate Table VII directly from Table VI.

We have plotted the values of the partial volumes of ammonium nitrate in solutions of different concentrations against the pressure in Fig. 1. The dotted curve shows the specific volume of solid ammonium nitrate as a function of the pressure. This diagram shows a marked contrast to the similar one for sodium chloride or for potassium sulfate. While the partial volumes of ammonium nitrate decrease as the pressure increases, except in the dilute solutions (15% or below) at low pressures, the partial volumes of the sodium chloride or potassium sulfate increase rapidly with pressure

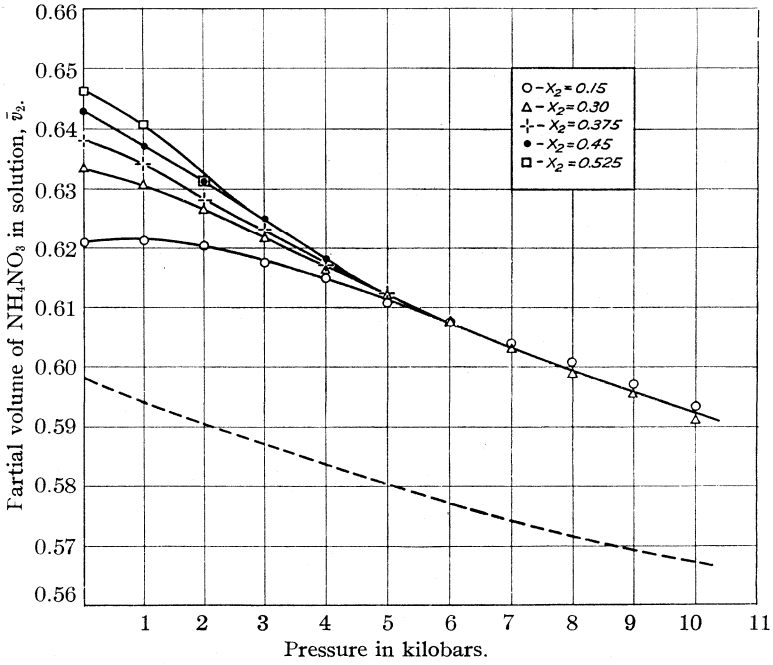

Fig. 1.—The partial volumes, $\bar{v}_2$, of ammonium nitrate in different solutions as a function of the pressure. The dotted curve shows the specific volume of the solid salt at different pressures.

except at the highest pressures in the most concentrated solutions. Furthermore, within the error of experiment our values of the partial volumes in different solutions seem to merge into one curve at the higher pressures, a curve whose slope is not very different from the slope of the volume–pressure curve of the solid salt. In other words, it seems that in aqueous solutions containing 15% or more ammonium nitrate the partial volumes of the salt are independent of the concentration above 5 kilobars and that the partial compressibility of the salt differs only slightly from the compressibility of the solid salt above this pressure. Ammonium nitrate adds another striking example in support of the supposition that at high pres-

sures and high concentrations aqueous salt solutions behave more and more like ideal solutions, at least in respect to volume changes.

Changes of the Chemical Potentials μ_1 and μ_2 in Solutions of Ammonium Nitrate.—Measurements made recently in this Laboratory show that the vapor pressures of solutions of ammonium nitrate may be expressed as a function of concentration within the error of experiment by the following simple equation

$$\log \frac{p}{p_0 X_1'} = 0.00093 + 0.31317\, X_2'^{3/2} - 0.1580\, X_2'^{5/2} \qquad (6)$$

The equation, which is valid over a range from 15 to 65% of ammonium nitrate, contains the quantities, p/p_0, the relative vapor pressure of the solution, X_2', the mole fraction of the ammonium nitrate calculated on the basis of the molecular weight being one-half of the usual formula weight, and X_1', which is equal to $(1 - X_2')$. This relation will be discussed in detail elsewhere—in this paper it is used to calculate $(\mu_1 - \mu_w)$, the difference between the chemical potential of water in any solution of ammonium nitrate and that of pure water at the same pressure and temperature.

At the low vapor pressures at which p/p_0 was determined, the chemical potential difference was given with sufficient accuracy by the equation

$$\mu_1 - \mu_w = \frac{2.303RT}{M_1} \log \frac{p}{p_0}$$
$$= \frac{2.303RT}{M_1} \left\{ \log X_1' + 0.00093 + 0.31317\, X_2'^{3/2} - 0.1580\, X_2'^{5/2} \right\} \qquad (7)$$

The difference between the chemical potential of the salt in any solution, μ_2, and in the saturated solution at 25°, $\mu_{satd.}$, was computed from the foregoing with the aid of Gibbs' equation (97), which for a binary system at constant temperature and pressure assumes the form

$$x_1 d\mu_1 = -x_2 d\mu_2 \qquad (8)$$

From equations (7) and (8) it follows that

$$\mu_2 = \frac{2.303RT}{M_2'} \left\{ \log X_2' - 0.93951\, X_2'^{1/2} + 0.57649\, X_2'^{3/2} - 0.1580\, X_2'^{5/2} \right\} + const. \qquad (9)$$

The value of μ_2 at the mole fraction corresponding to $x_2 = 0.6763$, the concentration of the saturated solution at 25°,[13] was taken as zero and hence $(\mu_2 - \mu_{satd.})$ was computed.

In order to bring these chemical potential differences from 20 to 25°, the partial enthalpy differences $(\bar{h}_1 - \bar{h}_w)$ and $(\bar{h}_2 - \bar{h}_{satd.})$ at the various concentrations were derived from the data of Cohen and Helderman[14] on the heats of solution of ammonium nitrate at 32.4° and brought to 22.5° by the heat capacity data of Cohen, Helderman and Moesveld.[15]

[13] E. Cohen and H. L. Bredée, *Z. physik. Chem.*, **117**, 148 (1925).

[14] E. Cohen and W. D. Helderman, *ibid.*, **113**, 154 (1924).

[15] E. Cohen, W. D. Helderman, and A. L. Th. Moesveld, *ibid.*, **112**, 139 (1924).

Equation (10) gives the exact formula for changing μ_2 from one temperature T_0 to another temperature T

$$(\mu_2 - \mu_{satd.})_T = \frac{T}{T_0}(\mu_2 - \mu_{satd.})_{T_0} - \frac{T - T_0}{T_0}(\bar{h}_2 - \bar{h}_{satd.})_{T_0} - \int_{T_0}^{T}\int_{T_0}^{T}\frac{\Delta\bar{c}_p}{T}\,dT dT \quad (10)$$

but by taking the value of $(\bar{h}_2 - \bar{h}_{satd.})$ at the intermediate temperature we avoided the necessity of using the last term.

In Table VIII we have incorporated values of the chemical potential differences in joules per gram at 20° as calculated by equations (7) and (9), and such values of these quantities at 25° as were necessary for this investigation.

TABLE VIII

CHEMICAL POTENTIAL DIFFERENCES AT 20 AND 25°. JOULES PER GRAM

x_2	$(\mu_1 - \mu_w)_{20}$	$(\mu_1 - \mu_w)_{25}$	$(\mu_2 - \mu_{satd.})_{20}$	$(\mu_1 - \mu_{satd.})_{25}$
0	0	0	∞	∞
0.10	(− 5.33)			
.15	− 8.18	− 8.39	−78.1	−81.3
.20	−11.16		−66.77	−69.35
.25	−14.34		−55.81	−57.96
.30	−17.76	−18.33	−46.76	−48.54
.35	−21.50		−38.98	−40.44
.40	−25.67		−32.03	−33.20
.45	−30.38		−25.67	−26.58
.50	−35.78		−19.71	−20.39
.55	−42.10		−13.97	−14.54
.60	−49.65		− 8.40	− 8.66
.65	−58.84		− 2.89	− 2.98
.6763	−64.56		0	0

The changes in the chemical potentials produced by a given rise in pressure at constant concentration are given by the general relation

$$\mu = (\mu)_0 + \int_0^P \bar{v}\,dP \quad (11)$$

where the subscript zero outside the parentheses, as always in this paper, means zero pressure. Terms of this nature will be introduced as required.

The Pressure–Solubility Curve of NH_4NO_3 IV.—If, at a given pressure P, a solution of ammonium nitrate of concentration x_2 is in equilibrium with solid NH_4NO_3 **IV**, whose chemical potential at that pressure may be written $(\mu_s)_P$, then according to Gibbs' fundamental equations

$$(\mu_2)_P = (\mu_s)_P \quad (12)$$

Now $$(\mu_2)_P = (\mu_2)_0 + \int_0^P \bar{v}_2 dP$$

and $$(\mu_s)_P = (\mu_s)_0 + \int_0^P v_s dP$$

$$\therefore \quad (\mu_2 - \mu_s)_0 = -\int_0^P (\bar{v}_2 - v_s)dP, \text{ if } (\mu_2)_P - (\mu_s)_P = 0 \quad (13)$$

i. e., $$(\mu_2 - \mu_{satd.})_0 = -\int_0^P (\bar{v}_2 - v_s)dP, \textit{ at the equilibrium concentration, } x_2 \quad (14)$$

Hence, as $(\mu_2 - \mu_{satd.})$ at atmospheric pressure is a function of x_2, say $F(x_2)$, and as $-\int_0^P (\bar{v}_2 - v_s)dP$ is another function of x_2, say $f(x_2)$, the problem of finding the equilibrium concentration at the pressure P resolves itself into determining a value of x_2 which satisfies the equation $F(x_2) = f(x_2)$ when the upper limit of the pressure is P. Graphically the problem may be solved by plotting $(\mu_2 - \mu_{satd.})_0$ and, for each pressure, $-\int_0^P (\bar{v}_2 - v_s)dP$ in the same units against the weight fraction and reading the concentration at which these two curves intersect, as is done in Fig. 2.

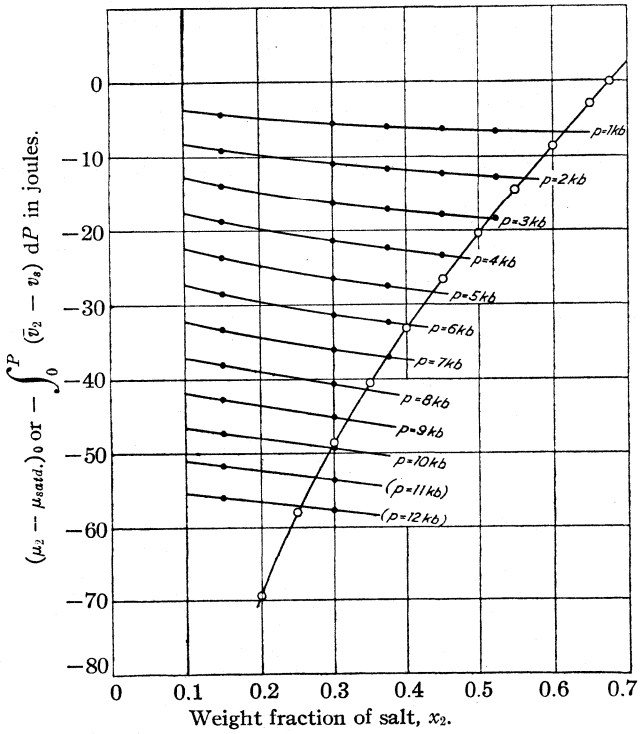

Fig. 2.—The curve with the open circles gives the chemical potential difference between ammonium nitrate in solutions of different concentration and ammonium nitrate in saturated solution, $(\mu_2 - \mu_{satd.})_0$, at 1 atmosphere and 25°. The other curves give the values of $-\int_0^P (\bar{v}_2 - v_s)dP$ at even kilobars as a function of the concentration. The abscissas of intersections of this family of curves with the curve of $(\mu_2 - \mu_{satd.})_0$ are the equilibrium concentrations at the various pressures.

For convenience in calculation, equation (14) was modified to equation (15)

$$(\mu_2 - \mu_{satd.})_0 = -[(\bar{v}_2)_0 - (v_s)_0]P - \int_0^P (\Delta_P\bar{v}_2 - \Delta_P v_s)\mathrm{d}P \qquad (15)$$

where the terms to be integrated are much smaller; indeed, the second term on the right-hand side of equation (15) is very significant only at the high pressures, and graphical integration was found to be more than adequate in accuracy. The specific volume of NH_4NO_3 **IV** at atmospheric pressure $(v_s)_0$ was taken as 0.5797 and $\Delta_P v_s$ was computed from the equation[16]

$$-\Delta_P v_s = 0.5797k = (668.9P - 13.86P^2)0.5797 \times 10^{-5} \qquad (16)$$

while $\bar{v}_2$ and $\Delta_P\bar{v}_2$ were taken from Tables II and VI, respectively.

TABLE IX

VALUES IN JOULES OF $-\int_0^P (\bar{v}_2 - v_s)\mathrm{d}P$ FOR DIFFERENT SOLUTIONS OF AMMONIUM NITRATE

P	x_2....0.15	0.30	0.375	0.45	0.525
0.001	0	0	0	0	0
1.0	− 4.35	− 5.43	− 5.90	− 6.2	− 6.53
2.0	− 9.03	−10.88	−11.62	−12.22	−12.71
3.0	−13.87	−16.23	−17.12	−17.97	−18.34
4.0	−18.78	−21.42	−22.40	−23.40	
5.0	−23.68	−26.44	−27.47		
6.0	−28.54	−31.30	−32.36		
7.0	−33.34	−36.01	−37.10		
8.0	−38.05	−40.58			
9.0	−42.67	−45.03			
10.0	−47.19	−49.34			
11.0	(−51.6)	(−53.5)			
12.0	(−55.9)	(−57.6)			

TABLE X

SOLUBILITY OF AMMONIUM NITRATE UNDER PRESSURE AT 25°

P	x_2
0	0.6763
1	.616
2	.563
3	.516
4	.473
5	.436
6	.403
7	.373
8	.345
9	.319
10	.297
11	(.275)
12	(.254)

Values in joules of the integral on the right-hand side of equation (14) are collected together in Table IX, and plotted against concentration for each value of the upper limit of pressure in Fig. 2. The original diagram on a large scale was used for the actual determination of the values of the equilibrium concentrations at each pressure which are summarized in Table X.

In effect we find for a given P the value of x_2 at which the μ of the solid salt is equal to that of the salt in solution. The same result may be obtained by finding, for a specified x_2, the value of P at which the μ's become equal, as was done in the previous investigations for determining the freezing-pressure curve of ice_{VI}. This would be accomplished by calcu-

[16] L. H. Adams and R. E. Gibson, *J. Wash. Acad. Sci.*, **21**, 388 (1931).

TABLE XI

THE FREEZING PRESSURES AT 25° OF ICE$_{VI}$ AND THE FREEZING TEMPERATURES AT ATMOSPHERIC PRESSURE OF ICE$_{I}$ IN CONTACT WITH SOLUTIONS OF AMMONIUM NITRATE. THE RATIO OF THE TEMPERATURE LOWERING TO THE PRESSURE ELEVATION IS GIVEN IN THE LAST COLUMN

x_2	P	$P - P_0$ (ice$_{VI}$)	$t_0 - t$ (ice$_{I}$)	$\frac{t_0 - t}{P - P_0} \times 10^2$
0	9,630	0	0	(0.53)[a]
0.15	10,930	1300	5.79	.44
.30	12,700	3070	11.35	.37

[a] Theoretical value calculated from dilute solution law.

lating $\mu_2 - (\mu_2)_r$ from $\bar{v}_2 - (\bar{v}_2)_r$ for each concentration (the subscript r denoting a reference concentration, say 15%) and determining from a plot the intersection of each curve with the curve for $\mu_s - (\mu_2)_r$. As a check on the computations, the solubility curve of ammonium nitrate was determined also by this method, with substantially the same results as those given by the first method, which, it may be noted, appears to be more convenient in the present instance.

The Solubility Curve of Ice$_{VI}$.—Pure water and ice$_{VI}$ coexist at equilibrium at 25° under a pressure of 9630 bars. Our problem was to find the pressures under which ice$_{VI}$ and a 15 or a 30% solution of ammonium nitrate are in equilibrium at this temperature. The chemical potential difference between water and ice$_{VI}$, *i. e.*, $(\mu_{VI} - \mu_w)$ has already been given as a function of the pressure,[17] and the chemical potential difference $(\mu_1 - \mu_w)$ for a given solution may be determined at any pressure by the relation

$$(\mu_1 - \mu_w)_P = (\mu_1 - \mu_w)_0 + \int_0^P (\bar{v}_1 - v_w)dP \qquad (17)$$

The terms in this equation are all known; $(\mu_1 - \mu_w)$ is given in Table VIII, $\bar{v}_1$ may be written as a tabular function of P from Tables II and VII, and v_w at different pressures is given in a previous paper.[18] In Fig. 3 $(\mu_{VI} - \mu_w)$ and $(\mu_1 - \mu_w)$ for 15 and 30% solutions of ammonium nitrate were plotted against the pressure. The abscissas corresponding to the intersections of the curves represented the pressures at which ice$_{VI}$ is in equilibrium with these solutions. It was found that ice$_{VI}$ is in equilibrium with a 15% solution of ammonium nitrate at 10,930 bars and with a 30% solution at 12,700 bars. The solubility of the salt was so diminished by pressure that only these two of the solutions studied were available for the construction of the solubility curve of ice$_{VI}$.

The Equilibrium Diagram

The two solubility curves when plotted on the same system of coördinates give the simple pressure–composition diagram shown in Fig. 4. The curves

[17] Adams, Ref. 1a, Table X.

[18] Adams, Ref. 1a, Table II.

divide the diagram into fields in which the phases noted coexist when the system is in equilibrium and they intersect at the point $x_2 = 0.253$, $P = 12.100$ kb. This point is the *pressure eutectic* for the system, NH_4NO_3–H_2O, at 298.1°K., and its coördinates give the only pressure and concentration at which NH_4NO_3 **IV**, ice_{VI}, and liquid solution may coexist in stable equilibrium at this temperature.

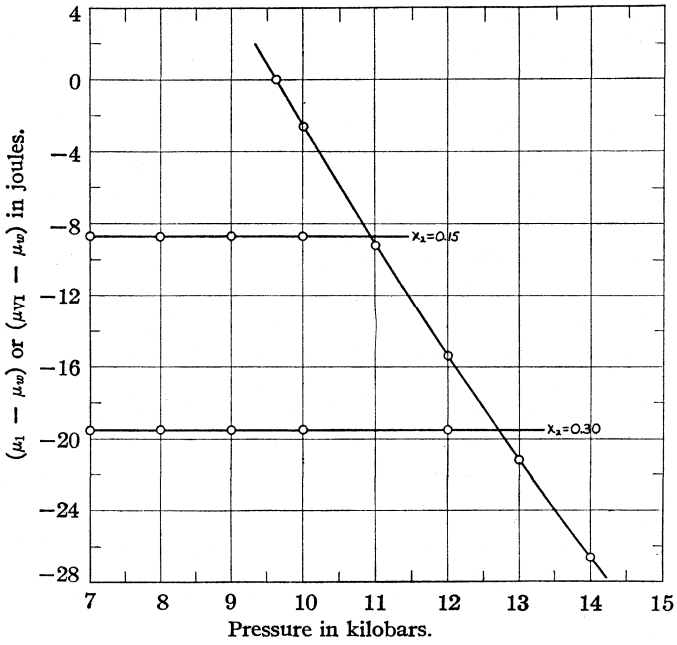

Fig. 3.—The differences between the chemical potential of water in 15 and 30% solutions of ammonium nitrate and of pure water are plotted as functions of the pressure. The abscissas of the intersections of these curves with the chemical potential–pressure curve of ice_{VI} represent the pressures at which ice_{VI} is in equilibrium with these two solutions.

This system differs in several respects from the systems NaCl–H_2O or K_2SO_4–H_2O, which are the subjects of the first two papers in this series. The solubility of ammonium nitrate at 25° diminishes continuously with increase of pressure, whereas the solubilities of the other two salts at first increase, then pass through a maximum and finally decrease as the pressure is raised. From this point of view the ammonium nitrate solutions behave more like ideal solutions. If we define an ideal solution as one which obeys Raoult's law in the generalized form

$$(\mu_2 - \mu_l) = \frac{RT}{M_2} \ln X_2 \qquad (18)$$

at all pressures at any temperature, it may be shown that $\bar{v}_2 = v_l$ at all

concentrations at that temperature. The reference state indicated by the subscript l is of necessity the pure liquefied component at the temperature and pressure of the experiment and M_2 is the effective molecular weight of that component. The initial slope of the pressure–solubility curve is given in general by the equation

$$\frac{dx_2}{dP} = -\frac{(\bar{v}_2 - v_s)}{\left(\frac{d\mu_2}{dx_2}\right)_P} \tag{19}$$

which for an ideal solution becomes

$$\frac{dx_2}{dP} = -\frac{\Delta v}{\left(\frac{d\mu_2}{dx_2}\right)_P} \tag{20}$$

where $\Delta v = v_l - v_s$, the volume change on melting of the pure solid.

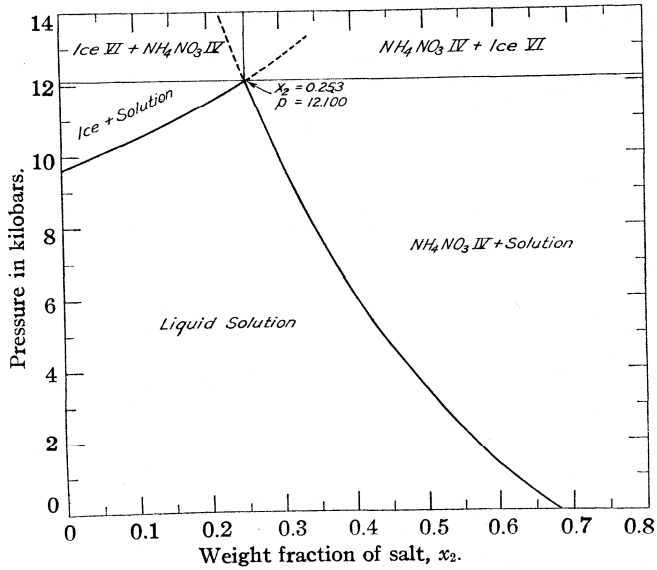

Fig. 4.—The pressure–concentration equilibrium diagram for the system, NH_4NO_3–H_2O, at 25°.

As the chemical potential μ_2 is always an increasing function of x_2 in a phase stable to continuous changes,[19] $(d\mu_2/dx_2)_{P,T}$ is always positive and the sign of the initial slope of the concentration–pressure curve therefore depends on the sign of Δv, the volume change on melting of the solid phase, being negative if Δv is positive and *vice versa*. Except in very rare cases solids expand on melting so that in general increase of pressure should decrease the solubility of a solid in an ideal solution. It should be remarked that the succeeding course of the pressure–solubility curve depends on the relative compressibilities of the solid and liquid forms of the com-

[19] J. Willard Gibbs, "Collected Works," Vol. I, p. 110, eqn. 171.

ponent—quantities that must be observed experimentally—they cannot be predicted from thermodynamics alone.

For purposes of comparison we have collected together in Table XII the data available on the initial values of dx_2/dP for different solutions. For most salts in aqueous solution this quantity is small and positive, whereas in the two solutions of organic solutes and solvents it is comparatively large and negative. The change in solubility of the ammonium nitrate resembles that of the organic compounds in that it is a relatively large decrease with increase of pressure, but it must be added that this decrease is not by any means as great numerically as in the case of the organic solutions. There seems to be little doubt but that aqueous solutions of ammonium nitrate behave more like ideal solutions over the whole range of pressure and concentration than do solutions of sodium chloride or of potassium sulfate.

TABLE XII

THE INITIAL SLOPES OF THE PRESSURE–SOLUBILITY CURVES OF DIFFERENT SOLUTES

Temp., °C.	Solute	Solvent	Soly. at 1 bar, g. per 100 g. soln.	Increase of soly. per 100 bars increase of pressure	Reference
25	NaCl	H_2O	26.42	0.083	Adams
25	K_2SO_4	H_2O	10.76	0.39	Adams
30	Tl_2SO_4	H_2O	5.80	0.33	I. C. T.[a]
25	$CdSO_4$	H_2O	43.44	0.088	I. C. T.[a]
25	$Ba(OH)_2$	H_2O	8.28	0.22	I. C. T.[a]
24	Mannitol	H_2O	17.11	0.072	I. C. T.[a]
25	$ZnSO_4$	H_2O	36.69	−0.013	I. C. T.[a]
30	CdI_2	H_2O	46.79	−0.38	I. C. T.[a]
30	m-$C_6H_4(NO_2)_2$	$CH_3COOC_2H_5$	34.44	−1.14	I. C. T.[a]
30	$C_{10}H_8$	$C_2H_2Cl_4$	35.08	−1.92	I. C. T.[a]
25	NH_4NO_3	H_2O	67.63	−0.63	Adams and Gibson

[a] "International Critical Tables," Vol. IV, p. 265.

Direct Determination of Equilibria

In the foregoing we have been able from the thermodynamic data to construct an equilibrium diagram for the system, NH_4NO_3–H_2O, on the assumption that the phases of the system were NH_4NO_3 **IV**, ice_{VI}, and liquid solution. The method we employed is based on exact thermodynamic principles and is as sound and trustworthy as direct observations themselves. However, the possibility that phases other than those assumed, for example a hydrate, might be formed under pressure must not be overlooked and the opportunity of making direct observations of pressures and concentrations on the equilibrium curves was welcomed as an important check on the validity of our assumptions about the phases. We were able to determine directly (a) the freezing pressure of the 15% solution, (b) the eutectic pressure, and (c) the solubility of NH_4NO_3 **IV**

at approximately 12,000 bars. The freezing pressure of the 15% solution was measured by a method which has already been described[20] and consists essentially of finding the intersection of the pressure piston-displacement curves for the solution alone and for an equilibrium mixture of ice and solution. The intersection of the "after melting" curve and the freezing curve (triangles) is shown in Fig. 5 at a pressure of 10,984 bars. The average of two determinations which differed by 40 bars gave 10,965 bars for the freezing pressure of the 15% solution of ammonium nitrate. This agrees well with 10,930 bars, the value of the freezing pressure of this solution as calculated from the thermodynamic data.

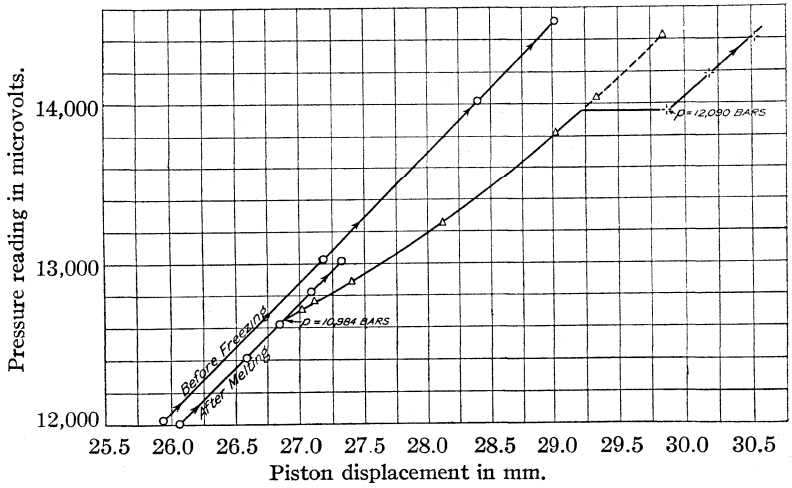

Fig. 5.—Graphical illustration of the direct determination of the freezing pressure of a 15% solution of ammonium nitrate and of the eutectic pressure in the system, NH_4NO_3–H_2O, at 25°.

The procedure for measuring directly the eutectic pressure has already been detailed.[21] The pressure is raised until so much ice has frozen out that the solution becomes sufficiently concentrated for the salt to separate—a super pressure of several hundred atmospheres often being needed. As long as three phases in equilibrium are present the pressure remains constant even though the piston displacement is changed.

Two direct determinations of this constant pressure gave as a mean 12,125 bars, the difference being 70 bars. The agreement between this figure and 12,100 bars, the pressure at which the two calculated solubility curves intersect, is most satisfactory.

In estimating the solubility of ammonium nitrate under pressure we placed a 30% solution in a cylindrical capsule and subjected it to a pressure

[20] Adams, Ref. 1a, p. 3811.

[21] Adams, Ref. 1b, p. 2241.

of approximately 12 kilobars. Although the solution was strongly supersaturated under these conditions, it did not usually begin to deposit salt until at least half an hour had elapsed. This delay in crystallization is in sharp contrast with the promptness with which crystals appear in a solution of ammonium nitrate which is only slightly supersaturated at atmospheric pressure. The solution was kept at high pressure for several hours. After the greater part of the crystallization (as judged by the fall in pressure) had taken place, the pressure was lowered by several hundred bars for a few minutes and then restored to the maximum value. We suspected that the salt might crystallize as long needles which might presumably grow to the top of the capsule. By lowering the pressure we hoped to dissolve these crystals partially and cause them to sink to the bottom of the capsule, where the small amount dissolved would also recrystallize when the system was again subjected to the highest pressure. After the capsule had been removed from the bomb a few cc. of solution was carefully withdrawn from the top layer and analyzed in a Rayleigh–Zeiss interferometer. In one experiment the uppermost layer of solution was found to contain 24.37% NH_4NO_3, while a sample drawn from immediately below it contained 24.40%. This convinced us that mixing had not proceeded to any appreciable extent and that in all probability the composition of the upper layer represented the composition of the solution which was in equilibrium with the solid salt at the maximum pressure. The method is not extremely precise but the results enable us to state with confidence as a result of several experiments that at 12,300 bars the solubility of ammonium nitrate is 24.9 ± 0.5 g. of salt per 100 g. of solution. The extrapolated solubility curve gives 24.8 as the value of this quantity.

The three direct determinations of the equilibrium pressures and concentrations are, therefore, in very good, one might say surprisingly good, agreement with the results of the thermodynamic calculations and confirm our confidence in the correctness of Fig. 4. It is, however, not impossible that the phases marked in this diagram are metastable and that other phases which exhibit extreme reluctance to appear are actually the stable ones, but, as far as our knowledge goes, none such are known or even suspected. Furthermore, as aqueous solutions of ammonium nitrate show small but positive departures from the Law of Ideal Solutions, and as the solid salt expands on dissolving, compound formation between these two components would not be expected.[22]

Summary

From new experimental data on the specific volumes of solutions of ammonium nitrate over the whole range of concentrations at 25° and 1

[22] See Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 72.

atm. pressure, and from direct measurements of the compressions of these solutions, we have calculated the partial volumes of ammonium nitrate and of water in different solutions under pressure from atmospheric to 10 kilobars. The partial volumes of the salt do not exhibit the large increases with rising pressure that were observed in solutions of sodium chloride or potassium sulfate except in the case of the 15% solutions where a small increase is observed at low pressures. Indications are that above 5 kilobars the partial volume of the salt in solutions containing more than 15% of ammonium nitrate is independent of the concentration.

From these data, together with the values of the chemical potential of the salt and water in the solutions at room temperature and pressure, we have calculated exactly the solubility curve of ammonium nitrate and the freezing curve of ice_{VI} up to a pressure of 12 kb. and have constructed an equilibrium diagram for the system, NH_4NO_3–H_2O, under pressure. The solubility of ammonium nitrate decreases continuously as the pressure is raised, diminishing from 67.6% at atmospheric pressure to 43.6% at 5 kilobars, 29.7% at 10 kilobars, and 25.3% at 12.1 kilobars, the eutectic pressure. At three points, namely, the freezing pressure of a 15% solution, the pressure eutectic at 25°, and the concentration of the solution in equilibrium with NH_4NO_3 IV at 12,300 bars, we have checked the diagram by direct observations of equilibria and found very satisfactory agreement.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

THE SYSTEM LEAD ACETATE, ACETIC ACID, WATER[1]

BY GRADY TARBUTTON AND WARREN C. VOSBURGH

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In connection with the study of certain voltaic cells it was found desirable to have further information concerning the system lead acetate, acetic acid, water. Sandved[2] found that the solubility of lead acetate trihydrate in mixtures of acetic acid and water increases with the proportion of acetic acid. He found a transition point at which the percentage of lead acetate was 67.90. Beyond this transition point the solubility data were somewhat uncertain, but he considered that anhydrous lead acetate was the stable solid form. He pointed out, however, that his data do not prove the non-existence of acid lead acetates.

Davidson and McAllister[3] studied the system lead acetate–acetic acid by the freezing point method. They obtained no evidence of solvates of lead

[1] Part of a thesis presented by Grady Tarbutton in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

[2] Sandved, *J. Chem. Soc.*, 2971 (1927).

[3] Davidson and McAllister, THIS JOURNAL, **52**, 512 (1930).

acetate. The compound that crystallized on the lead acetate side of the eutectic point was the unsolvated compound. They reported difficulty in getting the lead acetate to crystallize from a supersaturated solution, and had no points between 49° and the eutectic, about 2°.

The authors have attempted to prepare the cell with an acetic acid–water mixture or pure acetic acid as the solvent, and with anhydrous lead acetate as the solid phase in equilibrium with the saturated solution.

$$Pb(Hg) \mid Pb(C_2H_3O_2)_2 \text{ Satd.} \mid Pb(C_2H_3O_2)_2 \text{ Satd.}, Hg_2(C_2H_3O_2)_2 \mid Hg$$

If the solid phase in this cell is unsolvated lead acetate, the electromotive force should be independent of the composition of the solution. Sandved's data indicated a range of compositions within which this might be expected to be true. It was found, however, that when the cells had attained equilibrium, the electromotive force varied with the composition of the solution throughout the entire range, indicating that the solid phase was solvated. A further investigation of the solubility of lead acetate in acetic acid–water mixtures was therefore undertaken.

It has been found that two others olvates of lead acetate beside the familiar trihydrate exist, $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ and $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$. Anhydrous lead acetate in contact with a saturated solution is metastable.

Materials and Apparatus

Acetic Acid.—Chromic acid was added to C. P. glacial acetic acid in the proportion of 2 g. per 100 cc. and the acid distilled in an all-glass still. The first and last portions were rejected and about 80% collected.[4] The melting point of the product varied from 15.0 to 15.6° for different preparations.

For the experiments in which an acetic acid preparation of very small water content was desired, the water was removed from the purified acid by distilling with acetic anhydride. The quantity of water present was calculated from the freezing point,[5] and the required quantity of acetic anhydride added. Chromic acid was added as a catalyst, 2 g. per 100 cc., and the mixture refluxed for thirty minutes and then distilled, with protection from moisture.[6] The freezing point of the product was 16.48° as compared with 16.6° for pure acetic acid according to De Visser.[7]

Lead Acetate.—Some of the lead acetate was prepared by recrystallizing C. P. material three times. Other preparations were made by adding lead carbonate or litharge in excess to glacial or 6 molar acetic acid. The solution was concentrated by evaporation and crystallized. The product was recrystallized twice from dilute acetic acid solution.

Anhydrous Lead Acetate.—Several methods for the dehydration of lead acetate were tried. The trihydrate was kept in a vacuum over concentrated sulfuric acid with some glacial acetic acid present for eighteen days. After fourteen days it seemed to lose no more weight, but it still contained considerable water. In an oven at 40° with a current of dry air passing over it, the trihydrate lost most of its water in four or

[4] Orton and Bradfield, *J. Chem. Soc.*, **125**, 960 (1924).

[5] Seidell, "Solubilities," D. Van Nostrand Company, New York, 2d ed., Vol. I, p. 5.

[6] Orton and Bradfield, *J. Chem. Soc.*, 983 (1927).

[7] De Visser, *Rec. trav. chim.*, **12**, 118 (1893).

five days. The most satisfactory method when completely anhydrous lead acetate was desired was first to dry the trihydrate in a porcelain dish placed 45 cm. above a hot-plate, then fuse the product, a small quantity at a time. The water present boiled off and the salt resolidified. It was then heated again to fusion and poured into the acetic acid in which it was to be dissolved. Attempts to fuse the trihydrate without the preliminary dehydration resulted in charring.

Apparatus.—An electrically controlled oil thermostat having a capacity of about 50 gallons was used for maintaining constant temperature. The temperature was measured either by a thermometer certified by the Bureau of Standards, reading to 0.01°, or by one certified by the Physikalisch-Technische Reichsanstalt and correct to ±0.02°. The temperature did not fluctuate more than ±0.02°.

A device for agitating samples in the bath was constructed of a circular brass plate 14 cm. in diameter mounted on a shaft and having eight holes near its outer edge. In these holes test-tubes, 1.6 × 15 cm., could be mounted securely by means of cork stoppers. The shaft was suspended in the thermostat from another shaft by means of belts passing over pulleys on the two shafts. The samples to be analyzed were sealed in test-tubes and mounted in the disk parallel to the shaft and the whole device was made to rotate slowly in the bath.

Volumetric apparatus and weights were calibrated.

Methods of Analysis

Determination of Acetic Acid in the Presence of Lead Acetate.—When acetic acid in a solution containing a lead salt is to be titrated with standard sodium hydroxide solution, the lead must be removed before titration. It was found that lead can be removed satisfactorily as the oxalate by slowly adding an excess of a neutral solution of potassium oxalate and allowing the mixture to stand for three hours before titrating. No difficulty was found in getting a sharp end-point with phenolphthalein as the indicator. Experiments showed that the interference of lead acetate could be entirely prevented by this method.

Determination of Lead Acetate.—To a weighed sample of the solution to be analyzed was added 10 cc. of concentrated sulfuric acid and 10 cc. of concentrated nitric acid. The solution was slowly evaporated, without boiling, until fumes of sulfur trioxide were noticeable. It was then diluted to 100 cc. and allowed to cool to room temperature, when an equal volume of alcohol was added. The lead sulfate was filtered off, using either a Munroe or porcelain Gooch crucible, washed with 50% alcohol, dried at 110° to constant weight and weighed.

Solubility Determinations.—To prepare a saturated solution, a quantity of lead acetate was first dissolved at an elevated temperature in a mixture of acetic acid and water. The proportions were adjusted on the basis of preliminary experiments so that on bringing the temperature to 25° and seeding, a considerable excess would crystallize out,[8] but not so much that sampling the solution was difficult. Portions of the supersaturated solution were then sealed in test-tubes along with some seed

[8] Sandved found difficulty in getting lead acetate to crystallize from solutions of high acetic acid content. In this investigation not much trouble was experienced in this respect. A highly supersaturated solution was allowed to stand at room temperature for about twenty-four hours, and a large quantity of crystals was obtained. These crystals were preserved and used to seed other solutions. Crystals are obtained easily on seeding with the proper crystal form.

crystals. The tubes were rotated in the thermostat at 25° until equilibrium was attained.

It was found that equilibrium was reached within eight days if the excess solid was allowed to separate from the supersaturated solution at room temperature before placing in the thermostat, or within fourteen days if allowed to crystallize in the thermostat. It was shown that the same final state was attained by both methods. The samples selected for these experiments were among the most viscous. In view of the above results, all other samples were allowed to crystallize at room temperature and remain in the thermostat for at least fourteen days before analyzing.

At the proper times the test-tubes containing the samples were removed from the rotating device and clamped in an upright position in the bath. After allowing the solution to drain from the sides of the tube, the top was

TABLE I

ANALYSIS OF SATURATED SOLUTION AND WET SOLID

Sample	Sample, g.	0.2731 *N* NaOH, cc.	$PbSO_4$, g.	$HC_2H_3O_2$, %	$Pb(C_2H_3O_2)_2$, %
Satd. solution No. 13	1.4251	21.00	0.9079	24.15	68.31
		20.96	.9082	24.10	68.34
Wet solid No. 13	1.6982	21.25	1.1490	20.50	72.55
		21.25	1.1490	20.50	72.55

TABLE II

SOLUBILITY DETERMINATIONS AT 25°

	Saturated solution			Wet solid			
Sample	$HC_2H_3O_2$, %	$Pb(C_2H_3O_2)_2$, %	H_2O, %	$HC_2H_3O_2$, %	$Pb(C_2H_3O_2)_2$, %	H_2O, %	Solid phase
1	8.21	35.44	56.35	1.45	77.33	21.22	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
2	19.14	39.13	41.73	3.33	78.29	18.38	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
3	26.91	47.11	25.98	10.99	70.00	19.01	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
4	26.55	57.38	16.07	13.28	71.19	15.53	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
5	22.15	68.06	9.79	11.15	77.78	11.07	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$ +
6	22.40	67.75	9.85	15.20	76.93	7.87	$Pb(C_2H_3O_2)_2$ $0.5H_2O$
7	23.25	68.13	8.62	17.31	75.54	7.15	$Pb(C_2H_3O_2)_2$ $0.5H_2O$
8	23.07	68.15	8.78	17.53	75.30	7.17	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
9	23.25	68.15	8.60	7.27	88.43	4.30	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
10	23.28	68.06	8.66	16.26	76.65	7.09	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
12	24.11	68.35	7.54	21.46	71.67	6.87	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
13	24.13	68.33	7.54	20.50	72.55	6.95	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
14	25.89	69.10	5.01	23.29	71.76	4.95	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
15	25.59	70.12	4.29	23.34	72.57	4.09	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
16	25.50	70.54	3.96	18.61	77.78	3.61	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
17	25.49	70.81	3.70	15.75	81.20	3.05	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
18	25.51	70.71	3.78	19.63	77.00	3.37	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
19	25.20	71.54	3.26	19.27	77.59	3.14	$Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$
22	30.94	66.00	3.06	18.56	80.77	0.67	$Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$
23	31.71	65.66	2.63	23.70	74.54	1.76	$Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$
24	40.19	58.29	1.52	20.69	78.51	0.80	$Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$
25	41.82	57.06	1.12	22.41	76.85	.74	$Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$
26	44.56	54.95	0.49	...	...	...	$Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$

opened and as much of the liquid as possible drawn through a filter device (which had been brought to the bath temperature) into a small weighed flask. The test-tube containing the remaining wet solid was weighed, and after dissolving out the solid and drying, the empty tube was weighed.

The samples of both saturated solution and wet solid were diluted to 500 cc., and 100-cc. portions were measured out for analysis. Determinations of acetic acid and lead were made in duplicate by the methods described above. Results of duplicate determinations did not differ by more than two parts in a thousand in any case. The details of a typical analysis are given in Table I, the mean values of the results of all the analyses are given in Table II and are represented graphically in Fig. 1 by the method of Roozeboom.[9] The compositions of the solid phases were determined graphically from a large-scale plot.[10]

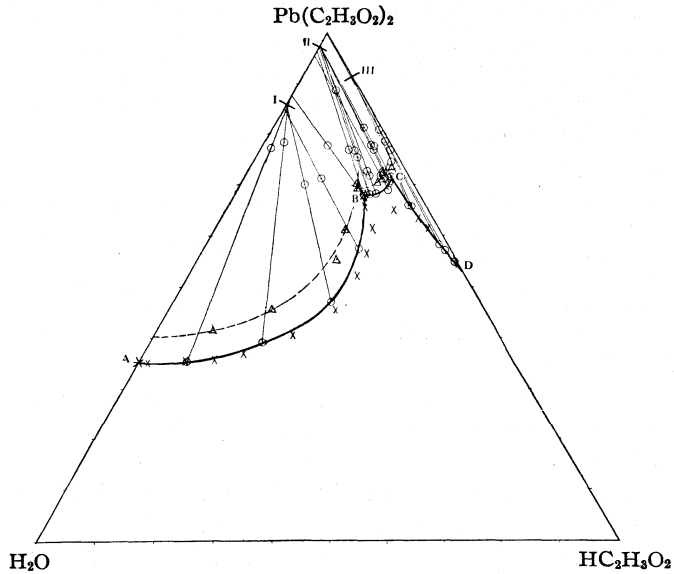

Fig. 1.—Composition of saturated solutions and solid phases. The results obtained at 30° are designated by triangles, those at 25° by circles and Sandved's results at 25° by crosses. The composition $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ is designated by I, $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ by II and $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$ by III.

Points I, II and III of Fig. 1 are the theoretical points for the compounds $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ and $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$, respectively. Compounds II and III have not been reported before as far as the authors are aware.

[9] Roozeboom, *Z. physik. Chem.* **15**, 147 (1894).

[10] Findlay, "The Phase Rule," Longmans, Green and Co., Ltd., London, 6th ed., 1927, p. 263.

Compound I, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, is well known and needs no discussion. It exists in stable equilibrium at 25° with solutions in which the ratio of acetic acid to water by weight is less than 2.3. The value for the solubility in pure water in Fig. 1 was taken from Jackson's[11] data.

Compound II, $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$, consists of thin needles, usually small when first formed but on standing in contact with a saturated solution they sometimes grow to about 12 mm. in length. This compound is capable of existing in stable equilibrium at 25° with saturated solutions in which the ratio of acetic acid to water is between 2.3 and 7.7. Solutions in equilibrium with Compound II are quite viscous, and it was difficult to separate a large proportion of the mother liquor from the solid phase. On this account the extrapolation from the composition of the wet solid to that of the dry solid was rather long.

To check the graphic extrapolation, the percentage of water was calculated from the analysis of each of Samples 7–19 by the algebraic extrapolation method described by Hill and Ricci.[12] Assuming that the compound contained no acetic acid, the average value for the percentage of water was 2.64, with an average deviation from the mean of ±0.66, as compared with the theoretical value of 2.69%. That Compound II was a solvated lead acetate was shown also by the variation of the electromotive force with the composition of the solution when voltaic cells were made with Compound II as the solid phase.

Compound III, $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$, can exist in stable equilibrium with solutions in which the ratio of acetic acid to water is larger than 7.7. The points representing the compositions of the saturated solutions and the solid phases lie so close to the side of the triangle that small errors in composition make a relatively large uncertainty in the convergence point.

In fact algebraic extrapolation showed that the solubility measurements were not sufficiently precise for the establishment of a formula. Therefore a direct analysis of the solid phase was made. The sample was dried in a vacuum desiccator over sodium hydroxide.[13]

Compound III is quite different in crystalline form from Compounds I and II; it crystallizes in plates. Its solubility decreases rapidly as the concentration of water approaches zero.

Several times when fused lead acetate was dissolved in acetic acid of small water content and the solution cooled, the crystals formed were thin needles and the mother liquor was extremely viscous. Only once in five times was Compound III obtained under these conditions. After that,

[11] Jackson, THIS JOURNAL, **36**, 50 (1914).

[12] Hill and Ricci, *ibid.*, **53**, 4306 (1931).

[13] Calculated for $Pb(C_2H_3O_2) \cdot 0.5HC_2H_3O_2$, lead acetate 91.58%; acetic acid 8.42%; found, lead acetate, 90.52, 90.53%; acetic acid, 8.92, 8.86%.

supersaturated solutions were seeded when Compound III was desired, and no trouble was experienced in getting it.

When a sample of the fine needle crystals in contact with a saturated solution was seeded with Compound III, the whole mass changed over to the plate form, showing that the latter form is the more stable. Anhydrous lead acetate did the same. It seems probable that the fine needle crystals are the anhydrous form and that it was this form that Davidson and McAllister obtained in their freezing point determinations. It was impossible to make a precise analysis of the solution saturated with the needle crystals because the very high viscosity interfered too much with filtration. The solution saturated with Compound III was much less viscous and gave no trouble.

A series of solubility determinations was made at 30.00° before all of the technique described above was perfected. The results are sufficiently precise, however, to give an idea of the effect of temperature on the solubility. The solutions were saturated by stirring mechanically for about fourteen days. It was found that at least ten days was required for constancy in acetic acid content to be attained. Samples were taken and analyzed as in the case of the solutions saturated at 25°. The results are given in Table III and by the broken line in Fig. 1.

TABLE III

COMPOSITION OF SATURATED SOLUTIONS OF LEAD ACETATE IN ACETIC ACID AT 30°

Sample	$HC_2H_3O_2$, %	$Pb(C_2H_3O_2)_2$, %	H_2O, %	Sample	$HC_2H_3O_2$, %	$Pb(C_2H_3O_2)_2$, %	H_2O, %
A	9.64	41.61	48.75	G	20.49	69.27	10.24
B	17.47	45.81	36.72	H	24.36	73.50	2.14
C	23.78	55.43	20.79	J	23.66	72.13	4.21
D	22.45	63.08	14.47	K	19.92	70.18	9.90
E	23.86	71.08	5.06	L	23.39	70.45	6.16
F	25.40	69.45	5.15				

The results given in Table III are subject to uncertainty in at least some cases. Some of the solutions were prepared with dried lead acetate. The anhydrous salt changed over to the stable form, but in at least one case the transition was incomplete. The values for solutions in equilibrium with the trihydrate are probably reliable since the trihydrate was used for saturating the solutions.

It was found to be quite difficult to prepare saturated solutions of lead acetate in fairly concentrated acetic acid at room temperature that would be saturated at 30° and yet not contain too much solid phase. The trouble arose because of the large increase of solubility with temperature.

Summary

The existence of the compounds $Pb(C_2H_3O_2)_2 \cdot 0.5H_2O$ and $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$ has been shown.

The former compound can exist in equilibrium with saturated solutions at 25° in which the ratio of acetic acid to water is between 2.3 and 7.7 by weight, and the latter can exist in equilibrium with saturated solutions in which the ratio is larger than 7.7.

Anhydrous lead acetate in contact with a saturated solution is metastable.

DURHAM, NORTH CAROLINA

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

THE ACTIVATION OF MOLECULAR OXYGEN BY ELECTRON IMPACT

BY GEORGE GLOCKLER AND JOHN L. WILSON[1]

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Introduction.—In the case of hydrogen[2] it was found that electrons of 11.4 e. volts or greater energy can transfer hydrogen molecules to an excited state ($^1\Sigma_g^+ \longrightarrow {}^3\Sigma_g^+$) and that such molecules can react with a copper oxide plate. Thus hydrogen molecules need not be ionized; excited states serve equally well as activated species. These studies were continued on oxygen and in the meantime Dalton[3] reported that oxygen molecules, activated by 8-volt electrons, react with a carbon surface. Wansbrough-Jones[4] studied the activation of oxygen, and detected no ozone below 25 e. volts nor below 0.8 mm. pressure. L. A. M. Henry[5] found however formation of ozone at much lower pressures than did Wansbrough-Jones, reporting critical voltages of 9.0 and 21.2 e. volts. In our own investigations on oxygen which were begun before any of the papers cited above appeared, it was decided to study the formation of ozone and the chemical reaction between a mercury surface and oxygen activated by electron impact and other materials. Since our results differ to some extent from those in the literature, they are reported in this paper. We have extended also the mode of interpretation of such experiments and interpret them in terms of efficiencies of energy transfer and of reaction.

Experimental Procedure

Both static and flow methods were used. At first we followed the reaction by freezing out the product formed and determined its behavior with potassium iodide solution. Such experiments, however, were not very reproducible although we obtained

[1] This article is based upon a thesis presented to the Faculty of the Graduate School of the University of Minnesota by John L. Wilson in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Glockler, Baxter and Dalton, THIS JOURNAL, **49**, 58–65 (1927).

[3] Dalton, *ibid.*, **51**, 2366–2374 (1929).

[4] Wansbrough-Jones, *Proc. Roy. Soc.* (London), **127A**, 530–539 (1930).

[5] Henry, *Bull. soc. chim. Belg.*, **40**, 339–360 (1931).

definite evidence of reaction in both methods with this chemical procedure. Since freezing out of the reaction product appeared difficult,[6] we considered other means of detection such as MoO_3, PbO, Ag, etc., and finally we decided that a mercury surface offered the best possibilities. Although Wansbrough-Jones reports no reaction between oxygen and mercury in dry oxygen, we have found that a mercury surface can react readily with oxygen molecules when these are excited by electron impacts. Our further experiments were carried out in a static system, the reaction being followed by measuring the drop of pressure as a function of the time at given accelerating voltages of the electrons. The general plan of experimentation was the one already described in the former paper. The experimental tube is shown in Fig. 1. The applied voltages were read on large scale standard voltmeters and we used an equipotential surface (oxide covered platinum) as a source of electrons. Both the reaction tube and the Pirani gage were immersed in liquid oxygen or nitrogen. The total volume of the closed system including reaction tube, gage and connecting tubing was 105 cc. The oxygen used was prepared from dry potassium permanganate mixed with barium peroxide, dried for months over potassium hydroxide and phosphorus pentoxide and admitted to the reaction system through a stopcockless valve.[7] The reaction vessel was thoroughly baked out at 400° after each assemblage before being used and the mercury distilled in with the pumps running. The hot filament will remove oxygen gas even though no accelerating field is applied and it was necessary to determine the "zero" rate of pressure drop (no accelerating voltage applied) and subtract it from the total pressure drop at various voltages to obtain the net reaction rates. No pressure drop is observed when the filament is cold. The zero rates were large due to the fact that the volume of the system was small and the surface of the electron emitting system was large.

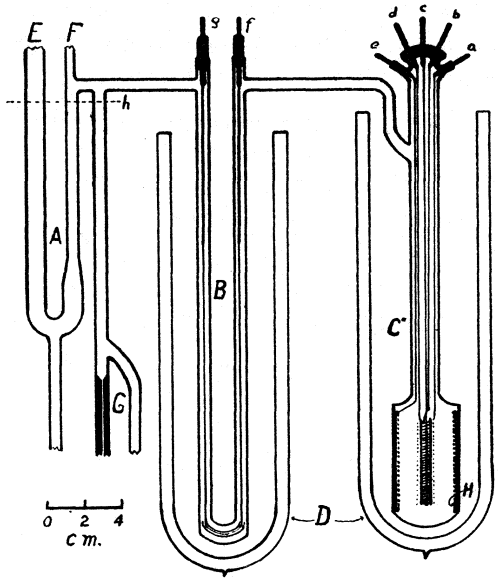

Fig. 1.—Reaction system: A, mercury cut-off; B, Pirani gage; C, reaction tube; D, Dewars; E, to pumps; F, to gas supply; G, McLeod gage; H, mercury surface; a–g, electrical connections; h, mercury level.

Application of accelerating voltages from 3.5 to 20 e. volts (corrected for initial velocity) produces an increased pressure drop if the reaction tube is immersed in liquid oxygen or nitrogen. However, this increased action is considerably greater if a mercury mirror is present in the reaction vessel than when it is absent. If however the tube is kept at room temperature or at 300°, then the accelerating field has no influence on the rate of pressure drop. Therefore experiments were carried out with the tube immersed in liquid oxygen and with a mercury mirror deposited inside the reaction vessel.

[6] Ozone vapor pressure is 0.035 mm. at −190°, Spannenberg, *Z. physik. Chem.*, **118**, 419 (1926).

[7] J. L. Wilson, *J. Phys. Chem.*, **35**, 3353 (1931).

Experimental Results

Mercury Surface.—Figure 2a shows the permanent drop in pressure as a function of the time with a mercury surface present in the tube. Many such experiments were carried out and the runs shown in Table I are only a sample of the results obtained. We can summarize these results by showing the number of molecules of oxygen which disappear per electron crossing the tube (Fig. 4). We find the following: (*1*) *electrons with velocities of 3–8 volts can cause oxygen molecules to disappear;* (*2*) *electrons above 8 volts velocity have a greater effect.* It becomes difficult to investigate the behavior of electrons of lower energy, because the emission from the filament is then very small.

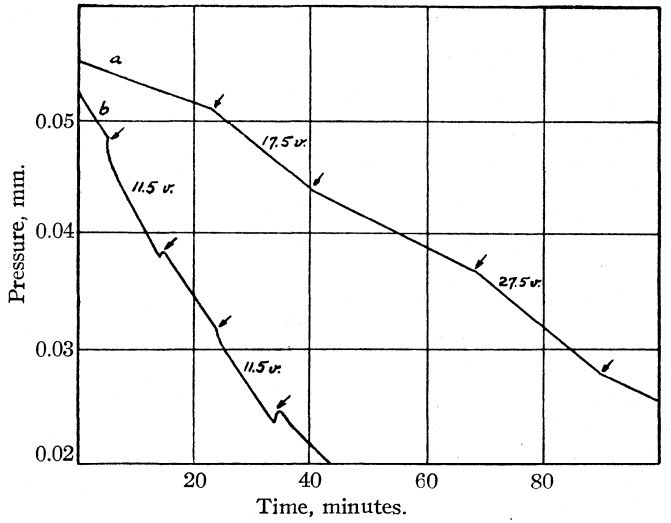

Fig. 2.—Pressure of oxygen as a function of time. Accelerating field on and off. (a) Mercury surface and low filament temperature. (b) Glass surface and high filament temperature.

Glass Surface.—We have also studied the removal of oxygen molecules upon a glass surface as well as upon mercury and we find that the zero rates are the same in the two cases, which means that they are not caused by the adsorption of oxygen but are due to the hot filament. The rates of pressure drop obtained are smaller than with mercury surfaces (Fig. 4). Figure 2b shows that with glass surfaces the rate of pressure drop is not constant while the accelerating field is applied, but increases as expected when the field was first put on, gradually decreasing to the zero rate, showing a steady state. This observation was not made with fresh mercury surfaces and we believe that the difference lies in the fact that excited oxygen molecules can react with mercury surfaces in a permanent fashion (acti-

vated adsorption)[8] while glass surfaces can only adsorb them into a more loosely bound state. The condition of the glass surface has a considerable effect. A freshly baked glass surface can remove more oxygen than a surface already partially covered (Fig. 4). With glass surfaces a further observation was made. When the accelerating field was removed, the pressure would rise to a point which would have been reached with the rate at no field, and when this situation has been attained the drop in pressure follows the zero rate as expected. Fresh mercury surfaces did not show this phenomenon. Furthermore, there was left a permanent brown deposit on the tube wall after the mercury had been removed (Fig. 3). No deposit was formed in the runs with glass surfaces. After a mercury surface had been used for many runs this behavior of pressure changes was also noted to a slight extent. A newly baked glass surface can adsorb activated oxygen molecules according to Henry, who baked out his apparatus before every run. We also found that a very fresh glass surface adsorbs better than a used one. We preferred to use a mercury surface because it is a more certain way of removing oxygen from the reaction tube.

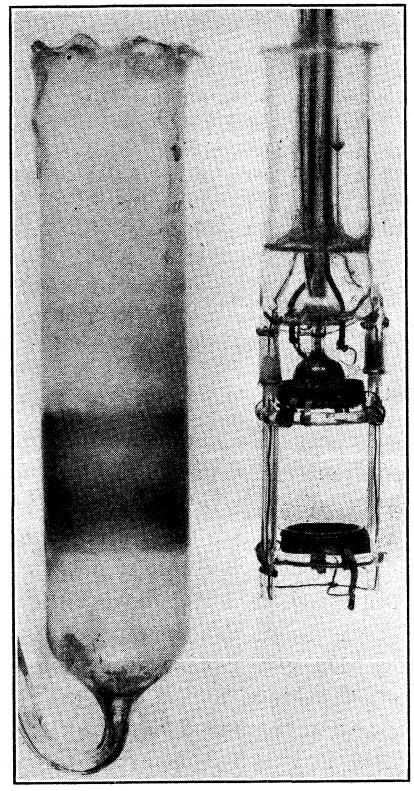

Fig. 3.—Permanent deposit of mercury oxide.

Efficiency of Mercury Surfaces.—We used the same mercury surface for several experiments at different voltages and convinced ourselves that the removal of oxygen had not decreased for any of the experiments. We repeated runs at the same voltage with a virgin and a used surface and found no difference in the capacity for adsorption. Calculations showed that we never exceeded a monomolecular layer.

Initial Velocity Correction.—This correction was determined by a series of ionization runs (Lenard curves) in oxygen and helium and in mixtures of the two gases. Furthermore, the minimum velocity which electrons must have to reach the plate was measured. Retarding voltages were applied

[8] M. Polanyi, *Z. Elektrochem.*, **35**, 561 (1929); H. S. Taylor, THIS JOURNAL, **53**, 578 (1931).

to the electron stream from which the initial velocity could be obtained. Five different ways of obtaining this correction gave consistent results and the correction amounts to 2.5 volts.

TABLE I

Expt.	v	i	P	$(\Delta P/\Delta t)$	E	$-M_{O_2}$	M/E	λ	Z	ZE	M/ZE
1	3.7	115	25.2	33.4	7.25	23.2	0.032	1.08	1.29	9.40	0.025
2	5.5	52	33.0	10.4	3.26	7.2	.022	0.82	2.24	7.30	.010
3	5.5	110	22.1	37.8	6.93	26.3	.038	1.23	1.00	6.93	.038
4	7.5	45	32.0	10.7	2.84	7.4	.026	0.85	2.08	5.91	.013
5	9.5	43	33.0	47.2	2.73	32.8	.120	.82	2.24	6.12	.054
6	11.5	58	35.0	77.4	3.65	53.7	.147	.78	2.47	9.02	.060
7	11.6	46	28.0	56.6	2.92	39.3	.134	.97	1.00	4.07	.084
8	11.5	126	26.0	89.4	7.95	62.0	.078	1.04	1.30	11.00	.056
9	11.5	120	26.2	100.0	7.56	69.5	.092	1.03	1.42	10.70	.065
10	14.7	42	30.0	41.7	2.62	28.9	.110	0.90	1.85	4.85	.060
11	17.5	50	33.0	43.5	3.15	30.2	.096	.82	2.22	7.00	.043
12	18.5	124	23.2	94.5	7.82	65.6	.084	1.17	1.10	8.60	.076

v = volts (corr.); i = current to plate (microamps.); P = press. (mm. Hg) $\times 10^3$; $(\Delta P/\Delta t)$ = (mm. Hg per sec.) $\times 10^7$; E = electrons per sec. $\times 10^{-14}$; $-M_{O_2}$ = molecules per sec. $\times 10^{-12}$; λ = M. F. P. of elec. (cm.); Z = impacts per electron with molecules; ZE = total impacts $\times 10^{-14}$.

Average Temperature in the Reaction Region.—A large temperature gradient exists in the reaction space because the hot filament is at about 900° while the walls of the vessel are at liquid oxygen temperature (−190°). We determined the average temperature of the gas experimentally as follows. The volume of the system was 105 cc. With the reaction system immersed in liquid oxygen the pressure was read with the filament off. The filament was then turned on and the pressure was read again. Assuming ideal gas laws it was possible to calculate the average temperature of the gas contained in the tube (147°K.). A calculation based on geometrical considerations and assuming the temperature of the filament to be 900–1200°K. checked the experimentally determined temperature satisfactorily.

Discussion of Results.—The results of electron-activated reactions can be stated by noting the pressure drop as a function of the time for a given electron current, by giving the number of molecules reacting per electron crossing the reaction tube or by calculating the number of molecules changed (M) per ion (N) produced by electrons, M/N.[9] The latter ratio has meaning only if the activating electrons have speeds greater than the ionization potential of the molecules of the gas and if in addition *the ions are the only agents causing reaction.* The meaning of N should include all possible active species such as vibrationally excited molecules, electronically excited molecules, ions and atoms. If in a given voltage range several of these activated species can be produced then N should represent their

[9] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., Inc., New York, 1928.

sum. We consider the mechanism of these activation reactions. The number of gas molecules (M) removed per second will depend upon the number of electrons (E) entering the reaction region per second, upon the number of impacts (Z) these electrons make with gas molecules, upon the efficiency (e) for inelastic collisions between electrons and gas molecules, upon the number of impacts (y) which the activated molecules make with normal gas molecules during their life in the reaction tube, and upon the efficiency of reaction (e') between excited and normal molecules. The number of efficient encounters (ye') between activated molecules (ZEe) and normal ones is limited by the energy available for activation. Thus we have

$$M = ZEeye'$$

The number of molecules reacting is produced by activations of various types depending on the velocity of the activating electrons

$$M = M_1 + M_2 + \ldots$$

Each group M_1, M_2, ... should be considered separately as above and for each group the various factors, e, y, e' may be different. However, because electron streams available at present have a rather wide velocity distribution and molecules of the type studied here (O_2) have many closely-spaced energy states it is not possible to study the problem in much detail. We therefore consider the situation in an average way over certain voltage ranges.

Molecules Reacting (M).—The number of molecules reacting per second is

$$M = \frac{\Delta P}{\Delta t}\frac{V \times 273 \times 6.06 \times 10^{23}}{22{,}400 \times 147 \times 760} = 6.95 \times 10^{18} \times \frac{\Delta P}{\Delta t}$$

These quantities are given in Table I. $(\Delta P/\Delta t)$ is the net pressure drop in mm. per second, V = volume of reaction vessel (105 cc.).

Electron Collisions (Z).—The number of collisions which an electron makes in crossing the tube is obtained by considering the process one of diffusion.[10] If "a" is the distance between the grid and plate (1 cm.), λ is the M. F. P. of the electron at pressure P (mm.), and for oxygen molecules the M. F. P. is 6.3×10^{-6} cm. at 760 mm. pressure, then

$$Z = \frac{3}{2}\frac{a^2}{\lambda^2} \qquad \lambda = \frac{0.0271}{P}$$

The distance between the emitting surface and the first grid was small (about 1 mm.) compared to the M. F. P. of the electrons (8 mm. in the pressure range used) so that about 90% of the electrons passed through the first grid and received their full energy before making a collision.

The Number of Electrons (E).—The number of electrons crossing the reaction vessel per second is given by $E = (6.06 \times 10^{23} \times i)/(96{,}540 \times 10^6) = 6.3 \times 10^{15} \times i$, where the current ($i$) is the electron current reaching the plate expressed in microamperes.

[10] G. Glockler, *Proc. Nat. Acad. Sci.*, **12**, 178 (1926).

The Ratio M/E.—The number of molecules removed per second depends upon the number of electrons crossing the tube per second and the ratio of these two quantities will depend upon the pressure and the efficiency of the mercury surface. This ratio (Fig. 4) is of no particular significance as far as reaction mechanism is concerned and we only discuss it here to point out that our work checks the results of Henry. He worked at about the same pressures and the distances between grid and plate were also nearly the same. His M/E ratios are of the same order of magnitude and his curve (Fig. 12 of his paper) shows the same trend for this ratio after resonances (8 volts) as our curve (Fig. 4). He also finds that at 12.5 volts (the ionization potential of oxygen molecules), no increase in the ratio is to be observed. Our results differ from Henry's in that we find some reaction occurring at lower voltages (3.5 to 8).

The Efficiency of Electron Collision (e).—We consider this question in relation to the energy of the impacting electrons and the possible excitation states of the oxygen molecules. Figure 5[11] shows that the oxygen molecule has many excited states. Although electrons cannot transfer energy to the hydrogen molecule below an electronically excited state (11.5 e. volts) (the dissociation energy is 4.32 e. volts), they can in the case of nitrogen and carbon monoxide excite vibrations of the atoms of these molecules with 5 volts energy.[12] It is therefore not improbable that low velocity electrons (3–8 e. volts) can transfer energy to the vibrational states of the oxygen molecules,[13] especially since they are said to have an electron affinity which would mean that the electrons can attach themselves to such molecules and their whole kinetic energy may then appear in the vibrational states of the resulting ion. Furthermore, the molecules of oxygen have metastable states ($^1\Sigma_g^+$) 1.62 e. volts above the normal state ($^3\Sigma_g^-$). Electrons may excite molecules to this metastable state in one of its vibrational configurations, although this state cannot be reached by light absorption. These excitations will take place with a certain efficiency of energy transfer, providing the possibility of activating oxygen molecules by low velocity electrons (3–8 e. volts). These efficiencies of inelastic electron collisions are not known but are probably small (0.1–0.001).

In the next voltage range (8–12 e. volts) it becomes possible to excite oxygen molecules to new electronic states with their accompanying vibrational and rotational energy levels. The efficiencies of such inelastic collisions have not been determined for many substances. For helium[14] it is known that the transition $1S \longrightarrow 2s$ (19.77 e. volts) can be brought about by electron impact with efficiencies of the order of 0.001. In

[11] Mulliken, *Review of Modern Physics*, **4**, 51 (1932).
[12] W. Harries, *Z. Physik*, **42**, 26–42 (1927).
[13] G. Hertz, *Verhandl. d. phys. Ges.*, **19**, 268 (1917).
[14] G. Glockler, *Phys. Rev.*, **33**, 175 (1929).

mercury vapor such efficiencies are of the order of a few per cent.[15] Transition probabilities for molecules are not known but are presumed to be of small magnitude. However, we can use our experimental data in an attempt to obtain some information concerning these efficiencies in the voltage range considered (8–12 e. volts).

Above 12 e. volts it becomes possible to ionize an oxygen molecule by electron impact. The probabilities of ionization impact between electron and oxygen molecules have been studied.[16] We use these probability factors to calculate the number of oxygen ions produced by one electron.

The quantities discussed so far give us the number of activated, excited or ionized molecules of oxygen produced by the electrons traversing the reaction region between grid and plate. In order to lead to reaction these energy rich species must either decompose into oxygen atoms which can be removed by the mercury surface or they will make further impacts with the normal molecules of the gas. We wish to know then what the possibilities for further collision may be between the activated species and the normal molecules.

Impacts between Activated and Normal Molecules (y).—The number of impacts which an excited molecule or ion will make with the normal molecules of the gas depends upon the diameters of the excited and the normal molecules and upon the average life (τ) of the excited state. The excited atoms have larger diameters[17] than the normal ones. For oxygen no experiments are known which would give the diameter of the excited states or ions. There are so many activated states possible that it is necessary to consider an average diameter. We shall assume that excited molecules have an average diameter $\sigma_1 = 10^{-7}$ cm. while the normal molecule has a diameter $\sigma_2 = 1.81 \times 10^{-8}$ cm. The diameter of the oxygen ion is taken equal to the diameter of the excited state. In order to calculate the number of impacts made between one of the activated molecules and the normal ones we obtain their mean free path λ^* from kinetic theory. We next consider that the average excited molecule or ion is created by electron impact anywhere in the reaction space between grid and plate and we desire to know the average distance (d^*) which it will have to travel to reach the wall. This distance d^* (=1.5 cm.) is obtained from a geometrical consideration.[18] Again, considering the process of one diffusion, we have

$$Z^* = \frac{3}{2} \times \frac{d^{*2}}{\lambda^{*2}} = \frac{3.38}{\lambda^{*2}}$$

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[15] H. Sponer, *Z. Physik*, **7**, 185 (1921); G. Hertz, *ibid.*, **32**, 298 (1925).

[16] Tate and Smith, *Phys. Rev.*, **39**, 270 (1932).

[17] Ruark and Urey, "Atoms, Molecules and Quanta," McGraw-Hill Book Co., New York, 1930, p. 497.

[18] *Loc. cit.*, Ref. 9, p. 94.

for the number of collisions with normal molecules made by an excited molecule in traveling the distance d^*. The actual zig-zag distance (D^*) traveled by excited molecules or ions while in the tube is

$$D^* = Z^*\lambda^*$$

and since their speed may be taken equal to the thermal velocity of the molecules (461 meters per second) we find how many seconds (t) they will be in the reaction tube if they do not return to normal or recombine in the case of ions

$$46{,}000 \text{ cm.} : 1 \text{ sec.} :: D : t$$

The excited molecules will not live long enough to reach the wall unless they are in metastable states. Their existence is terminated after the period (τ) when they return to normal. The average duration in an upper quantum state has been calculated[19] to be of the order of 10^{-7} sec. However, the return to normal means emission of radiation and we must consider the possibility of "light-imprisonment" which will increase "τ." If we take $\tau = 10^{-6}$ seconds[20] we can calculate the number of collisions (y) which an excited molecule will make during its average life in the reaction tube (Table II)

$$Z : t :: y : \tau$$

Recombination of Ions.—If the excited states are ions it becomes of importance to know whether or not they recombine in the gas phase. The recombination coefficient (α) is usually[21] given as 1.32×10^{-6} for oxygen at atmospheric pressure and room temperature. It is both a function of pressure and temperature and we estimate for oxygen at low pressure[22] and at the average temperature of our reaction tube: $\alpha = 148 \times 10^{-10} \times (273/147)^3 = 10^{-7}$ so that ions will recombine at a rate given by

$$\frac{d\nu_1}{dt} = -10^{-7} \times \nu_1 \times \nu_3$$

where ν_1 = concentration of ions and ν_3 = concentration of electrons. From the number of electrons (E) crossing the reaction region per second, we find the number of ions produced per second (N^*) and we suppose that these ions have to reach the wall by a process of diffusion. They travel the distance d^* in the time t, so that their drift-speed is d^*/t. We have then

$$\frac{N^* d^*}{V} = \nu_1 \times \frac{d^*}{t} \text{ or } \nu_1 = \frac{N^* t}{V}$$

The concentration of slow electrons ν_3 is twice the concentration of the positive ions, for at every inelastic impact two electrons are created per ion.

[19] R. C. Tolman, *Phys. Rev.*, **23**, 693 (1924).

[20] Foote and Mohler, "Origin of Spectra," Chapt. IV; Koenig and Ellett, *Phys. Rev.*, **39**, 576–584 (1932).

[21] K. K. Darrow, "Electrical Phenomena in Gases," Williams and Wilkins Co., Baltimore, Md., 1932, p. 263.

[22] J. J. and G. P. Thomson, "Conduction of Electricity through Gases," Cambridge University Press, 1928, p. 37.

The initial electron traveling with full velocity across the reaction tube has little chance to recombine with the positive ions. Recombinations $R(t)$ occurring in the time t in the whole reaction volume are

$$R(t) = 2 \times 10^{-7} \times N^* \times t^2$$

From the values of Z^* and $R(t)$ it is seen that the ions have a fair chance to recombine and thereby react and that they have opportunity to make impacts with other molecules while in the state of ions.

TABLE II

Expt.	n_2 O_2 molecules in V. $\times 10^{16}$	λ^* M. F. P. of activated mol. cm.	Z^* No. of coll. between O_2 and O'_2	D^* (cm.)	$t \times 10^{-3}$ (sec.)	$y = Z^*\tau/t$	$R(t)$	$N^* \times 10^{12}$	M/N
1	17.5	0.038	2340	89.1	1.94	1.21			
2	22.9	.029	4020	116.4	2.53	1.59			
3	15.4	.043	1830	78.7	1.71	1.07			
4	22.2	.030	3750	112.5	2.45	1.53			
5	23.0	.029	4020	116.4	2.53	1.59			
6	24.3	.027	4630	125.0	2.66	1.74			
7	19.4	.034	2920	99.0	2.15	1.36			
8	18.0	.037	2470	91.4	1.99	1.24			
9	18.2	.036	2600	93.6	2.04	1.27			
10	20.8	.032	3300	105.3	2.29	..	4.03	3.93	7
11	22.9	.029	4020	116.4	2.53	..	19.6	15.30	2
12	16.1	.041	2010	82.5	1.79	..	22.1	34.45	2

Reaction Caused by Slow Electrons (3–8 E. Volts).—We see from Fig. 4 that there is some pressure drop observed when electrons of velocity 3–5 e. volts impact on oxygen molecules. Oxygen molecules can thus be activated by such slow electrons so that they may react with a mercury

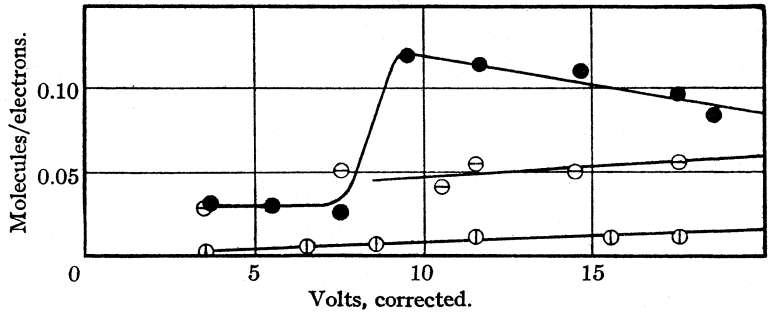

Fig. 4.—Molecules reacting per electron: ●, on fresh mercury surface; ⊖, on freshly baked glass surface; ⓘ, on used glass surface.

surface. The only state to which oxygen molecules can be raised in this voltage range is the metastable state $^1\Sigma_g^+$ in its various vibrational configurations. These excited molecules cannot decompose in the gas phase into atoms until the activating electrons have reached 5.2 e. volts of energy which corresponds to the heat of dissociation. Since the activated mole-

cules are in metastable states we may suppose that they can withstand impacts (y) in the gas phase and that they arrive at the wall in the metastable condition and there react with the mercury-surface

$$O_2 \text{ (activated to } {}^1\Sigma_g^+) + Hg \text{ (surface)} \longrightarrow 2HgO$$

whereas ordinary oxygen molecules do not react rapidly with mercury. If the impacting electrons have energies greater than 5.2 e. volts and if they can transfer this energy to the oxygen molecules we may expect dissociation into two normal atoms. In this voltage range 5–8 e. volts not more than one molecule can be dissociated. The mechanism of activation considered in the voltage range 3–5 e. volts can still be operative and we must content ourselves with an "average" picture of the reaction mechanism over the range 5–8 e. volts. We have discussed above the efficiencies of electron impact (energy transfer by the electrons) and we shall calculate the "average" chance that a molecule shall suffer an inelastic impact *and* react at the mercury surface. This averaging process is also made necessary since our electron stream has a fairly wide velocity distribution. In the range 3–8 e. volts we have then

$$M = ZEee'$$

Since only enough energy is available to dissociate one molecule, impacts (y) are of no importance unless they become large in numbers and cause molecules (5–8 e. volts) to return to normal before reaching the mercury surface. From Fig. (6) we find $M = 0.02 \times Z \times E$ and we obtain $e \times e' = 0.02$. The main interest in this combined probability is its small magnitude as is expected from general considerations. The efficiencies "e" are known to be small and the probabilities of reaction "e'" are of small value as expected. These reaction efficiencies are of fundamental importance, as they are analogous to specific reaction rates. Their knowledge enables us to predict reactions and they are quantities independent of impacts and of all external situations. They concern only the activated state and its reaction partner. They are quantities which can be deduced from a complete theory of molecular structure.

We have considered the possibility of successive impacts between initial electrons and oxygen molecules but they are negligible in our experiments. It is not possible to extend these studies below 3 e. volts for the emission from the filament becomes too small. We can then summarize our finding: "*In the velocity range 3–8 e. volts, electrons can transfer energy to oxygen molecules, activating them so that they can react with a mercury surface. The average probability of reaction is small as expected.*" Further research will enable us to obtain the quantities "e" and "e'" with greater accuracy and it will also be possible to decide the minimum heat of activation if the experiments can be extended to the lower voltages.

Reaction in the Range 8-12 E. Volts.—Such electrons can activate oxygen molecules from the normal state ${}^3\Sigma_g^-$ to the electronically excited

state $^3\Sigma_u^-$ (Fig. 5). We may suppose that the probabilities of such transitions are greater than for the type $^3\Sigma_g^- \longrightarrow {}^1\Sigma_g^+$ since the energy transfer is to a state which is not metastable. We actually find that the number of molecules reacting per electron impact increases markedly as would be expected on the above argument. As above we will discuss the reaction "on the average" in this voltage range. Oxygen molecules in the $^3\Sigma_u^-$ state can decompose spontaneously into a normal and an excited atom. If further impacts (y) have no influence then

$$M = ZEee'$$

and with $M = Z \times E \times 0.06$ we find $ee' = 0.06$. Again we note that this product of probabilities is small in magnitude as expected. We may next consider various possibilities of reaction including other normal molecules and their impacts (y) with the excited molecules during their average life (τ). Although we have not studied the reaction in sufficient detail to carry out such an analysis, we can however give a picture of the activation reaction in this voltage range as follows: "*Electrons of energy 8–12 e. volts can cause activation of oxygen molecules with greater efficiency than can be obtained with slower electrons. The combined probability of excitation followed by reaction is 6%.*"

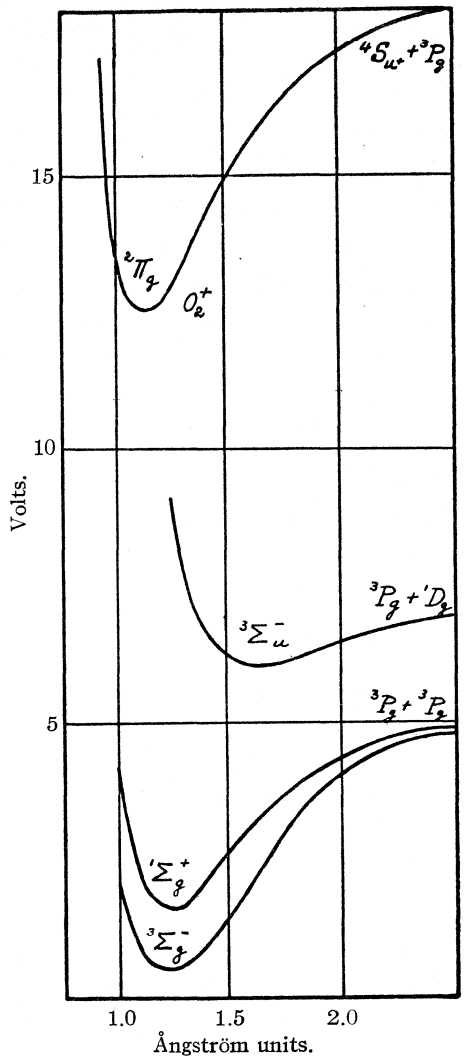

Fig. 5.—Energy diagram of oxygen molecule.

Reaction above Ionization.—When 12.5 volt electrons impact with oxygen molecules they have enough energy to ionize them. We find that reaction does occur but that the rate of pressure drop *does not increase markedly* when ionization voltage is reached. The number of molecules removed per electron crossing the tube is the same as in the lower voltage range (8–12 e. volts). This must mean that ions are not very much better activating centers for reaction than are excited states. At our low

pressures the oxygen mole-ions make many collisions (Z^*) before recombination $R(t)$ (Table II). It may easily be possible to have several molecules removed per ion because there is sufficient energy available for activation or dissociation when the electron returns. Again we must consider an average situation and taking

$$M = (ZEe)(ye')$$

we have $M = 0.06ZE$ and $M/N = M/(ZEe) = 4$ so that $ye' = 4$ and since the number of impacts an ion makes before a recombination occurs is of the order of 100 we have $e' = 0.04$. The only conclusion is that $e' < 1$. Further detailed analysis is not possible at present; however, we have pointed

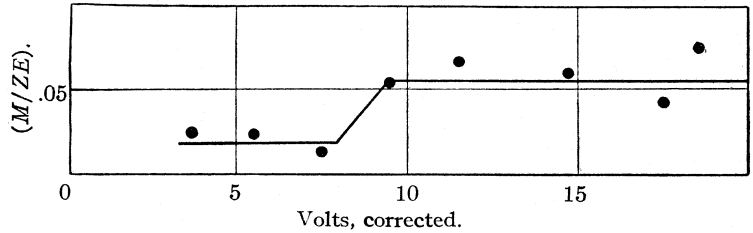

Fig. 6.—Molecules reacting per electron impact as a function of electron speed.

out the proper method of analysis and especially is it of importance to realize that such activation reactions should be interpreted in terms of efficiencies. We can summarize our findings as follows if we assume a certain mechanism predominant in a given voltage range.

Volts	Reaction	Combined efficiencies of energy transfer and reaction (yee')
3–8	$E_{fast} + O_2(^3\Sigma_g^-) \longrightarrow E_{slow} + O_2(^1\Sigma_g^+) + 2Hg \longrightarrow 2HgO$	0.02
8–12	$E_{fast} + O_2(^3\Sigma_g^-) \longrightarrow E_{slow} + O(^3P_g, {}^1D_g) + 2Hg \longrightarrow 2HgO$	.06
12–20	$E_{fast} + 2O_2(^3\Sigma_g^-) \longrightarrow E_{slow} + [O_2^+, O_2] + 4Hg \longrightarrow 4HgO$	.06

Further research may enable us to determine these efficiencies separately and we expect to study these activation reactions on the basis of the considerations outlined here.

Production of Ozone.—We have found that above the ionization potential the reaction product when adsorbed on glass showed chemical reaction with potassium iodide solution (iodine is liberated) but oxygen atoms may well cause this *same reaction as does ozone*

$$O_3 + 2KI + 2HCl \longrightarrow I_2 + 2KCl + O_2 + H_2O$$
$$O + 2KI + 2HCl \longrightarrow I_2 + 2KCl + H_2O$$

so no direct proof has been obtained for the presence of ozone. We may expect that ozone is not produced because triple collisions between oxygen atoms and oxygen molecules are needed to remove the energy of the reaction

$$O_2 + O \longrightarrow O_3; \quad H = 25{,}000 \text{ cal.}$$

in the gas phase. Although we do not have enough triple collisions to produce ozone, we must have taking place in our reaction tube the primary process (atom formation or production of an activated state) which would yield ozone had we the needed triple collisions. In further studies it will be necessary to distinguish between ozone and oxygen atoms.

Photochemical Reaction.—It is of interest to compare other activation reactions with our mode of activation by electron impact. While photochemical formation of ozone has not been observed below 2537 Å.,[23] which is equivalent to 4.9 e. volts, we find reaction below this voltage. This situation can be understood when it is recalled that the transitions considered by us involve metastable states which cannot be reached by light absorption but can be excited by electron impact. No conflict exists between the photochemical action and our activation reaction. Photochemical actions are not studied below 1800 Å. or 6.7 e. volts but activation by controlled electrons allows us to cover a much wider energy range than is available to the photo-chemist. A comparison of quantum yield and efficiency of our activations will be made when we have more detailed information.

Radon Reactions.—Oxygen has been studied by Lind and others[9] under the influence of ionization produced by the alpha particles of radon. The reaction process is expressed by the ratio of molecules reacted or formed (M) to ions produced (N) and it is found that the M/N ratio is variable since deozonization usually takes place under the conditions of the experiment. With a rapid flow Lind and Bardwell[24] obtained $M/N = 2$. We find $M/N = 4$ if we assume that all of the reaction depends on the ions formed. This M/N ratio is not known with any accuracy from our experiments, but at least it can be seen that there is no disagreement with radon reactions. From our point of view we consider the further analysis of the M/N ratio into terms of efficiency necessary and we shall consider this question in another place.

Summary

The activation of oxygen molecules by electrons of known speeds (3–20 e. volts) has been studied. The activated species have been removed by further reaction on a mercury surface. Activation is possible in the whole range of energies studied and is interpreted on the basis of the energy diagram of molecular oxygen derived from its band spectrum. In the low-velocity region (3–8 e. volts) metastable ($^1\Sigma_g^+$) oxygen molecules serve as the activated state, in the region from 8–12 e. volts, electronically excited molecules ($^3\Sigma_g^-$) are the activated species and above the ionization potential (12.5 e. volts) ions (O_2^+) enter the reaction ($M/N = 4$). These various

[23] Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., Inc., New York, 1928, p. 221.

[24] S. C. Lind and D. C. Bardwell, THIS JOURNAL, **51**, 2751 (1929).

activations are discussed in terms of probabilities of energy transfer from electrons to normal molecules and of probabilities of further reaction between activated states and the mercury surface.

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ENERGY EXCHANGE IN UNIMOLECULAR GAS REACTIONS

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§1. Introduction

There is a large number of substances which decompose in the gas phase, and whose rate constants show a characteristic behavior in that they tend to approach a constant value as one goes to high pressures, but fall in value as one goes to low pressures.[1] According to the currently accepted theories, it is supposed that in these reactions the activated molecules receive their energy by collision with other molecules. As one goes to lower pressures the time between collisions becomes greater; when it becomes of the same order of magnitude as the average time necessary for an activated molecule to decompose, the falling off of the rate constant first becomes noticeable.[2]

Now it is found that it sometimes is possible to restore the rate constant to its high pressure value by the addition of an inert gas, which is able to exchange energy (without any chemical reaction taking place) with the molecules which are to decompose. Thus Hinshelwood and his co-workers have found that the rate constants for a number of ethers are increased by addition of a sufficient amount of hydrogen, the hydrogen being in most cases about as effective pressure for pressure as the reacting gas itself. They have also found that the rate constant is but little affected by the addition of helium, nitrogen, carbon dioxide and other gases composed of relatively heavy atoms;[2] also, strangely enough, in one or two cases, organic compounds have been reported ineffective.[3]

[1] As a matter of fact, in many cases, including those in which we shall be most interested here, this is a statement of a theoretical expectation rather than an experimental fact, since the limiting high pressure rate has not been reached experimentally.

[2] For a general discussion and references see Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932. It may be well to state explicitly that I assume the current explanations of the phenomena of unimolecular reactions, including the phenomena with inert gases present, although I am not certain but that further experimental work may show that some of the individual cases cited as illustrative of these principles really are more complex than they are now thought to be. In this connection note Rodebush and Copley, THIS JOURNAL, **54**, 2560 (1932), and Vernon and Daniels, *ibid.*, p. 2563.

[3] For example, Steacie, *J. Phys. Chem.*, **36**, 1562 (1932), reports that dimethyl and diethyl ether will not activate each other. These results have not been verified

As a start toward the development of an adequate theory of the exchange of energy in these gas reactions, we shall in this paper discuss the effects of hydrogen and helium.[4] These will be the simplest cases to investigate, as they will involve only the exchange of rotational and translational energy; it seems probable that the vibrational energy of hydrogen will not enter into the problem appreciably.

Even this simplest case is in reality exceedingly complicated. It will, therefore, be necessary to simplify the problem considerably. So, in order to get a rough idea of how the process of energy exchange between the translational motion of the colliding particles and the vibrational motion of the decomposing molecule takes place, we shall consider the case of the collision of a simple particle with an oscillator whose equilibrium position is fixed in space (representing one of the oscillators in the reacting molecule—the particular one hit by the colliding particle). We shall further assume that the oscillator is vibrating along some particular line in space, and that the particle is moving in the same line—thus we get a head-on collision.[5] Crude though this model is, it will undoubtedly give us an indication of what actually does take place.

§2. The Rotational Energy of the Colliding Molecule

When the colliding molecule is diatomic as in the case of hydrogen, the collision process is somewhat more complicated than in the case considered above on account of the possibility of exchange of rotational energy. If the position of the colliding molecule were so fixed that its axis lay along the line of the collision, and if no exchange of vibrational energy takes place, then the collision should take place about as represented above. But collisions will take place in which the colliding molecule is oriented in various ways. Furthermore, the colliding molecule may hit the oscillator in such a way that the two atoms in the colliding molecule straddle the oscillator; or the collision may perhaps be rather a collision between one of the atoms in the molecule and the oscillator. If the latter were the case, and if the colliding molecule were oriented across the line of the collision, the collision should be very much like the collision described before, but with the mass of the atom involved substituted for the mass of the whole colliding molecule. The problem is thus reduced back to the situation originally considered of a particle colliding with an oscillator.

Of course, this discussion is based on much too crude a picture of a dumb-bell molecule; and, indeed, Eyring and Slater[6] have concluded that for ordinary collisions

by Kassel, THIS JOURNAL, **54**, 3949 (1932), however, to whom I am indebted for being allowed to see his results before publication. Also, Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **115A**, 215 (1927), have reported methane ineffective in the case of methyl ether, and in one or two instances Hinshelwood and his co-workers have reported the reaction products as slightly effective (propionic aldehyde) or even retarding (diethyl ether).

[4] I have treated this problem in a rather hasty way in a previous article, *Chem. Rev.*, **10**, 125 (1932); there, however, I assumed that exchange of energy could only take place with the outside hydrogens of the organic molecule, an assumption which now seems to me to be too restrictive.

[5] See Zener, *Phys. Rev.*, **37**, 556 (1931).

[6] See Eyring, *Chem. Rev.*, **10**, 116 (1932); Eyring, THIS JOURNAL, **54**, 3191 (1932).

between two hydrogen molecules with a relative kinetic energy equal to the average at room temperature they act much like two spheres. It hardly seems possible at the present time to give a very satisfactory discussion of this question; these rough considerations will, however, provide the reason for making calculations, in the subsequent pages, in which the mass of the colliding particle is set equal to that of a hydrogen atom.

§3. The Transfer of Energy between a Colliding Particle and an Oscillator

The one-dimensional problem of a particle colliding with an oscillator, just outlined, has been treated by Zener,[5] by the following method. If the oscillator is in a certain energy state, it will exert a certain average force on the colliding particle which may be supposed for the moment to be held at a fixed distance from the point of equilibrium of the oscillator. This force depends on the distance of the particle, and one may thus construct a potential energy curve for the particle, there being a different potential energy curve for each state of the oscillator. Now the fact that the oscillator is actually in motion introduces a perturbation into the problem, which may be shown to result in an exchange of energy between the oscillator and the particle, and the probability of such an exchange may be calculated.

This may be formulated in the following manner. We let the distance of the oscillator from its center of equilibrium be x, and the distance of the colliding particle from the same point be r, the distance between the colliding particle and the oscillating particle being thus $r - x$; the eigenfunction which describes the state of the oscillator we call ϕ. If the colliding particle is far away, ϕ will very approximately satisfy the wave equation of a harmonic oscillator

$$\frac{h^2}{8\pi^2 m}\frac{d^2\phi}{dx^2} + (E - 2\pi^2\nu_0^2 m x^2)\phi = 0 \tag{1}$$

where m is the mass of the oscillating particle, ν_0 its frequency, E its energy and h Planck's constant.

The effect of a collision of the colliding particle will be to change the oscillator from one state, say ϕ_n with energy E_n, to another, say $\phi_{n'}$, with energy $E_{n'}$, the difference of energy being taken up in the translational energy of the colliding particle. Suppose we represent the mutual potential energy of the colliding and the oscillating particles, which will be a function of $r - x$, by V. Then the average potential energy, when the colliding particle is fixed at a definite value of r and the oscillator is in a definite quantum state, n, will be a function of r given by

$$u_{nn} = \int_{-\infty}^{\infty} \phi_n^2 V\, dx \tag{2}$$

The wave function of the colliding particle R_{nm} will, in zero approximation, obey the wave equation

$$\frac{h^2}{8\pi^2 M}\frac{d^2R_{nm}}{dr^2} + (T_{nm} - u_{nn})R_{nm} = 0 \tag{3}$$

where M is the mass of the particle and $T_{nm} = W_{nm} - E_n$ (W_{nm} being the total energy of the system). The wave function of the combined system will be, in zero approximation

$$\psi_{nm} = \phi_n R_{nm} \tag{4}$$

The normalization of the function R_{nm} which is one of a continuous series of eigenfunctions is accomplished in the following manner. We assume that r cannot become greater than a certain large value, r_∞. Then the continuum is changed into a close-spaced set of discrete states, the energy between two adjacent energy levels being

$$\epsilon_{nm} = 2\pi T_{nm}^{1/2}/r_\infty K \tag{5}$$

where $K^2 = 8\pi^2 M/h^2$. R_{nm} is then normalized so that

$$\int_0^{r_\infty} R_{nm}^2 dr = 1 \tag{6}$$

Now the wave equation for the whole system is

$$\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2} + \frac{h^2}{8\pi^2 M}\frac{\partial^2\psi}{\partial r^2} + (W - 2\pi^2\nu_0^2 m x^2 - V)\psi = 0 \tag{7}$$

When (4) is substituted into (7) it is found that the latter is not exactly satisfied. Treatment of the extra terms by the usual first order perturbation method shows that transitions are induced from the state nm to others, for example $n'm'$, with the same total energy. The transition probability is given by

$$\gamma_{nm,\,n'm'} = 4\pi^2 v_{nm,\,n'm'}^2/\epsilon_{nm}\epsilon_{n'm'} \tag{8}$$

where

$$v_{nm,\,n'm'} = \int_0^{r_\infty} R_{nm} R_{n'm'} u_{nn'} dr \tag{9}$$

where

$$u_{nn'} = \int_{-\infty}^{\infty} \phi_n \phi_{n'} V\, dx \tag{10}$$

$R_{n'm'}$ satisfies an equation like (3) but with $u_{n'n'}$ substituted for u_{nn} and $T_{n'm'} = E_n - E_{n'} + T_{nm}$ for T_{nm}.

§4. Calculation of Transition Probabilities

The evaluation of $\gamma_{nm,\,n'm'}$ resolves itself into several parts. First we calculate u_{nn}, $u_{n'n'}$ and $u_{nn'}$. The first two of these enable us to get R_{nm} and $R_{n'm'}$. Then, finally, we can find $v_{nm,\,n'm'}$ and $\gamma_{nm,\,n'm'}$. All of these calculations require us to make approximations. In order to check up on these we shall try different methods of approximation, the results of which we can then compare.

The interaction, V, of the colliding and oscillating particle can be approximated by a function of the form

$$V = Ce^{-\alpha(r - x)} \tag{11}$$

C is a constant and α is a parameter which determines what we may call the "sharpness" of the collision.[5] The determination of these constants will be discussed in a later section.

With this expression for V, and remembering that the solutions of

equation 1 are the Hermite orthogonal functions, it is easy to arrive at expressions for u_{nn}, $u_{n'n'}$ and $u_{nn'}$. These expressions will all be of the form $e^{\alpha^2/4\beta - \alpha r}$ times a polynomial in $\alpha/\beta^{1/2}$ where

$$\beta = 4\pi^2 m\nu_0/h \tag{12}$$

But the insertion of a function of this form into equation 3 will not give an equation which can be solved for R_{nm}. It is necessary, therefore, to find some other type of approximation for u_{nn}. This is accomplished in the following way. We set

$$u_{nn} = A/(r - B)^2 + u_\infty \tag{13}$$

The constants A, B and u_∞ are then adjusted so that u_{nn}, du_{nn}/dr and d^2u_{nn}/dr^2 have the proper values (*i. e.*, the values equal to those found by the use of equation 11 in evaluating u_{nn}) at that value of r, which we call r_0, at which $T_{nm} = u_{nn}$. The values of A, B and u_∞ are

$$A = 27T_{nm}/2\alpha^2 \tag{14}$$
$$B = r_0 - 3/\alpha \tag{15}$$
$$u_\infty = -T_{nm}/2 \tag{16}$$

This gives an approximate value of u_{nn} which will be good in the region of r which is most important in determining the value of the integral in equation 9. In particular, it will differ from the true u_{nn} in two respects. First, it has the wrong asymptotic value. Second, it becomes infinite when $r = r_0 - 3/\alpha$. These differences lie outside the important region of r, as noted.

Having thus set up an expression of u_{nn}, we write for $u_{n'n'}$ simply

$$u_{n'n'} = \rho u_{nn} \tag{17}$$

where ρ is a constant equal to the ratio $u_{n'n'}/u_{nn}$ obtained by setting (11) in (2) and the similar expression for $u_{n'n'}$. We have

$$A' = \rho A \qquad B' = B \qquad u'_\infty = \rho u_\infty \tag{18}$$

where A', B' and u'_∞ are the parameters in the expression for $u_{n'n'}$.

With these values of u_{nn} and $u_{n'n'}$ we can express R_{nm} and $R_{n'm'}$ in terms of Bessel functions[7]

$$R_{nm} = (\pi Kz/r_\infty)^{1/2}\,(3T_{nm}/2)^{1/4}\,J_\nu(K\sqrt{3T_{nm}/2}\,z) \tag{19}$$
$$R_{n'm'} = (\pi Kz/r_\infty)^{1/2}\,(T_{n'm'} - u'_\infty)^{1/4}\,J_\mu(K\sqrt{T_{n'm'} - u'_\infty}\,z) \tag{20}$$

where the J's are Bessel functions of orders and arguments indicated, $z = r - B$, and

$$\nu = (K^2A + 1/4)^{1/2} \tag{21}$$

and

$$\mu = (K^2A' + 1/4)^{1/2} \tag{22}$$

Now if we let σ be the ratio $u_{nn'}/u_{nn}$ obtained through the substitution of (11) in (2) and (10) we may write

$$v_{nm,\,n'm'} = \sigma \int_0^{r_\infty} R_{nm}R_{n'm'}\,u_{nn}dr \tag{23}$$

[7] Watson, "Bessel Functions," Cambridge University Press, 1922, p. 95.

We may substitute for R_{nm} and $R_{n'm'}$ from (19) and (20) and for u_{nn} from (13). The most convenient quantity to get is $v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2}$ using (23) and (5). We set

$$\begin{aligned} a &= (\nu + \mu)/2 \\ b &= (\nu - \mu)/2 \\ c &= \nu + 1 \\ S &= 3T_{nm}/2(T_{n'm'} - u'_\infty) \end{aligned} \tag{24}$$

We consider the case where $S < 1$. Then the result of the integration indicated in (23) is[8]

$$v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = \frac{\sigma K^2}{6^{1/2}}\left(\frac{T_{nm}}{T_{n'm'}}\right)^{1/4} S^{\nu/2 - 1/4} \times$$
$$\left[-\frac{S}{K^2}\frac{\Gamma(a+1)}{\Gamma(c)\,\Gamma(-b)}F(a+1,\,b+1,\,c,\,S) + \left(\frac{3}{2}\right)\frac{A}{2}\frac{\Gamma(a)}{\Gamma(c)\,\Gamma(1-b)}F(a,b,c,S)\right] \tag{25}$$

In this expression the Γ's represent the usual gamma functions, with the arguments indicated, while the F's are hypergeometric functions.

It will be noted that the first term in the brackets arises from the second term in the expression for u_{nn} (equation 13), which is responsible for the fictitious asymptotic value of u_{nn}. If, therefore, this term should prove to be relatively large, we should hesitate to use equation 25. It is small, however, provided S is not too close to 1, which will be true in the cases we shall consider in this paper. If this is true the hypergeometric function is about equal to 1, and the absolute value of the ratio of the second term to the first becomes roughly $3AK^2/4Sab = 3/S(1-\rho)$, by equations 24, 21, 22 and 18. In the least favorable cases we shall have to consider this ratio, as may be verified from the subsequent calculations, will be around 20. So the first term of (25) may be neglected. Further, it will never cause more than about 4% error to set $(3T_{nm}/2T_{n'm'})^{1/4}$ equal to $S^{1/4}$. Also, for the hypergeometric function, in the range of the parameters we shall need to use, it will be a good approximation to set[9] $(1 - aS/c)^{-b}$. Equation 25 thus becomes (using equation 14)

$$v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = 3.74\,\sigma\frac{K^2T_{nm}}{\alpha^2}S^{\nu/2}\frac{\Gamma(a)}{\Gamma(c)\,\Gamma(1-b)}(1 - aS/c)^{-b} \tag{26}$$

As a check on (26) another approximation for u_{nn} may be used in equation 23, still using the values of R_{nm} and $R_{n'm'}$ (which I think are certainly as good as we can get) given by (19) and (20). For the new approximation we shall set

$$u_{nn} = 27T_{nm}/\alpha^3 2^3 \tag{27}$$

[8] Ref. 7, p. 401.

[9] This may be verified readily by comparison of the series expansions of the hypergeometric function and the function which is substituted for it. In doing this it is necessary, of course, to have at hand the values of the various parameters involved. Sufficient data are presented in the subsequent calculations so that these parameters may be calculated if it is desired to verify this procedure.

It may be verified that this expression gives the same values for u_{nn} and du_{nn}/dr, and 4/3 the former value for d^2u_{nn}/dr^2 at $r = r_0$. This approximation gives (making the allowable approximation $(T_{n'm'} - u'_\infty)^{1/4}/T_{n'm'}^{1/4} = 1$)

$$v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = 4.57\,\sigma\,\frac{K^3 T_{nm}^{3/2}}{\alpha^3}\,S^{\nu/2-1/2}\,\frac{\Gamma(a-1/2)}{\Gamma(c)\,\Gamma(3/2-b)}\,F(a-1/2,\,b-1/2,\,c,\,S) \tag{28}$$

The hypergeometric function may be set equal $[1 - (a - 1/2)S/c]^{-b+1/2}$. As a matter of fact, I have set it equal to 1 in using this equation, as this is a sufficiently good approximation.

§5. Interaction of the Oscillator with the Rest of the Molecule[10]

We now attempt to take into account the fact that the oscillator actually struck by the colliding particle is but part of a molecule whose motion should rightly be described in terms of its normal coördinates. As long as the molecule is not too highly excited, its wave equation will be separable in the normal coördinates, the motion of each coördinate will be quantized as an harmonic oscillator and have its own frequency, and the normal coördinates will be linear functions of the natural coördinates which describe the actual positions of the atoms in the molecule. Suppose the number of coördinates which we have to consider (*i. e.*, the equivalent number of coupled linear oscillators, provided each contributes approximately an equal amount to the motion of the natural coördinate which gives the position of the atom actually struck in the collision) is q. We consider now the probability that the normal oscillator connected with *one*[11] of the q normal coördinates changes its quantum state. Then it may be readily shown that, to a good approximation, the results of the previous section will remain valid, if, in calculating the ratios ρ and σ, we simply substitute $\alpha^2/q\beta$ for α^2/β. The physical significance of this is clear. β is a parameter the inverse square root of which gives the extension in space of the motion of the oscillating particle. But the particular oscillating particle which is hit in the collision must now share its energy, so to speak, with other oscillators, and it is the energy of all these oscillators which is transferred at the collision. There will be less vibration of the particular atom in the molecule which is hit by the colliding particle, due to the energy of any given normal vibration, than there would be if all that energy were located in the given particle. Therefore β must be correspondingly larger. In general ρ will be found to be nearer 1 than in the previous section because the motion of the particular particle in the molecule which is struck will

[10] The problem considered in section 5 has something in common with the problem of accommodation coefficients recently considered by Jackson, *Proc. Camb. Phil. Soc.*, **28**, 136 (1932), and Zener, *Phys. Rev.*, **40**, 178, 335 (1932) and, since the submission of this article, Jackson and Mott, *Proc. Roy. Soc.* (London), **137A**, 703 (1932).

[11] We remember, of course, that there are now different ways in which such transitions can occur, a factor taken into account afterward.

not differ as much after the transition; the effective potential energy curves u_{nn} and $u_{n'n'}$ of the colliding particle before and after the collision will therefore be nearer alike.[12]

The mathematics of the situation is as follows. We will use the symbols $\xi_1, \xi_2, \ldots \xi_q$ to designate the normal coördinates, and $x_1, x_2, \ldots x_q$ to designate the "natural" coördinates. One of the latter, say x_1, will be the quantity that we have previously designated as x; that is, it is the displacement of the oscillator actually hit by the colliding particle in the direction along which it is hit. Now we shall be interested in the behavior of the coördinate x_1 when one of the normal modes of vibration is excited. (We can then find its behavior when more than one are excited, by simple addition.) To get this information we shall need to inquire into the dynamics of the molecular motion, and for the moment we shall look at it from a classical point of view.

The ξ's will be linear functions of the x's and we may write

$$\xi_i = \Sigma_j a_{ij} x_j, \text{ and} \tag{29a}$$

$$x_j = \Sigma_i b_{ji} \xi_i \tag{29b}$$

where $a_{ij} = \partial\xi_i/\partial x_j$ and $b_{ji} = \partial x_j/\partial\xi_i$. Although the ratios of the various b_{ji} (with a given i) are determined by the dynamical situation, the absolute values are not. We shall, therefore, apply what we may term a normalizing condition, which will determine the absolute values. If only one ξ_i is excited then $x_j = b_{ji}\xi_i$ and $x_j^2 = b_{ji}^2\xi_i^2$; we shall now demand that on the average x_j^2 goes through the same range as ξ_i^2, so that on the average b_{ji}^2 is 1. This means that

$$\Sigma_j b_{ji}^2 = q \tag{30}$$

where q is the number of values j can take.[13]

Now the kinetic energy for the given normal mode of vibration is $\mu_i\dot{\xi}_i^2/2$, where μ_i is the reduced mass for the mode of vibration. But since the x_j are ordinary Cartesian coördinates of the actual particles of the system, we must have, $\mu_i\dot{\xi}_i^2/2 = \Sigma_j m_j\dot{x}_j^2/2$, if only one normal mode of vibration is excited. Here the m_j are the masses of the various parts of the system. But since only the one mode of vibration is excited, we must have, by (29b), $\dot{x}_j = b_{ji}\dot{\xi}_i$ and, hence, $\mu_i\dot{\xi}_i^2/2 = \Sigma_j m_j b_{ji}^2\dot{\xi}_i^2/2$ which enables us to define our reduced mass (in a rather unusual way) as

$$\mu_i = \Sigma_j m_j b_{ji}^2 = q\bar{m}_j \tag{31}$$

where $\bar{m}_j$ is a sort of average of the masses of the parts of the system.

The wave equation for a normal mode of vibration of frequency ν_0 will be like equation 1, except that ξ_i, say, will replace x and μ_i will replace m. If the eigenfunction is $\phi^i(\xi_i)$ then the eigenfunction for the complete system, including all normal vibrations, will be of the form $\Pi_i\phi^i(\xi_i)$.

In place of equation 2 we now have

$$u_{nn} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}[\Pi_i\phi_n^i(\xi_i)]^2\, V d\xi_1 d\xi_2 \ldots d\xi_q \tag{32}$$

Using equation 11 (remembering that x_1 takes the place of x) and equation 29b we get, after a slight rearrangement

$$u_{nn} = Ce^{-\alpha r}\Pi_i\int_{-\infty}^{\infty}[\phi_n^i(\xi_i)]^2\, e^{\alpha b_{1i}\xi_i}\, d\xi_i \tag{33}$$

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[12] This becomes clear in the subsequent applications—see equations 39 and 41.

[13] q will be equal to $^1/_2$ the value of the quantity called n by Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

and similarly for $u_{n'n'}$. If the states n and n' differ in only one $\phi^i(\xi_i)$ which we designate simply with i, then we may write instead of the ratio ρ of equations 17 and 18

$$\rho_i = \frac{u_{n'n'}}{u_{nn}} = \frac{\int_{-\infty}^{\infty} [\phi^i_{n'}(\xi_i)]^2 e^{\alpha b_{1i}\xi_i} d\xi_i}{\int_{-\infty}^{\infty} [\phi^i_n(\xi_i)]^2 e^{\alpha b_{1i}\xi_i} d\xi_i} \tag{34}$$

Similarly in place of the ratio σ may now be written

$$\sigma_i = \frac{\int_{-\infty}^{\infty} [\phi^i_n(\xi_i)][\phi^i_{n'}(\xi_i)] e^{\alpha b_{1i}\xi_i} d\xi_i}{\int_{-\infty}^{\infty} [\phi^i_n(\xi_i)]^2 e^{\alpha b_{1i}\xi_i} d\xi_i} \tag{35}$$

Now $\phi^i_n(\xi_i)$ will be the same function of ξ_i as the previously considered function ϕ_n is of x, except that β_i will be substituted for β, where

$$\beta_i = 4\pi^2\mu_i\nu_0/h \tag{36}$$

The original expressions for ρ and σ will be functions of α^2/β. (This follows from the statement just before equation 12.) From their relation to the new ρ_i and σ_i defined in equations 34 and 35 it may readily be seen that the latter will be functions of $\alpha^2 b^2_{1i}/\beta_i$. Now b^2_{1i} will be of the order of 1, from equation 30, while β_i will be of the order βq by (31), (36) and (12). Thus we may say, roughly, that ρ_i and σ_i are the same functions of $\alpha^2/q\beta$ as ρ and σ are of α^2/β. We shall see in section 6 how our results are affected by making this change.

§6. Results of the Calculation

The vibration frequencies of organic molecules have been discussed by Andrews.[14] In our calculations we shall try assigning a number of values to ν_0, *i. e.*, 500, 1000 and 1500 wave numbers (cm.$^{-1}$) which are reasonable frequencies corresponding to various types of vibration of the component atoms.

Andrews also has considered the force constants of the oscillators in organic molecules. The force constant, k_i, for a particular normal mode of vibration, is given by the expression $k_i = 4\pi^2\nu_0^2\mu_i$, while if we consider only a single oscillator as in section 4 we have

$$k = 4\pi^2\nu_0^2 m \tag{37}$$

The constant which Andrews has attempted to evaluate is k. We have made calculations in which we have assigned to this quantity the values 0.6×10^5, 1.2×10^5 and 5.0×10^5 dynes per cm., which, from Andrews' work, would appear to cover satisfactorily the range likely to occur in organic molecules. Our procedure is to get β from the equation (derived from 12 and 37)

$$\beta = k/h\nu_0 \tag{38}$$

using the given values of k and ν_0. If we wish to take into account the considerations of section 5 we multiply this value of β by q.

Next we consider the extent to which the vibrations of an activated molecule are likely to be excited; we are particularly interested in the

[14] Andrews, *Phys. Rev.*, **36**, 544 (1930).

ethers, as these are the cases in which data on the effect of inert gases are available. Hinshelwood and his co-workers have found their activation energies to be around 50,000 calories per mole,[2] and in general the number of normal modes of vibration which seems to be associated with the decomposition, in these cases, is around five. Thus in the activated molecule each one of these normal modes of vibration is excited on the average by an amount equivalent to 10,000 calories per mole. If the frequency is 1000 wave numbers, corresponding to about 2850 calories per mole, it will be seen that this means that it is in its third or fourth quantum state. As this would seem to be a good average value, we have made calculations in which we assume that the vibrator goes from its fourth to its third quantum state giving up the energy to the colliding particle (we choose to consider deactivation rather than activation, this being in general more convenient from a theoretical point of view); but we have also investigated the case in which the oscillator goes from its first to its 0th (lowest) quantum state.

We come now to the properties of the colliding particle. Its initial kinetic energy T_{nm} we set equal to the average translational energy of one component of the motion of a particle in thermal equilibrium at a temperature like those at which the reactions occur, say 800 Å., *i. e.*, about 800 calories per mole.

We assign to M the value, in atomic weight units, of 1, 2 or 4, according to whether we are investigating the exchange of rotational energy by hydrogen, of translational energy by hydrogen, or of translational energy by helium. (It would, of course, be proper to take into account the motion of the organic molecule by using a reduced mass. This would lessen the difference between hydrogen and helium slightly.)

Finally we come to the evaluation of the constant α, which gives the sharpness of collisions. The question of the interaction between molecules has been discussed by Lennard-Jones,[15] who gives a formula for the force between two hydrogen molecules as a function of the distance between them. It will almost certainly produce no appreciable error to use this same curve for evaluating the force between a colliding hydrogen molecule and the oscillator in the organic molecule, as the force between two atoms does not seem to depend much on how they are bound to other atoms. Even though the colliding particle exchanges energy with the carbon–carbon vibrations, the force must probably be transmitted through hydrogen atoms. If now we set $\alpha = 5 \times 10^8$ cm.$^{-1}$, use this in equations 14 and 15, and calculate u_{nn} from equation 13, we get a function of r which coincides reasonably well with what we would get from Lennard-Jones, in the important range of r. This is illustrated by Fig. 1, in which the curve is the potential energy function from Lennard-Jones, and the circles

[15] Fowler, "Statistical Mechanics," Cambridge University Press, 1929, Chapter X.

represent points calculated in the way described. In the case of helium we have no very good way to calculate α. Helium may likely make a sharper collision than hydrogen. If, on the other hand, we use Lennard–Jones' curve for the collision of two helium atoms, we will undoubtedly get too sharp a collision, *i. e.*, too large a value of α. A mean between the curve for two hydrogen molecules and that for two helium atoms will probably be about right, and indicates a value for α for the collision of helium with an organic molecule of about 0.5×10^8 higher than the corresponding value with hydrogen. We have carried out calculations for a series of different values of α, to show how this parameter affects the results.

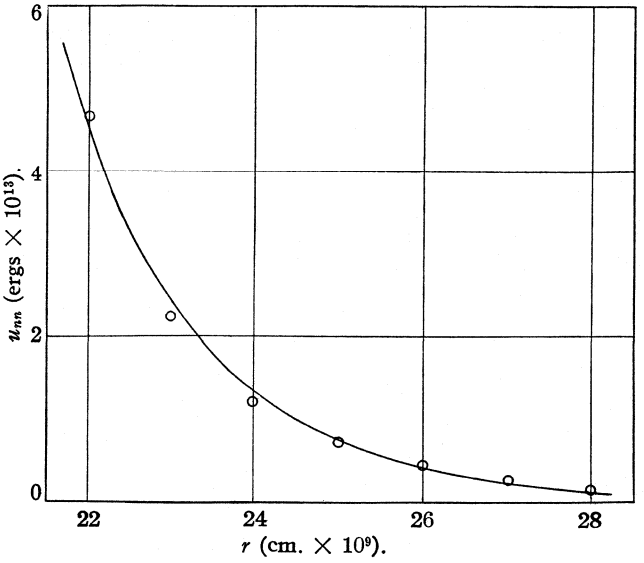

Fig. 1.

In Table I are given the results when we assume that ϕ_n, the eigenfunction of the initial state, is the eigenfunction of the first excited state of a harmonic oscillator, and $\phi_{n'}$ is the lowest state and use equation 26 for the calculation. It is here assumed that there is but a single oscillator, the results of section 5 not being taken into account. In this case it is easily shown that

$$\rho = (1 + \alpha^2/2\beta)^{-1} \tag{39}$$

$$\sigma = (\alpha^2/2\beta)^{1/2}(1 + \alpha^2/2\beta)^{-1} \tag{40}$$

In Table II we have used equation 28 instead of equation 26. It will be seen that the results correspond fairly well to the results in Table I for somewhat higher values of α. This is to be expected, inasmuch as the potential given by equation 27 goes up much more steeply for small values of r than that given by equation 13. It is certainly unlikely that any

TABLE I

VALUES OF $\gamma_{nm,n'm'}$ CALCULATED FROM EQUATION 26 (M IN ATOMIC WEIGHT UNITS, ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

M ↓	$\alpha \times 10^{-8}$ ↓	$\nu_0 \rightarrow$ / $k \times 10^{-5} \rightarrow$	500 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
1	7		0.40	0.31	0.10	0.13	0.14	0.070	0.053
1	6		.36	.25	.08	.11	.11	.047	.040
1	5		.27	.18	.060	.075	.070	.027	.024
1	4		.18	.11	.034	.037	.032	.012	.010
2	7		.31	.27	.10	.052	.072	.045	.012
2	6		.26	.21	.070	.035	.049	.027	.0067
2	5		.17	.13	.042	.019	.024	.011	.0033
2	4		.08	.063	.020	.0068	.0077	.0034	.0009
4	7		.15	.16	.074	.0077	.019	.018	.0006
4	6		.10	.11	.044	.0041	.009	.008	.0003
4	5		.051	.053	.021	.0017	.0034	.0025	.0001
4	4		.021	.019	.0070	.0004	.0007	.0004	.0000

TABLE II

VALUES OF $\gamma_{nm,n'm'}$ CALCULATED FROM EQUATION 28 (M IN ATOMIC WEIGHT UNITS, ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

M ↓	$\alpha \times 10^{-8}$ ↓	$\nu_0 \rightarrow$ / $k \times 10^{-5} \rightarrow$	500 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
1	6		0.42	0.29	0.087	0.25	0.21	0.080	0.16
1	4		.27	.17	.047	.10	.08	.027	.047
2	6		.39	.29	.100	.12	.13	.059	....
2	4		.17	.12	.036	.027	.025	.010	.0064
4	6		.22	.20	.080	.024	.037	.023	.0039
4	4		.060	.048	.017	.0026	.0034	.0017	.0002

general conclusions as to trends which would be drawn from the one set of calculations would not be drawn from the other also. This gives us some confidence that these conclusions will be significant.

In Table III we have taken ϕ_n as the fourth excited state and $\phi_{n'}$ as the third, and we have used the considerations of section 5. In this case it may be shown that, approximately (neglecting terms in the numerator and denominator containing higher powers of $\alpha^2 b_{1i}^2/\beta_i$)

$$\rho_i = \frac{1 + 1.50\ \alpha^2 b_{1i}^2/\beta_i}{1 + 2.00\ \alpha^2 b_{1i}^2/\beta_i} \sim \frac{1 + 1.50\ \alpha^2/q\beta}{1 + 2.00\ \alpha^2/q\beta} \tag{41}$$

and

$$\sigma_i = \frac{\alpha b_{1i}\,(1.41 + 1.06\ \alpha^2 b_{1i}^2/\beta_i)}{\beta_i^{1/2}\,(1.00 + 2.00\ \alpha^2 b_{1i}^2/\beta_i)} \sim \frac{\alpha\,(1.41 + 1.06\ \alpha^2/q\beta)}{q^{1/2}\beta^{1/2}(1.00 + 2.00\ \alpha^2/q\beta)} \tag{42}$$

where β is to be given the same value as in the case in which the considerations of section 5 were not taken into account.[16] Now the transition

[16] The method of evaluating the matrices like u_{nn} and $u_{nn'}$ and, thus, ρ and σ is the following. We can express the eigenfunction ϕ_n, as a function of the variable $\beta^{1/2}x = \xi$, as $\phi_n(\xi) = \pi^{-1/4}2^{-n/2}(n!)^{-1/2}H_n(\xi)e^{-\xi^2/2}$, where $H_n(\xi)$ is a Hermite poly-

TABLE III

VALUES OF $\gamma_{nm,n'm'}$ CALCULATED FROM EQUATION 44 (M IN ATOMIC WEIGHT UNITS ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

M ↓	$\alpha \times 10^{-8}$ ↓	$\nu_0 \rightarrow$ / $k \times 10^{-5} \rightarrow$	500 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
1	7		2.75	1.58	0.44	1.68	1.06	0.320	1.09
1	6		2.27	1.29	.34	1.27	0.76	.220	0.75
1	5		1.68	0.91	.24	0.78	.45	.125	.41
1	4		1.04	0.55	.138	.36	.20	.050	.155
2	7		2.81	1.63	.45	1.20	.75	.230	.601
2	6		2.09	1.19	.31	0.74	.44	.129	.325
2	5		1.31	0.71	.185	.35	.206	.057	.129
2	4		0.61	0.33	.082	.11	.061	.016	.031
4	7		2.16	1.25	.347	.53	.332	.102	.185
4	6		1.35	0.76	.203	.253	.152	.044	.072
4	5		0.66	.36	.093	.084	.049	.0135	.0188
4	4		.22	.118	.030	.016	.0086	.0023	.0022

VALUES OF $\gamma_{nm,n'm'}$ CALCULATED FROM EQUATION 44, BUT WITH T_{nm} = 2400 CALORIES, PER MOLE. ν_0 = 1000 CM.$^{-1}$

$\alpha \times 10^{-8}$ ↓	$k \times 10^{-5} \rightarrow$	$M = 1$ 0.6	$M = 1$ 5.0	$M = 2$ 0.6	$M = 2$ 5.0	$M = 4$ 0.6	$M = 4$ 5.0
6		6.70	1.16	4.75	0.83	2.09	0.36
4		2.38	0.35	0.99	.14	0.215	.032

probability calculated with the aid of these equations will be the probability that *one* of the normal modes of vibration will change its energy in the collision. Since there are actually q modes of vibration, the final $\gamma_{nm,n'm'}$ must be multiplied by q; or we can get an effective σ_i by multiplying it by $q^{1/2}$.

The actual value of q will be about 5; but we have already considered a case where q is equal to 1 and, involving lower quantum numbers, is much

nomial (see Sommerfeld, "Atombau und Spektrallinien," Ergänzungsbd, Braunschweig, 1929, pp. 19, 57). $\phi_n(\xi)$ differs from $\phi_n(x)$ in the normalizing factor, as $\phi_n(\xi)$ is normalized for integration with respect to ξ. Now, for example, consider $u_{nn'}$. We have

$$u_{nn'} = \pi^{-1/2}2^{-\frac{n+n'}{2}}(n!n'!)^{-1/2}e^{-\alpha r}\int_{-\infty}^{\infty} H_n(\xi)H_{n'}(\xi)\,e^{-\xi^2}e^{\alpha x}\,d\xi \qquad (43)$$

By making the substitutions $\gamma = \alpha/2\beta^{1/2}$ and $\zeta = \xi - \gamma$ this takes the form

$$u_{nn'} = \pi^{-1/2}2^{-\frac{n+n'}{2}}(n!n'!)^{-1/2}e^{-\alpha r}e^{\gamma^2}\int_{-\infty}^{\infty} H_n(\zeta+\gamma)H_{n'}(\zeta+\gamma)\,e^{-\zeta^2}\,d\zeta \qquad (43a)$$

Now $H_n(\zeta+\gamma)$ and $H_{n'}(\zeta+\gamma)$ may be expanded in terms of $H_n(\zeta)$ and $H_{n'}(\zeta)$, respectively, and their derivatives, by use of Taylor's theorem, and the derivatives of the Hermite polynomials may then be expressed in terms of Hermite polynomials of lower order (Courant and Hilbert, "Methoden der mathematischen Physik," Berlin, 1924, p. 76, equation 60) whence the integral reduces to a sum of integrals, all of which involving Hermite polynomials of different order vanish (Courant and Hilbert, equation 64), while the others are the standard normalization integrals (Courant and Hilbert, equation 65).

TABLE IV

σ_i, EFF., CALCULATED WITH THE AID OF EQUATION 42 (ν_0 IN CM.$^{-1}$, k IN DYNES PER CM., α IN CM.$^{-1}$)

$\alpha \times 10^{-8}$ ↓	$\nu_0 \rightarrow$ / $k \times 10^{-5} \rightarrow$	500 0.6	500 1.2	500 5.0	1000 0.6	1000 1.2	1000 5.0	1500 0.6
7		1.073	0.815	0.430	1.356	1.073	0.592	1.521
6		0.954	.719	.370	1.230	0.954	.513	1.397
5		.825	.609	.310	1.082	.825	.434	1.245
4		.680	.496	.249	0.913	.680	.349	1.062

more sensitive to changes in ρ than the present one; furthermore, the differences between the results for given $h\nu_0$, given α, and given M, but differing k, are largely due to differences in σ. We shall therefore set $\rho_i = 1$ and write from equation 26

$$v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2} = 3.74 \frac{\alpha}{\beta^{1/2}} \frac{1.41 + 1.06\,\alpha^2/5\beta}{1.00 + 2.00\,\alpha^2/5\beta} \frac{K^2 T_{nm}}{\alpha^2} \frac{S^{\nu/2}}{\nu} \qquad (44)$$

This is the effective value of $v_{nm,\,n'm'}/(\epsilon_{nm}\epsilon_{n'm'})^{1/2}$ in which σ has been multiplied by $q^{1/2}$. Since ρ is set equal to 1 we have $\nu = \mu$, the gamma functions give the factor $1/\nu$ and the hypergeometric function becomes equal to 1. The results of the application of this formula have been given in Table III.[17]

It will be noticed that in some of these cases the transition probability has a value greater than 1. Such a result is of course impossible, and it means that the interaction between the oscillator and the colliding particle is so great that equation 8, which is based on the theory of small perturbations no longer holds. It may, in fact, well be that, even in cases where the transition probability comes out small, the perturbations are too large to apply the theory of small perturbations. For I have shown in the discussion of a similar problem that in the "case of poor resonance" such a thing may occur.[18] Now poor resonance means that there is a considerable exchange of translational to internal (which in the present case would be vibrational) energy, or *vice versa*, and this occurs in the cases considered in this paper. However, a method of treating the case of poor resonance when the perturbations are large has been developed.[19] This will now be applied and the results may then be compared with those we have already obtained. The latter have been presented in some detail because I believe that the relative values may have some significance; also, I think they may probably be used with slight modification in the case where the colliding particle may also have vibrational energy which it can exchange, a case which I hope may be the subject of future considerations.

[17] Because it may possibly be questioned whether one ought to set T_{nm} equal to 1/2 the Boltzmann constant times the absolute temperature rather than 3/2 this product, a few calculations are included in which T_{nm} is given the larger value.

[18] Rice, *Phys. Rev.*, **38**, 1951 (1931).

[19] Rice, *ibid.*, **38**, 1953 (1931); London, *Z. Physik*, **74**, 143 (1932).

§7. Modification for Large Interactions

In this calculation we consider two solutions of our equation 1, ϕ_n and $\phi_{n'}$ as before, but we first apply the perturbation V holding r fixed. Thus for the perturbed equation we have

$$\frac{h^2}{8\pi^2 m}\frac{d^2\phi}{dx^2} + (E - V - 2\pi^2\nu_0^2 m x^2)\,\phi = 0 \tag{45}$$

in which r may appear as a parameter, but x is the only variable. We assume that ϕ_n and $\phi_{n'}$ are the *only* solutions of equation 1 that need to be considered. This is not true, but is necessary for purposes of simplification. Application of perturbation theory then shows that there are two solutions of (45) which we shall call χ_1 and χ_2 and which are given by[20]

$$\begin{aligned}\chi_1 &= \phi_n \cos\omega + \phi_{n'} \sin\omega \\ \chi_2 &= -\phi_n \sin\omega + \phi_{n'} \cos\omega\end{aligned} \tag{46}$$

where

$$\omega = \frac{1}{2}\arctan\frac{2u_{nn'}}{E_n - E_{n'} + u_{nn} - u_{n'n'}} \tag{47}$$

The energies which go with these solutions are, respectively

$$\begin{aligned}U_1 &= \frac{1}{2}\left\{E_n + u_{nn} + E_{n'} + u_{n'n'} + [(E_n + u_{nn} - E_{n'} - u_{n'n'})^2 + 4u_{nn'}^2]^{1/2}\right\} \\ U_2 &= \frac{1}{2}\left\{E_n + u_{nn} + E_{n'} + u_{n'n'} - [(E_n + u_{nn} - E_{n'} - u_{n'n'})^2 + 4u_{nn'}^2]^{1/2}\right\}\end{aligned} \tag{48}$$

We can now set up equations of the following form to give the translational motion of the colliding particle under the forces due to these potential energy fields

$$\frac{h^2}{8\pi^2 M}\frac{d^2 G_{kl_k}}{dr^2} + (W_{kl_k} - U_k)\,G_{kl_k} = 0 \tag{49}$$

where k takes the value 1 or 2, and l_k is the quantum number which then determines W_{kl_k}, the total energy. The eigenfunction giving the state of the whole system will be $\chi_k G_{kl_k}$. If such a wave function is substituted in the exact wave equation (7), however, it will be found not to satisfy it exactly. Treatment of the perturbation problem shows that if we start with the function χ_1 the probability per collision of going over to χ_2 (or *vice versa*) is given by

$$\gamma_{12} = 4\pi^2 p_{12}/\epsilon_1\epsilon_2 \tag{50}$$

where p_{12} is the matrix component of the perturbation energy. If we simplify the subscript notation, calling the first (complete but unperturbed) eigenfunction $\chi_1 G_1$ and the second $\chi_2 G_2$ then

$$p_{12} = -K^{-2}\int_0^{r_\infty} dr \int_{-\infty}^{\infty} dx \chi_1 G_1 [G_2(\partial^2\chi_2/\partial r^2) + 2(\partial G_2/\partial r)(\partial\chi_2/\partial r)] \tag{51}$$

Substituting for χ_1 and χ_2 from (46) and (47), performing the differentiations and the integration with respect to x (taking into account the orthogonality of ϕ_n and $\phi_{n'}$ and the fact that they are normalized, and

[20] London, Ref. 19.

using some simple trigonometric identities) and integrating with respect to r by parts twice,[21] this can be written

$$p_{12} = K^{-2} \int_0^{r_\infty} \omega[G_2(d^2G_1/dr^2) - G_1(d^2G_2/dr^2)]dr$$

Using (49) this reduces to[22]

$$p_{12} = -\int_0^{r_\infty} \omega(W_1 - U_1 - W_2 + U_2)G_1G_2dr \qquad (52)$$

Now it will be seen from equation 48 that since $u_{nn'}$ increases as r decreases U_2 may eventually reach a maximum. This would mean that though at first there is a repulsive force between the oscillator and the colliding particle, it becomes, if we go to small enough values of r, attractive. Such a result is, from a physical viewpoint, ridiculous. It apparently occurs because we have only taken into account the two states ϕ_n and $\phi_{n'}$, whereas in reality all states of the harmonic oscillator must be considered. When the perturbation becomes large, as at small values of r, a number of them will be of importance. However, with this method it will be very difficult to handle more than two states at a time. In this situation it seems best to make an attempt at an approximation by neglecting $u_{nn'}$ in equation 48, setting[23]

$$\begin{aligned} U_1 &= E_n + u_{nn} \quad \text{and} \\ U_2 &= E_{n'} + u_{n'n'} \end{aligned} \qquad (53)$$

Furthermore, we have seen that when all the necessary considerations are taken into account it is a good approximation to set $\rho = 1$, that is, $u_{nn} = u_{n'n'}$. Thus (52) becomes, if we let $T_1 = W_1 - E_n$ and $T_2 = W_2 - E_{n'}$

$$p_{12} = -(T_1 - T_2) \int_0^{r_\infty} \omega G_1G_2dr \qquad (54)$$

where G_1 and G_2 obey (49) with the values of U from (53) inserted.

This gives us the transition probability per collision from χ_1 to χ_2, but since at large distances χ_1 becomes equal to ϕ_n and χ_2 to $\phi_{n'}$ this will be the transition probability we desire. It is not pretended that this method gives better than a rough approximation, but it seems to me that there is no question that even this approximation will throw valuable light on the process of transfer of energy between molecules.

There is no way to evaluate (54) except by numerical methods. G_k (where $k = 1$ or 2) may be approximated by the Wentzel–Kramers–Brillouin approximation method,[24] which gives the following results. We set $r = r_k$ for the point where $W_k = U_k$ (that is $T_k = u_k$ if $u_k = u_{nn}$

[21] The integrated parts vanish at the limits.

[22] This is essentially equivalent to the equation for B_l on p. 165 of London's article. As it was not necessary for the purposes I had in mind at the time, I did not write out the expression 46 explicitly, and so did not get p_{12} into the form (52).

[23] The small disturbance due to the finite value of p_{11} and p_{22} is also neglected.

[24] See Kramers, *Z. Physik*, **39**, 828 (1926).

or $u_{n'n'}$ according as k is 1 or 2) and we assume the G's normalized in the same way as the R's, according to equation 6, and we take r_∞ to be very large; we may then write

$$G_k = 2^{1/2} r_\infty^{-1/2} T_k^{1/4} (T_k - u_k)^{-1/4} \cos\left\{ K \int_{r_k}^{r} (T_k - u_k)^{1/2} dr - \pi/4 \right\} \quad (55)$$

if $r \gg r_k$, and

$$G_k = 2^{-1/2} r_\infty^{-1/2} T_k^{1/4} (u_k - T_k)^{-1/4} \exp\left\{ -K \int_{r}^{r_k} (u_k - T_k)^{1/2} dr \right\} \quad (56)$$

if $r \ll r_k$. If r is in the neighborhood of r_k we may write

$$G_k = 2^{-1/2} r_\infty^{-1/2} \pi^{-1/2} K^{1/2} T_k^{1/4} \left\{ 3^{-1/6} \Gamma\left(\frac{1}{3}\right) (K^2 u_k')^{-1/6} + 3^{1/6} \Gamma\left(\frac{2}{3}\right) (K^2 u_k)^{1/6} (r - r_k) \right\} \quad (57)$$

where $u_k' = -du_k/dr$.

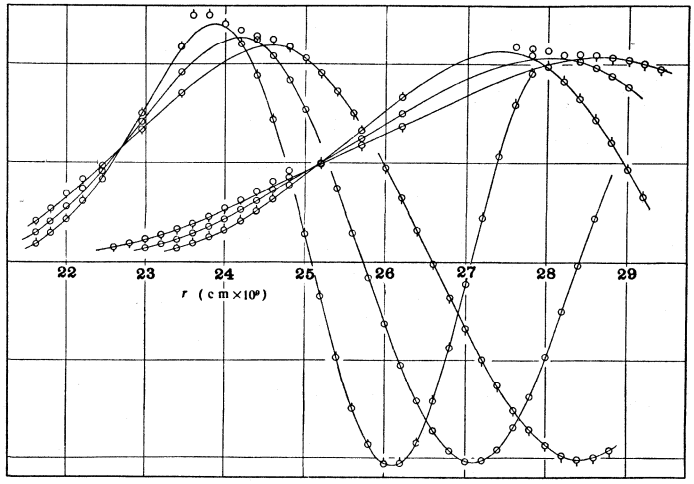

Fig. 2.—Evaluation of G_k: ○, $M = 1$; ○, $M = 2$; ○, $M = 4$.

It is now necessary to evaluate G_k numerically. This we have done, using equations 53 (and $\rho = 1$) for determining U_k (U_1 or U_2). u_{nn} as a function of r we have taken directly from Lennard-Jones' expression for the force between two hydrogen molecules as a function of the distance between them. Since the equations 55, 56 and 57 do not cover the whole range of r it is necessary to interpolate between the various regions graphically. The method by which this has been done is shown in Fig. 2, in which portions of all the various G_k curves used in the subsequent calculation are exhibited. The three points near the first point of inflection of each curve ($r = r_k$) are, in each case, calculated from equation 57; the other points are calculated from either 55 or 56. The actual curves which have been used are shown. Values from these curves have been sub-

stituted into equation 54, ω has been calculated from (47) and p_{12} found by numerical integration. I have assumed that the value of $u_{nn'}$ to be used in (47) is obtained from u_{nn} by multiplication with the proper *effective* value of σ_i, as listed in Table IV. Calculations have been made for σ_i effective, equal to 0.5 and to 1.0.

On account of the labor involved in this process the calculations have been made for only a few cases. Throughout we have used the same curve for u_{nn} and have taken $T_1 = 0.5 \times 10^{-13}$ ergs (723 calories per mole) and $T_2 = 2.5 \times 10^{-13}$ ergs. The difference, $T_2 - T_1 = h\nu_0$, corresponds to an oscillator frequency of 1018 cm.$^{-1}$. The results of the calculations (γ_{12}) are given in Table V.

TABLE V

VALUES OF γ_{12} CALCULATED BY THE METHOD OF SECTION 7

$\sigma_{i,\text{ eff.}}$	$M \rightarrow$ 1	2	4
0.5	0.14	0.058	0.011
1.0	.32	.096	.007

Comparison with the values of Table III for $h\nu_0 = 1000$ cm.$^{-1}$ and $\alpha = 5 \times 10^8$ cm.$^{-1}$ indicates that the correction for large perturbations is scarcely necessary when $\sigma_{i,\text{ eff.}} = 0.5$, but is of some importance when it is around 1.

Some information about how γ_{12} varies with the sharpness of collision may be found without further calculation by the following means. If we suppose that u_k has approximately the form $C_k e^{-\alpha r}$ we may make the substitution $y = \alpha r$ and write equation 49 in the form

$$\frac{h^2\alpha^2}{8\pi^2 M}\frac{d^2G_k}{dy^2} + (T_k - C_k e^{-y})G_k = 0$$

whence it is seen that, for given T_k and C_k, G_k will depend on α and M only in the combination α^2/M. Changing C_k is equivalent only to changing the zero point for y, which can make but very slight difference in the eigenfunction G_k, except to shift it along correspondingly. So if we have two eigenfunctions, G_1 and G_2, so long as the ratio C_1/C_2 remains fixed (for instance if $\rho = 1$) the product G_1G_2 depends on α and M only in the combination α^2/M. If the same substitution, $y = \alpha r$, is made in (54), then it is readily seen, from (54), (50) and the fact that ϵ_1 and ϵ_2 are inversely proportional to $M^{1/2}$, that γ_{12} depends on α and M only in the combination α^2/M, except in so far as σ changes. Since Table V tells something as to how γ_{12} changes with σ, and with M when σ is fixed, one may estimate, with its aid and that of Table IV how γ_{12} will change when α changes and M remains fixed.

§8. Discussion

The experimental facts, as far as they concern the effects of hydrogen and helium as activating and deactivating agents, are easily summarized.

Experiments have been made with hydrogen in the decompositions of dimethyl ether, diethyl ether, methyl ethyl ether, methyl propyl ether and propionic aldehyde. In all these cases, except methyl ethyl ether the hydrogen is about as effective pressure for pressure, in causing activation or deactivation as the organic molecule itself. In the case of methyl ethyl ether it apparently has somewhat less, but at least at the lower partial pressures of ether, a marked effect; at the higher partial pressures, it seems to retard slightly the rate in this case, but what this may mean is not clear.

In the case of dimethyl ether and diethyl ether, helium is said to be ineffective as an activator or deactivator. From the experiments[25] I should estimate that it is not more than about $^1/_{15}$ to $^1/_{20}$ as effective, pressure for pressure, as hydrogen. This estimate, however, is based on only one experiment in the case of dimethyl ether and two in the case of diethyl ether.

It has been customary in work on the kinetics of unimolecular reactions to assume that deactivation takes place at every collision of an activated molecule with an inactivated one of the same species. It was recognized, of course, that this could be only an approximation, and it was evident that the rate constants of the ethers fall off at a higher pressure than is to be expected for molecules of their complexity if we make the assumption of deactivation at every collision. However, it has been pointed out that this may be due to an impedance of energy transfer inside the molecule[26] or an ineffectiveness of certain of the vibrations of the molecule as far as the particular reaction is concerned;[27] so it is not necessarily to be ascribed to a failure of the assumption that deactivation takes place at every collision. The present results would seem to indicate that the assumption of deactivation at every collision is quite a reasonable one, as far as order of magnitude is concerned. For it seems to be definitely indicated that hydrogen will deactivate at a substantial fraction, say $^1/_{10}$ to $^1/_{20}$, of the collisions it makes; so the organic molecules, which are as effective, pressure for pressure, but which, on account of their slower average velocity, make only one-third to one-fourth as many collisions, will, within such a factor as is relatively unimportant in chemical kinetic considerations, deactivate at every collision with an activated molecule. (This is based on Table V.)

It should, perhaps, be remarked that removal of one quantum of energy (about 2850 calories per mole) from an oscillator of frequency around 1000 cm.$^{-1}$ is adequate to deactivate effectively an activated molecule. That is, it brings an average activated molecule into an energy range where the molecules are essentially maintained at their Maxwell–Boltz-

[25] Hinshelwood, *Proc. Roy. Soc.* (London), **114A**, 94 (1927); Hinshelwood and Askey, *ibid.*, **115A**, 223 (1927).

[26] Rice and Ramsperger, THIS JOURNAL, **50**, 619 (1928).

[27] Rice, "Réunion Internationale de Chimie Physique," Paris, 1928, p. 305.

mann quota. Since similar discussions have been given before,[28] no detailed explanation will be given here, but the truth of the statement for practically any pressure is easily seen, if one accepts the theory of unimolecular reactions developed by Rice and Ramsperger, from their curves[29] giving the relative amount of reaction due to molecules of various energies.

And since the above results indicate that the supposition that only a limited number of the various modes of vibration are concerned with the reaction in the case of the ether decomposition is probably correct, it seems entirely reasonable to suppose that these particular vibrations have frequencies around 1000 cm.$^{-1}$, which is about that of a carbon–carbon or carbon–oxygen vibration when the vibration takes place in the line joining the two atoms.[30]

On this basis it would appear that the results of section 7 are fairly satisfactory in that they give a marked difference between hydrogen ($M = 2$) and helium ($M = 4$), even though it is not quite as large as the observed difference. On closer examination, however, several doubtful points come to light.

In the first place the small values of γ_{12} for $M = 4$ in Table V are due to extensive cancellation of positive and negative parts in the integral for p_{12}. For example, in the case $M = 4$, $\sigma = 0.5$ the integral p_{12} is composed of three principal positive portions, equal to 3.5 p_{12}, 1.5 p_{12} and 0.05 p_{12}, respectively, from which are subtracted two principal negative portions equal to 4.0 p_{12} and 0.04 p_{12}, respectively. The value of p_{12} will therefore be very sensitive to slight changes in the various quantities involved; thus if the curves for U_1 and U_2 as functions of r are shifted slightly with respect to one another, large changes in p_{12} will occur. It is true that if these curves are shifted slightly apart (which is probably the right direction) p_{12} and hence γ_{12} will be decreased, but on the whole it will be easier to cause increases in p_{12} than decreases. However, the important point is that when we have $M = 4$ we are already in the region of extensive cancellation of positive and negative portions of the integral, which is what is necessary to make it small.

A more unsatisfactory feature is our inability to make a fair comparison between the α for hydrogen and that for helium, and an estimate of the effect of changes in rotational energy in the case of hydrogen. These two points are, of course, intimately associated, as both the value of α and the

[28] Rice and Ramsperger, THIS JOURNAL, 49, 1625 (1927); Rice, "Réunion Internationale de Chimie Physique," Paris, 1928, p. 316.

[29] Rice and Ramsperger, THIS JOURNAL, 49, 1625 (1927).

[30] It is not to be supposed, of course, that these are necessarily the only sorts of motion involved. For example, the transverse hydrogen vibrations have a slightly higher frequency and may be of some importance. In fact, in the case of dimethyl ether one cannot make up enough vibrations involving only the carbon–oxygen longitudinal motion.

possibility of exchange of rotational energy in the case of hydrogen are connected with the electron distribution in the hydrogen molecule. Although a direct collision of a helium atom would undoubtedly be sharper than one of a hydrogen molecule, it is by no means certain that this is true in the present case where transfer of energy from the carbon–carbon vibrations are concerned. For it is quite possible that the smaller size of the helium atom would enable it to get down into the interstices between the hydrogen atoms in the organic molecule, and so, in a certain number of its collisions, find it was bouncing off a softer cushion. In any event, it may well be that the possibility of a hydrogen molecule changing its rotational energy would make up for any smaller ability to exchange energy due to the blow being softer than in the case of helium.

But by far the most disconcerting factor, if one is interested in using the above results to explain the difference between hydrogen and helium, is a possibility that up to this point has been entirely neglected. This is the chance that transitions will occur in which two of the normal oscillators change their quantum states, one gaining, the other losing, energy. Since it is not possible for a given molecule to have around five oscillators of just the same frequency, it is quite possible that such a double jump would result in quite an appreciable transfer of energy to the colliding particle, though the amount of energy transferred would of course be much smaller than when only one oscillator changed its quantum number. A smaller exchange of energy is naturally less effective in producing deactivation, but on the other hand it will be found to take place with a greater probability, in spite of the fact that two oscillators are involved, and since for these transfers there is little difference between hydrogen and helium, the difference previously found will be to a large extent, masked.

An estimate of the probability of a transition involving a double jump may be made without too much calculation, using the method of section 7, if u_k is given approximately by $C_k e^{-\alpha r}$. If we write equation 49 in the form

$$\frac{h^2}{8\pi^2 M T_k}\frac{d^2G_k}{dr^2} + (1 - C_k e^{-\alpha r} - \log T_k)\, G_k = 0$$

it is seen that a change of T_k has approximately the same effect on G_k as a change in M, with a shift in the abscissas. And a new value of σ_i, eff., is easily calculated by a slight extension of the methods previously used. Table VI gives some values of σ_i, eff., for ν_0 equal to 1000 cm.$^{-1}$ (this being assumed to be average frequency of the oscillators participating). These values are obtained from the values of σ_i by multiplying by $10^{1/2}$ instead of $5^{1/2}$, since 10 is the number of different pairs of 5 oscillators which is possible. (It is quite probable, of course, that not all the pairs would be effective, as with some pairs the available difference of energy would be too small to be at all effective in deactivation.) I have made a calculation of γ_{12}, taking $M = 4$, and $T_2 = 1.25 \times 10^{-13}$ ergs, as G_2 can then be obtained, as noted above, from the curves formerly used for $M = 2$ and $T_2 = 2.5 \times 10^{-13}$. This makes $T_2 - T_1 = 0.75 \times 10^{-13}$ ergs, instead of 2.0×10^{-13}. For σ_i, eff., = 0.187 and 0.375, respectively (values used because then ω does not need to be recalculated), I have obtained $\gamma_{12} = 0.077$ and

0.24, respectively. Values of γ_{12} for $M = 2$ will not be greatly different when the ratio of T_2/T_1 is so small. It is thus apparent that even though removal of 0.75×10^{-13} ergs is not as effective in deactivating as removal of 2.0×10^{-13} ergs, still the difference between hydrogen and helium will be pretty well swamped if these double jumps can occur.

TABLE VI

σ_i, EFF., FOR DOUBLE JUMPS FOR $\nu_0 = 1000$ CM.$^{-1}$ (k IN DYNES PER CM., α IN CM.$^{-1}$)

$\alpha \times 10^{-8}$ ↓ / $k \times 10^{-5}$ →	0.6	1.2	5.0
7	1.377	0.844	0.250
6	1.119	.661	.188
5	0.865	.491	.133
4	.602	.331	.086

The alternative possibility is that the various normal modes of vibration are not as closely related as we have assumed, and that if the colliding molecule strikes the organic molecule in a certain way it interacts essentially only with a single oscillator, even though this be a normal oscillator.

On account of the points which have just been discussed, I do not feel that it is justifiable to make any claims that the difference here found between hydrogen and helium really represents completely the difference observed experimentally and I present the results merely as suggesting a possibility. There is a hope, however, that it may be possible, with these results as a basis, to find out something about the effect of exchanges of smaller amounts of energy experimentally. For there are a number of reactions, for example the decomposition of azomethane, in which we judge, from the pressure at which the rate constant begins to fall off, that all possible oscillators, including those of considerably lower frequency than 1000 cm.$^{-1}$, are involved. If it is true that the difference between hydrogen and helium indicates that quantum jumps of two vibrators simultaneously do not often occur, then the difference between the two gases should be much less in these cases where transfers of much smaller amounts of energy are possible without the double jumps occurring. Unfortunately Ramsperger[31] has found that hydrogen seems to react with azomethane; nevertheless, it would be very interesting to try the effect of helium, as we may guess it would be appreciably greater than in the case of the ethers. But even in the case of the ethers, and assuming that the double jumps do not occur, it is evident, if the theory here presented is at all correct, that helium should have an appreciable, even if small, effect—one which slightly more sensitive methods of experimentation should detect. If it should be detected, it would then be interesting to try neon with apparatus of the same sensitivity. Here the mass is great enough to cause it to be so poor an activator that no effect should be detectable even with the most sensitive apparatus possible to devise.

[31] Ramsperger, private communication.

Another experiment of extreme interest, should it become possible, would consist in the investigation of a hydrogen gas composed of the newly discovered heavier isotope of hydrogen. Some of the experiments indicated, Dr. D. V. Sickman and I hope to carry out shortly.

I wish to express my thanks to Dr. Sickman for assistance in some of the calculations.

INDEX OF SYMBOLS

The number gives the equation in or near which the symbol is defined

a	24	q	30	$v_{nm,\,n'm'}$	9	ν	21
a_{ij}	29a	r	1	V	2	ν_0	1
A, A'	13, 18	r_∞	5	W, W_{nm}	7, 3	$\xi_1, \xi_2, \ldots \xi_q, \xi_i$	29a
b	24	r_0	14	W_1, W_2	49	ρ, ρ_i	17, 34
b_{ji}	29b	r_k	55	x	1	σ, σ_i	23, 35
B, B'	13, 18	$R_{nm}, R_{n'm'}$	3, 10	$x_1, x_2, \ldots x_q, x_j$	29a	$\phi, \phi_n, \phi_{n'}$	1
c	24	S	24	z	20	$\phi_n^i(\xi_i)$	32
C, C_k	11, 58	$T_{nm}, T_{n'm'}$	3, 10	α	11	χ_1, χ_2	46
$E, E_n, E_{n'}$	1	T_1, T_2	54	β, β_i	12, 36	ψ_{nm}, ψ	4, 7
G_1, G_2, G_k	51, 55	u_k	55	$\gamma_{nm,\,n'm'}$	8	ω	47
K	5	$u_{nn}, u_{n'n'}$	2, 10	γ_{12}	50		
m, m_j	1, 30	$u_{nn'}$	10	$\epsilon_{nm}, \epsilon_{n'm'}$	5, 8		
M	3	$u_\infty, u_{\infty'}$	13, 18	μ	22		
p_{12}	50	U_1, U_2, U_k	48, 49	μ_i	30		

§9. Summary

The rate constants for many unimolecular gas reactions decrease at low pressures, as the number of activating collisions becomes small. In a number of decompositions of organic compounds addition of sufficient hydrogen restores the rate constant to its high pressure value, the hydrogen being able to cause activation. Helium, however (in common with a number of other gases), apparently does not have this ability.

In order to gain a better understanding of these phenomena, an attempt has been made in the present paper to investigate the dynamics of energy exchange between organic molecules of the type which undergo decomposition in the gas phase and other simple molecules, in particular hydrogen and helium, which may activate or deactivate the organic molecules. Deactivation of an organic molecule may take place, for example, if some of its vibrational energy is changed into translational energy of the colliding atom or molecule. The calculations are based essentially on a simple one-dimensional model in which it is assumed that a particle collides with an oscillator along the line in which the latter is vibrating; some discussion has been given, however, of the modifications which should be introduced on account of the complexity of the organic molecule. The first calculations have been made on the basis of the Born collision method; since it was found, however, that probabilities of energy exchange greater than 1 occurred, a modification was introduced, following

recent work of the writer, and of London, which allowed an approximate calculation for large perturbations. It was still found that the probability that hydrogen should deactivate an activated molecule was such as to be consistent with the assumption that an activated molecule is deactivated every time it hits an unactivated molecule of the same kind, within a factor of around ten (this conclusion being drawn after a discussion of experimental results which give the relative probability that a hydrogen molecule and an unactivated molecule of the same kind will deactivate the activated molecule).

The various factors which affect the probability of transfer of energy have also been investigated. It was found that, in general, increasing the frequency of the oscillator decreases the probability, increasing the force constant of the oscillator decreases the probability, increasing the "sharpness" of the collision (*i. e.*, the steepness with which the force between the oscillator and the colliding particle goes up as they approach) increases the probability, and increasing the mass of the colliding particle decreases the probability. The latter effect was of interest in connection with the observed difference between hydrogen and helium, and a study was made of the effect of the mass of the colliding particle when other things were varied. However, on account of various complications, it was not possible to decide whether the observed difference between hydrogen and helium actually found a complete explanation in the calculated results.

Note added in proof, Oct. 17, 1932.—Since this article was submitted Jackson and Mott, Ref. 10, have shown how to solve the differential equation 3 and evaluate the integral in (10), for the particular case, $\rho = 1$, when u_{nn} is left in the exponential form instead of being put in the form (13). A few rough calculations made from their formula seem to show about as satisfactory agreement with Table III as is shown between Tables I and II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

THE VELOCITY AND MECHANISM OF RACEMIZATION. II. MANDELIC ACID

BY ALAN NEWTON CAMPBELL AND ALEXANDRA JEAN ROBSON CAMPBELL

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As a continuation of the work described in Part 1,[1] we have investigated in a similar manner the racemization of mandelic acid in the presence of acid and alkali. The apparatus and methods are described in Part 1.[1] We chose mandelic acid in contrast to Rochelle salt, because the mechanism must necessarily be simpler, in so far as there is no possibility of meso formation. We supposed, as a result of our work already described, that complex formation was a necessary condition of racemization, but we have

[1] Campbell and Campbell, THIS JOURNAL, **54**, 3834 (1932).

found no experimental evidence of the existence of a complex in the case of mandelic acid, although the existence of a very loose complex is not excluded.

The *l*-mandelic acid was prepared from amygdalin by a method described elsewhere.[2]

Rotatory Power.—The specific rotations of mandelic acid in acid and in alkali were first determined, as described in Part I. Light filter No. 3 was used (transmission: 7608–5800 Å.) and the temperature of measurement was 26.5°. In view of the cost of amygdalin all solutions used in this work were decimolar with respect to mandelic acid. The results are contained in Table I.

TABLE I

SPECIFIC ROTATIONS OF DECIMOLAR MANDELIC ACID IN VARIOUS MEDIA

Medium		Medium	
11.24 *N* HCl	−159°	Water	−129°
4.49 *N* HCl	−145	0.935 *N* NaOH	−106
2.38 *N* HCl	−140	1.97 *N* NaOH	−107
1.25 *N* HCl	−136	2.72 *N* NaOH	−113
Water	−128	6.97 *N* NaOH	−113

It is apparent that the rotation of mandelic acid passes through a minimum in about 1 normal sodium hydroxide, after which it increases only very slightly. In alkaline media we are dealing principally with the mandelate ion, the concentration of which will decrease slightly with increasing concentration of sodium hydroxide. In acid solution the mandelic acid will be present almost entirely as non-dissociated molecules. Perhaps one might say that there is no indication of complex formation in the alkaline solutions, but some indication of it in the acid solutions.

H^+ and OH^- Concentrations.—The H^+-ion concentrations were determined, in acid by means of the quinhydrone electrode, in alkali by means of the manganese hydroxide electrode. The combinations

Hg/Hg_2Cl_2 in satd. KCl/HCl/Quinhydrone

and

Hg/Hg_2Cl_2 in satd. KCl/0.1 *M* Mandelic acid in HCl/Quinhydrone

yielded identical e. m. f.'s throughout, as did the combinations

Hg/Hg_2Cl_2 in satd. KCl/NaOH/Manganese hydroxide

and

Hg/Hg_2Cl_2 in satd. KCl/0.1 *M* Mandelic acid in NaOH/Manganese hydroxide

There is no evidence of complex formation from this source.

Conductometric Experiments.—The molecular conductivity of *M*/10 sodium mandelate was determined, in the usual manner, together with the molecular conductivities of 2.72 *N* sodium hydroxide, 6.97 *N* sodium hydroxide, and 11.24 *N* hydrochloric acid. Decimolar *l*-mandelic acid

[2] *Trans. Faraday Soc.*, **26**, 561 (1930).

was then dissolved in each of these three media and the molecular conductivity again determined. No special precautions were taken in the work. The measurements were made in a thermostat at 25°. The experimental value for "medium + $M/10$ mandelic acid" (column 3) was compared with the sum of the molecular conductivity of the sodium hydroxide medium alone and the conductivity of the fraction of a mol of sodium mandelate contained in a volume which contained one mol of sodium hydroxide (column 4). The results are contained in Table II.

TABLE II

Nature of medium	μ obs. Medium alone	μ obs. Medium + $M/10$ m. a.	μ for medium + μ for $M/10$ m. a.	Difference	Ratio
Water	...	48(NaM)	...	..	..
2.62 N NaOH	158	166	160	−6	1.04
6.97 N NaOH	106	95	107	12	0.89
11.24 N HCl	44.5	44	45	1	.98

The deviation from additivity is hardly sufficient to indicate complex formation.

Velocity of Racemization.—The apparatus and method of work are described in Part 1.[3] At the temperature of experiment (96.2°) no racemization could be detected in acid solutions of strength below 11.24 N hydrochloric acid. When working with mandelic acid in 11.24 N hydrochloric acid (concentrated acid) it was observed that the solution developed a distinct yellow-green color, together with a pronounced smell of phenylacetic acid. It was thought that decomposition had taken place in the sense of the equation

$$C_6H_5CH(OH)COOH + 2HCl = C_6H_5CH_2COOH + H_2O + Cl_2$$

This was tested for by taking a measured volume of the solution after a series of racemization measurements, adding potassium iodide and titrating the liberated iodine with standard thiosulfate. In two such experiments the results corresponded to 10.4 and 6.9% decomposition, respectively, an amount insufficient to account for the total decrease in rotation, but amounting to a considerable fraction of it. The only method of correcting for this decomposition which occurred to us was to take the mean of the two results (8.65%), multiply the differences between the zero reading and subsequent readings by 0.0865 and add this to the experimental reading. Correcting in this way, and graphing the results in the manner previously described, series of k values are obtained which are reproduced in Fig. 1. The k value curves for $M/10$ mandelic acid in 0.935, 1.97, 2.72 and 6.97 N sodium hydroxide are also given.

It should be observed that the greater solubility of r-mandelic acid as compared with that of l-mandelic acid obviates certain complications

[3] THIS JOURNAL, **54**, 3834 (1932).

which were to be expected in the case of tartrate racemization. An inspection of the curves shows that racemization of mandelic acid in alkali is much more rapid than in acid, and that in both cases it is much more rapid than with Rochelle salt. A more detailed examination shows that in the case of the acid racemization the velocity "constant" is strictly a constant for the first eleven hours of heating, after which it shows a small but steady decrease, possibly connected with the decomposition of the mandelic acid.

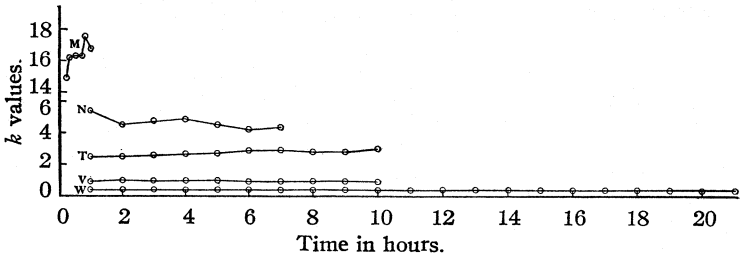

Fig. 1.—M, 6.97 *N* NaOH; N, 2.72 *N* NaOH; T, 1.92 *N* NaOH; V, 0.935 *N* NaOH; W, 11.24 *N* HCl.

In the alkaline solutions, the deviations are irregular and presumably due to experimental error. It was not possible to carry out measurements in alkali of higher concentrations, because, first, mandelic acid became sparingly soluble in, for instance, 9 *N* sodium hydroxide, and, second, because the velocity became inconveniently great: in 6.97 *N* sodium hydroxide, racemization is complete after little more than an hour's heating. We conclude that the process of racemization of mandelic acid, in both acid and in alkali, is simply represented by the equation

$$l\text{-Mandelic acid} \longrightarrow d\text{-Mandelic acid}$$

Attempts to Isolate a Complex.—On the basis of our supposition that racemization was necessarily preceded by formation of a complex, we made attempts to isolate the supposed complex between mandelic acid and hydrochloric acid. In the first place we evaporated a solution of mandelic acid in concentrated hydrochloric acid to dryness in a stream of hydrogen chloride, in a weighed dish. Nothing but mandelic acid was obtained. In the second place an all-glass system was built up consisting of a flask containing dry mandelic acid connected to a hydrogen chloride generator and closed manometer. On forcing in hydrogen chloride gas, the pressure rose progressively to two atmospheres, when the experiments were discontinued, without indication of a rest point. These experiments likewise yield no evidence of complex formation.

Summary

The velocity of racemization of mandelic acid in hydrochloric acid and in sodium hydroxide has been studied, using an apparatus previously de-

scribed. The variations in the constant are purely sporadic. Mandelic acid racemizes much more readily in sodium hydroxide solution than in acid solution, and in both much more readily than Rochelle salt. There is nothing to show that the racemization of mandelic acid is any other than is represented by the simple scheme

$$l\text{-Mandelic acid} \longrightarrow d\text{-Mandelic acid}$$

The existence of a complex has been investigated by the methods of hydroxyl-ion concentration and by measurements of conductivity but neither method gives any certain indication of complex formation. Attempts to isolate a complex have failed. It is shown that the racemization of mandelic acid in strong hydrochloric acid is accompanied by a certain amount of decomposition, together with liberation of free chlorine: possibly the decomposition product is phenylacetic acid.

WINNIPEG, CANADA

[CONTRIBUTION FROM THE ALABAMA EXPERIMENT STATION]

QUANTITATIVE DETERMINATION OF CALCIUM BY THE MAGNETO-OPTIC METHOD

BY EDNA R. BISHOP AND C. B. DOLLINS

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Allison and Murphy have described a magneto-optic[1] method of chemical analysis in which compounds are detected by characteristic light minima produced by the time lag of their Faraday effect. Since very minute traces of a compound will produce its characteristic minima regardless of what other substances may be present, it seemed desirable to study the quantitative possibilities of this method.

Technique.—In general, the method consists of finding the smallest amount of material that will produce light minima characteristic of a calcium compound. This will represent a definite concentration of calcium which is determined by using solutions of known concentration and, from this, the amount in an unknown sample is calculated.

The water used is redistilled from Pyrex glass apparatus. Great care is exercised to guard against any possible contamination. Standard volumetric apparatus is used.

The fact that some calcium is dissolved from glass is recognized. The water was always tested before making an analysis and consistently gave no calcium minima. The reproducibility of results and checks with permanganate titration indicate that the amount dissolved is either negligible or constant.

To test the rate of solution of calcium from glass, water redistilled from Pyrex was left standing in a Pyrex beaker under a bell jar and in a 100-cc. normax flask and tested from day to day for calcium chloride. To ensure the presence of chloride without the addition of any calcium the water was exposed to fumes from concentrated hydrochloric acid. The water in the normax flask gave negative results until the fifth day, when the

[1] Allison and Murphy, THIS JOURNAL, 52, 3796 (1930).

minimum of the more abundant isotope was read. The second minimum became visible on the seventh day. The amount of calcium in the water kept in Pyrex was still below the threshold value. Water was evaporated down to one-fourth its volume in a Pyrex beaker, which would not only concentrate any calcium which might be present but increase its rate of solution. This water showed bare threshold minima for calcium chloride. Some singly distilled water which had been standing around a laboratory in a Pyrex flask for two months was examined. Threshold minima were observed but disappeared when the water was diluted with an equal amount of freshly distilled water, showing that the concentration was equal to or greater than 3.74 g. $Ca/10^{12}$ cc. of water but less than twice that amount.

Stock solutions are prepared by dissolving a weighed sample in a 100-cc. volumetric flask. Any calcium-free compound may be added to give a desired anion. A series of dilutions is then made by diluting 1 cc. of the stock solution to 100 cc., 1 cc. of the resulting solution to 100 cc., etc., until the most dilute contains 1 part or less of calcium in 10^{12} of water. The most dilute solution is examined for calcium chloride or phosphate minima. If the minima are not seen, then each successive increasing concentration is examined until they do appear. Let the concentration in which the minima appear to be $1/10^{n+1}$ of the stock solution. A 10-cc. buret is then filled with $1/10^{n+2}$ solution which is added in 0.5-cc. portions to a cell containing approximately 50 cc. of water and examined for calcium chloride or phosphate minima after each addition until they appear. This gives the concentration range in which to work. An accurate solution is then prepared corresponding to the most concentrated that did not produce minima. By means of a specially calibrated pipet, 49.75 cc. of this solution is placed in a cell and a 10-cc. buret is filled with $1/10^{n+2}$ solution. The solution in the buret is added drop by drop to the cell until each minimum just appears. The volume necessary to detect the minimum of each isotope is read separately and the average of the two readings used. The amount added from the buret will be less than 0.5 cc. so that the final volume in the cell will differ from 50 cc. by less than 0.25 cc. or 0.5%. Therefore the concentration, c, at which the minima appear will be the concentration placed in the cell increased by as many tenths as there were twentieths of a cc. added from the buret.

Sensitivity.—The sensitivity, s, of the apparatus is the lowest concentration of a given element at which its characteristic minima can be detected. In order to determine the sensitivity of the apparatus for calcium, solutions were prepared as follows: 0.8–0.9 g. of calcium acetate was heated in an electric muffle to form the oxide, which was dissolved in hydrochloric acid and diluted to 200 cc. in a volumetric flask. The concentration of calcium in each of two solutions was determined on two 25-cc. aliquots by precipitation of the oxalate and titration with permanganate. These solutions were then analyzed by the magneto-optic method as outlined above. The average of the concentration at which the two minima were read was used as the sensitivity. Thirteen determinations gave values from 3.64 to 3.80 $\times 10^{-12}$ g. Ca/cc. with an average of 3.74 $\times 10^{-12}$ g. Ca/cc. for the sensitivity.

Effect of the Presence of Other Compounds.—To study the effect of the presence of other compounds on the sensitivity, the three types that were considered most likely to interfere were investigated. To study common ion effect, hydrochloric acid was added. To see if a closely related cation would affect the results, magnesium chloride was added. To investigate any possible competition of anions for the calcium, sulfuric acid, nitric acid and phosphoric acid and sodium ammonium phosphate were added. The compound whose influence was being studied was added in making the $1/10^{7}$ dilution so that it was present in the order of 10^{10} times as much as the calcium. None of the compounds studied had any effect on the sensitivity. The results are included in the thirteen values summarized above.

Sensitivity for Other Calcium Compounds.—Calcium chloride solutions to which sodium sulfate, nitric acid and sodium ammonium phosphate had been added were determined simultaneously as described above for all four calcium salts.[2] Several determinations showed that the minima due to each of these compounds became visible at the same concentration and that this concentration was identical with that found when only the chloride was present.

The minima read are in each case characteristic of the *compound* or an ion pair acting together. The calcium ion, however, seems to function simultaneously with every anion that may be present and the concentration at which the minima become visible is a function solely of the calcium-ion concentration and independent of the kind of anion with which it functions. All anions were present in excess. There is, however, a difference in the sharpness of the minima and hence the ease with which they can be read. The order of decreasing sharpness is phosphate, chloride, sulfate and nitrate. The nitrate presents the added difficulty of very closely spaced minima.

Determination of Calcium in Plant Ash.—A weighed sample (0.05 to 0.1 g.) of dried, ground plant material was ashed in an electric muffle, dissolved in hydrochloric acid, filtered and diluted to volume in a 100-cc. volumetric flask. This sample was then analyzed by the magneto-optic method as indicated above. At first determinations were made as the chloride but in later work sodium ammonium phosphate was added during the dilutions and calcium phosphate minima were read because of their greater sharpness.

The percentage of calcium in the sample is given by

$$\frac{s}{c}\frac{v}{m}100 = \%\ \mathrm{Ca}$$

where s is sensitivity $= 3.74 \times 10^{-12}$ g. Ca/cc., c is concentration with respect to stock solution at which the minima became visible, m is weight of sample in stock solution in grams and v is volume of stock solution in cc.

All samples were unknowns to the observer and were designated simply by number. Several determinations were run of each solution. Other portions of each sample were ashed and determined by permanganate titration. The results are shown in Table I.

TABLE I

PERCENTAGE CALCIUM IN SOME VEGETABLE SAMPLES

Vegetable	Sample no.	Magneto-optic method: No. of detns.	Min.	Max.	Av.	Permanganate titration
New Zealand spinach	56	4	0.933	1.02	0.973	
						0.900
	63	4	0.942	1.04	0.994	
Turnip tops	57	5	1.87	2.12	2.01	
						2.04
	55	4	1.96	2.03	2.00	

Since none of the compounds tested affects the determination, it seems probable that this method may be used for the determination of calcium in any type of sample by using appropriate methods of obtaining a calcium

[2] We are indebted to Dr. Fred Allison for furnishing us with the unpublished scale readings of calcium phosphate, namely, 23.20 and 23.52.

phosphate or chloride solution. The size of sample weighed could be reduced to advantage by the use of a micro-balance. Great care is necessary to prevent calcium contamination. The time necessary to make one determination after the stock solution is prepared varies from two to four hours and requires considerable practice and skill in manipulation of the apparatus. This method is recommended for those cases where the amount of calcium is too small to determine by the usual chemical methods.

We wish to express our appreciation to Dr. Allison for the use of his apparatus and for the many courtesies he has extended to us throughout the work.

Summary

A quantitative method for the determination of calcium by the magneto-optic method has been outlined.

The sensitivity of the apparatus to calcium is 3.74×10^{-12} g. Ca/cc. when the minima are read for either phosphate, chloride, sulfate or nitrate. This varies slightly with the observer.

Of these minima, the phosphate is the most satisfactory to read and the chloride is second.

The presence of excess chloride, nitrate, sulfate, phosphate, magnesium, sodium, or ammonium does not affect the results.

Duplicates will check each other and values obtained with permanganate titration within 10%.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS]

THE EFFECT OF AMMONIA ON THE POSITIVE ION EMISSIVITY OF IRON, NICKEL AND PLATINUM

BY A. KEITH BREWER

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In a recent article[1] it was shown that adsorbed gases in certain cases affect the photoelectric threshold of metal surfaces in a manner identical to that occasioned by adsorbed alkali ions. To illustrate, the emission characteristics of iron in 5 mm. of ammonia at 80° are identical to iron 0.02 covered with K^+ ions; on the other hand, ammonia has only a small effect on the emissivity of platinum.

An obvious interpretation of these results is that some of the adsorbed ammonia molecules are dissociated into ions by the electrical forces at the iron surface and that the change in work function is due to the presence of the positive ions so formed. This interpretation is not necessarily the only one, however, since it is within the range of possibility that a layer of

[1] A. Keith Brewer, THIS JOURNAL, **54**, 1888 (1932).

highly polarized molecules adsorbed on the surface could produce the same effect. It is the object of this research to distinguish, in so far as is possible, between these two mechanisms of adsorption.

Apparatus.—The apparatus was essentially the same as that described in the previous communication; a resistance leak of 1.73×10^{10} ohms, made by the S. S. White Dental Manufacturing Company, was substituted for the 10^{11} ohm resistance, since extreme sensitivity was not necessary in the present instance.

The filaments tested were pure iron, nickel and platinum in the ribbon form and a potassium aluminum oxide promoted iron catalyst coated on platinum in the usual manner.[2] The gases were prepared in the manner described before.

Method of Procedure.—All filaments were heated in hydrogen for several hours and then glowed in a vacuum until outgassing practically ceased. Care was taken, however, not to heat the iron catalyst appreciably above redness. The thermionic currents were measured for both ascending and descending temperatures, the latter giving the more consistent results. All thermocouple measurements were checked at high temperatures with an optical pyrometer.

Results

The effect of various pressures of nitrogen, hydrogen, and ammonia on the thermionic emission of positive ions from iron is shown in Fig. 1.

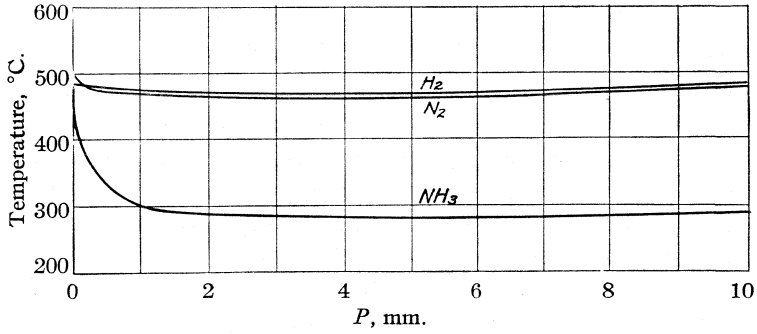

Fig. 1.—The effect of gas pressure on the temperature for equivalent thermionic currents from iron.

These results were taken with a pure iron filament which had been heated to about 800° in a good vacuum for several hours before each series of runs. The data do not represent the point where emissivity becomes detectable but rather the temperature at which the positive ion current was 8×10^{-13} amp. Each gas was studied over the pressure range of 10 cm. to about 10^{-6} mm. No conspicuous effect was observed above 1 cm. except a

[2] C. H. Kunsman, *J. Franklin Inst.*, **204**, 635 (1927).

slight rise in the temperature necessary to obtain the equivalent thermionic current.

The important thing to note is that an equivalent positive ion current can be obtained at 200° lower temperature in the presence of ammonia than in a vacuum; indeed a positive ion emissivity was detected at temperatures as low as 250°. The effect of nitrogen and hydrogen is small, both showing only a slight enhancement of the current over that obtained in a vacuum.

The effect of accelerating voltage on the positive ion emissivity from iron in these three gases at 1 cm. pressure is shown in Fig. 2.

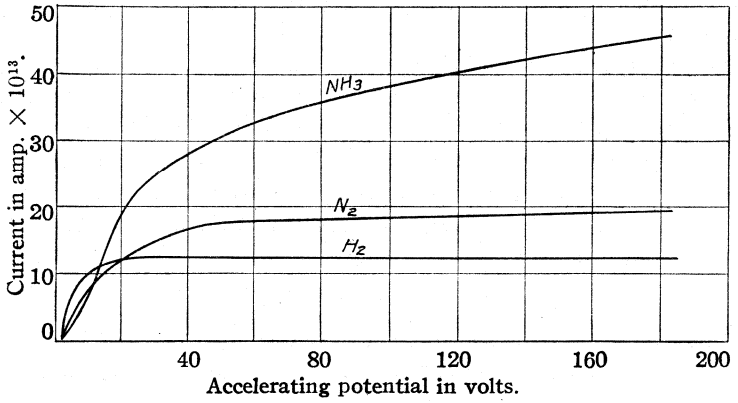

Fig. 2.—Effect of accelerating potential on the thermionic current: iron filament; gas pressure, 1 cm.

The curves for nitrogen and hydrogen were taken at the same temperature, while the ammonia curve was taken at about 200° lower. The curve for hydrogen shows saturation and is identical in shape to that obtained in a vacuum. Nitrogen gives only a partial saturation while ammonia completely fails to saturate. At only slightly higher pressures, the current in ammonia is proportional to the voltage. Thus since saturation is not obtainable with ammonia, the true difference in the relative emissivities of the gases would be greater than that shown in Fig. 1, especially at the higher pressures. Doubtless the failure to saturate is responsible for the flattening out and even turning up of the curves in Fig. 1 above about 5 mm. pressure.

The results obtained with a pure nickel filament are shown in Fig. 3. The accelerating potential was 45 volts, as was the case for iron.

It will be noted that the results for positive ion emission are quite similar to those obtained with iron. The outstanding difference is the lowering of the equivalent temperature for hydrogen, while nitrogen shows only a small effect. Ammonia again has a very pronounced effect on the emissivities, the equivalent temperature being almost as low as for iron.

Curves are included to show the effect of nitrogen and hydrogen on the negative ion, probably electron, emission. It will be noted that nitrogen has only a small effect, while hydrogen lowers the equivalent temperature about 140°. The curve for ammonia can only be approximated due to the rapid decomposition at the higher temperatures. The temperature–current curves for ammonia show a detectable emission current at about 550°, where a decay with time sets in which becomes rapid at 655°; at 700° the electron emissivity almost entirely disappears. It is interesting to note that this is the temperature range over which Kunsman[3] found the rate of decomposition of ammonia on nickel to be appreciable.

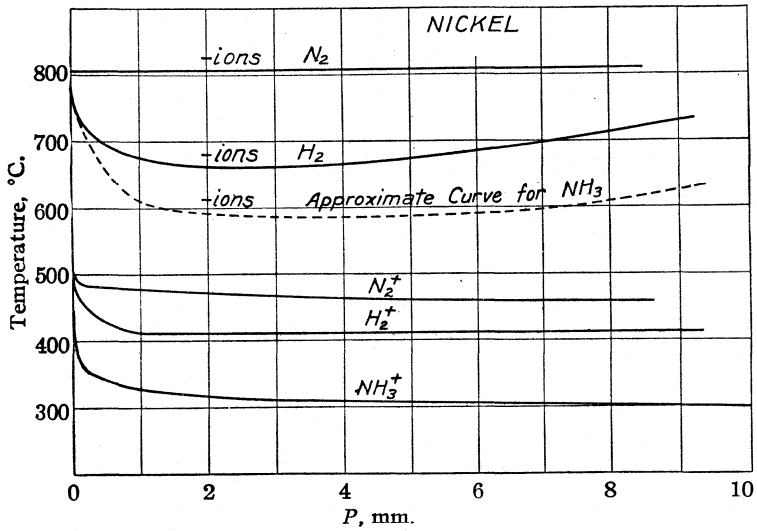

Fig. 3.—Effect of gas pressure on the thermionic emission of positive and negative ions from nickel.

The results obtained with platinum under conditions identical to those described for iron and nickel are shown in Fig. 4.

The salient features are that nitrogen has little or no effect on the positive ion emissivity, while hydrogen lowers the equivalent temperature more than 100°. The effect of ammonia on the positive ion emission was very similar to its effect on the electron emission described for nickel. A small emission current was detected at 325°, which increased only seven-fold at 500°. From 500 to 600° the current increased only two-fold, but from this point on the increase was characteristic of thermionic emission. At all temperatures below 600° the positive ion current in ammonia was not constant but decreased with time.

The data showing the effect of gases on the electron emission from plati-

[3] C. H. Kunsman, THIS JOURNAL, 50, 2100 (1928).

num were unsatisfactory due to the fact that the equivalent emission temperatures fluctuated between such wide limits. In general, however,

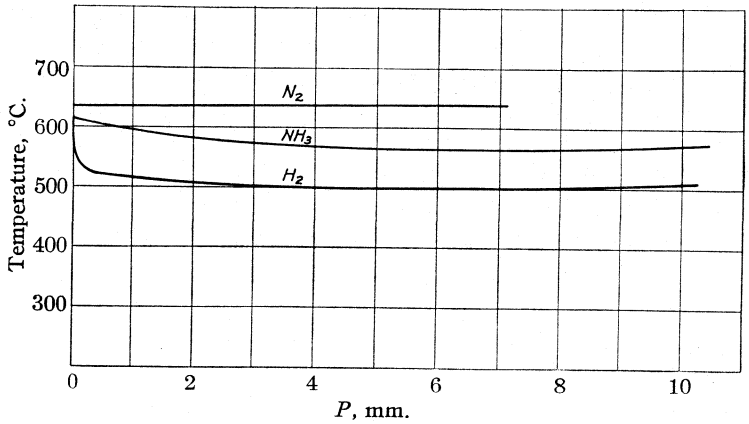

Fig. 4.—Effect of gas pressure on the temperature for equivalent thermionic currents from platinum.

nitrogen decreased the emissivity while hydrogen and ammonia showed an enhancement.

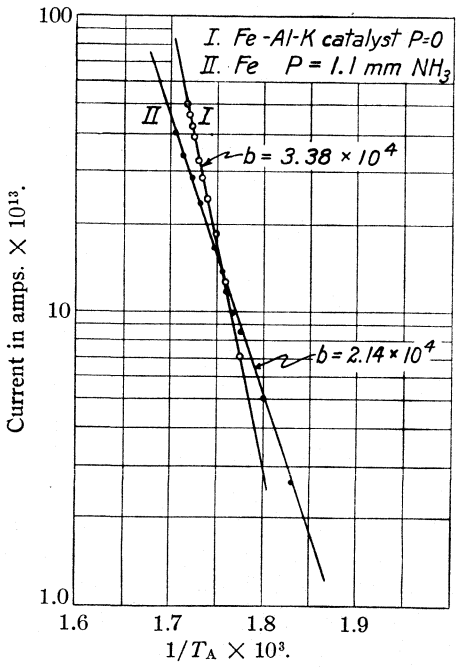

Fig. 5.—Emissivity curves for iron in ammonia, and for an Fe-Al-K catalyst.

A comparison of the positive ion emissivity of pure iron in ammonia with a potassium impregnated iron catalyst in a vacuum is given in Fig. 5.

The catalyst was No. 922, the photoelectric properties of which were described in a previous communication;[4] it was shown to have an appreciable potassium content at the surface. This catalyst was chosen particularly because of its excellent emission properties for positive ions.

The effect of the ammonia pressure for all pressures above 0.1 mm. on the positive ion work function was negligible. The emissivity at all pressures followed very closely, the Richardson equation $i = AT^{1/2}e^{-b/T}$ the value of b varying between 2.08×10^4 and 2.17×10^4.

[4] A. Keith Brewer, This Journal, **53**, 74 (1931).

The interesting thing to note is that pure iron in ammonia is a slightly better emitter of positive ions at low temperature than is iron impregnated with potassium. The temperature coefficient for the catalyst is somewhat higher, however, so it is the better emitter at high temperatures. It should be recalled that special care was taken in the preparation of the catalyst filament so that its emissivity would not be impaired.

Discussion of Results

The presence of positive ions adsorbed on a surface (adions) can be detected either by the lowering of the electron work function or by an enhancement of the positive thermionic current. This is clearly illustrated in the study of platinum coated glass filaments,[5] where it was shown that the electrolysis of K^+ ions to the emitting surface resulted in an enhancement of the thermionic and photoelectric emission of electrons as well as the thermionic emission of positive ions.

The mechanism by which adions lower the electron work function has been discussed in detail for photoelectric emission.[1] This mechanism, which is essentially the same for thermionic emission, is that adsorbed ions possess the properties of a positive grid placed about one molecular diameter from the surface, the effective potential of the grid being determined by the concentration of the ions. The work ϕ_0 expressed in volts which an electron must do to escape from a pure surface is now decreased by ϕ_G, the potential of the grid, so the observed work ϕ will be

$$\phi^- = \phi_0^- - \phi_G$$

This accounts for the results given in Fig. 3, where the equivalent temperature for the negative thermionic current is materially lowered by hydrogen and ammonia. The temperature lowering is due to a decrease in the work necessary to remove an electron brought about by the presence of positive ions adsorbed on the surface. These results are similar to those obtained for the photoelectric emission of electrons, where the lowering of the work function indicated the presence of adsorbed positive ions.

The detection of the presence of positive adions by the enhancement of the positive ion current can be seen from the following discussion. Consider a surface on which the concentration of ions is n per sq. cm. Let the velocity component of the ions be u, v and w, where w is normal to the surface. Since only the w component aids in the escape of the ions, and since due to the work function of the surface only those ions having a velocity component between w_0 and ∞ can overcome the surface forces, the number of ions leaving 1 sq. cm. of surface per second is given by[5]

$$N = n\sqrt{\frac{kT}{2\pi m}}\, e^{-mw_0^2/2kT}$$

[5] A. Keith Brewer, *J. Phys. Chem.*, **32**, 1006 (1928)

where T is the absolute temperature, m the mass of the ion and k is the Boltzmann constant. Since $1/2\, mw_0^2 = e\phi$, the equation can be simplified to the form

$$i = n\sqrt{\frac{kT}{2\pi m}}\, e^{-e\phi/kT} = AT^{1/2}\, e^{-b/T}$$

where $i = N$ ions per second and b is Richardson's work function. From this it follows that i increases directly with n. It is not a proportionality, however, since the positive ion grid while lowering the work function for electrons raises it for positive ions, *i. e.*, $\phi^+ = \phi_0^+ + \phi_G$, where ϕ^+ is again the observed work function in volts. ϕ_G will not be as effective for an ion adsorbed on the surface, however, as for an ion coming from within the metal, since the apparent distance of the ion grid from the surface is no greater than the dimensions of the ion; hence the ion will not necessarily pass through the entire grid field.

In practice the detection of gas ions on a metallic surface by an increase in the positive ion current is complicated by the fact that positive ions are always given off from hot surfaces even in the best vacuum and after a thorough baking out. These inherent ions, consisting of dissolved alkali, adsorbed gases and charged atoms of the metal itself, can be detected by a sensitive measuring apparatus, similar to that used in the present case, at temperatures from 450 to 600°, depending on the metal.

For the reasons just given, it is impossible to say with certainty whether positive adions exist in cases where the gas has only a slight effect on the emissivity of the metal, for instance, hydrogen on iron and nitrogen on platinum. In cases like hydrogen on platinum and nickel, and ammonia on iron and nickel, however, the enhancement is so great that it seems impossible to dispute the presence of positive adions.

The presence of adions from the adsorbed gas is again brought out by the temperatures for the two curves in Fig. 5; the emissivity is shown to be almost identical for ammonia on iron and for potassium on iron. The photoelectric studies[4] of catalyst 922 show it to possess the properties of a surface two per cent. covered with K^+ ions. Using this as a basis of comparison it might be assumed that two per cent. of the ammonia molecules of the surface are ionized at any given instant when the ammonia pressure is above 0.1 mm. Since i increases with n if the change in ϕ_G with n is neglected, it follows from a comparison with ammonia that the concentration of hydrogen ions on nickel is about one per cent. of the total adsorbed molecules, assuming the surface to be completely covered with adsorbed hydrogen.

The fact that iron in an atmosphere of ammonia gives off positive ions as copiously as do the best of potassium impregnated iron emitters, raises the question as to whether the ions come from the ammonia which has actually dissolved in the iron or from the adsorbed film of ammonia

on the iron surface. An idea of the point of exodus of the ions can be had from the work function of the surface, *i. e.*, from the value of b.

b is a measure of the work done in removing an ion from some point near the surface to a point outside the sphere of electrostatic image attraction (10^{-4} cm. from the surface). The electrostatic image attraction is given by $F = e^2/4x^2$ where x is the distance of the ion from the surface. The work done in removing an ion from the plane $x = 0$ would be infinite, but owing to the finite dimensions of the ion there is always a lower limit to x; also the intrinsic force at the surface is operative at distances of less than one molecular diameter. The work done in removing an ion from a point at distance d from the surface to a point outside the range of surface forces is given by

$$w = (1/4)\int_d^\infty (e^2/x^2)\,dx = e^2/4d$$

Since $w = bk$ where k is Boltzmann's constant, it is possible to calculate d when b is known, by the equation $d = e^2/4bk$. The value of $b = 2.1 \times 10^4$ obtained for ammonia on iron gives d to be 1.9×10^{-8} cm. This value assumes that the image force is the only one that is appreciable at distance d and also that none of the work represented by b goes into dissociation of the ammonia molecule into ions.

The x-ray values for the diameter of NH_3 are 3.4×10^{-8} cm., while the kinetic theory value is 4×10^{-8} cm. If it is assumed that the positive charge is located at the outermost point on the ion, 4×10^{-8} cm. from the surface, then it follows that b must represent work other than that of removing the ion from the surface against image forces. Since ϕ_G is small for the removal of a charge from a point d cm. from the surface when d is of the order of atomic diameter, it is reasonable to assume that the excess energy may have gone largely into completing the dissociation of the ammonia. On the other hand, if it is assumed that the positive charge is located near the center of the ammonia molecule, which is the natural assumption to make on the basis of a nucleus hypothesis of atomic structure, then it follows, since d is almost exactly one-half the molecular diameter, that the ammonia is largely dissociated by the surface forces and that the most of the work done by thermal agitation is the removal of the ion from the surface. This latter interpretation, rather than the former, is in agreement with the photoelectric results obtained for ammonia on iron, wherein it was found that the concentration of positive ions on the surface decreased rapidly with rising temperature.

The values of b obtained for nitrogen and hydrogen on iron, however, suggest that part of the work done in removing an ion from the surface may be consumed in completing the dissociation of the gas. For instance, the values of b for hydrogen and nitrogen are 3.45×10^4 and 3.66×10^4, respectively; there is but little change from 1 cm. to atmospheric pressure.

The values of d computed from these quantities are 1.2×10^{-8} and 1.16×10^{-8} cm. for H_2^+ and N_2^+. It must be assumed therefore, for nitrogen, since d is less than the ion radius, that either thermal energy is consumed in completing the dissociation or the ions come from the gas which has dissolved in the iron. It is not possible at present to distinguish between these two suppositions.

The voltage–current curves shown in Fig. 2 are also indicative of the presence of adions on the surface. The fact that ϕ_G due to the adions is not constant over the surface, but is highest near the ions and diminishes to a small value at distances greater than 10 molecular radii removed, causes the effective work function of the surface to vary from point to point over the surface. This variation found on composite surfaces is always evidenced by a failure to obtain saturation.

Application to Surface Catalysis.—The photoelectric studies of the effect of adsorbed ions[1,6] has shown that the force field about positive adions is appreciable at distances ten times the ion radius. Recently Becker[7] has obtained an identical value from thermionic studies for the dimensions of this force field. Becker has shown further that the evaporation of neutral atoms is effected by the electrical fields at the surface and that the net force on an atom is much the same as on a negatively charged particle, the evaporation curves obtained for atoms being similar to those obtained for electrons. It seems probable that force fields of this type (combined image, intrinsic and adion) may be the basis of activated adsorption described by Taylor[8] and by Benton.[9]

As far as the mechanism of catalysis is concerned, the interpretation is primarily the same as that suggested from the photoelectric studies. If there is any connection between the dissociation of the adsorbed gas into ions and the mechanism of chemical action, then the data indicate that iron and nickel are excellent catalysts for the decomposition of ammonia, while platinum is comparatively poor. This is in agreement with the results of Kunsman on the decomposition of ammonia on these metals. Further, the data suggest that nickel and platinum might be excellent hydrogenation catalysts, which again is in agreement with experience. In brief it seems probable that a gas which appears to be appreciably dissociated into ions on a given metal, as is evidenced by a lowering of the work function for electrons or by an enhancement of the positive ion current, might be catalyzed by that surface in the case of reactions initiated by the gas in question. An exception to this may arise when one of the other gases present is selectively adsorbed; this is illustrated by the inhibition of the

[6] A. Keith Brewer, *Phys. Rev.*, **38,** 401 (1931).
[7] J. A. Becker, *Trans. Faraday Soc.*, **28,** 148 (1932).
[8] Taylor, *Chem. Rev.*, **9,** 1 (1931).
[9] Benton and Ulrich, THIS JOURNAL, **54,** 1820 (1932).

ionization of ammonia on platinum due to the hydrogen liberated from the decomposed ammonia.

These results are offered simply as an added proof of the contention that gases are dissociated into ions on metallic surfaces. If the present interpretation is correct, this dissociation as well as the types of surface forces outlined here must be taken into consideration in formulating a mechanism for adsorption and for surface catalysis.

The writer wishes to acknowledge the interest Dr. C. H. Kunsman has taken in this research.

Summary

Results are given showing the effect of nitrogen, hydrogen and ammonia on the thermionic emission of positive ions from iron, nickel and platinum.

The surprising fact noted is that at low temperatures a pure iron filament in ammonia emits positive ions more copiously than does even the best of potassium impregnated positive ion sources. Nickel also is only slightly less efficient than iron but the positive ion current from platinum is not materially increased.

Hydrogen exhibits an appreciable enhancing effect on platinum and nickel, for both positive and negative thermions. Nitrogen, however, shows only a slight effect on iron and nickel, and none on platinum.

The mechanism by which positive adions lower the work function for electrons and enhance the emissivity for positive ions is described.

Work function values for ammonia on iron indicate that the ion is emitted from a point 1.9×10^{-8} cm. from the surface. Since this distance is approximately equal to the radius of the ammonia molecule, it is interpreted as indicating that ions before emission resided on the surface in the completely dissociated state.

The bearing of these results on adsorption and surface catalysis is suggested.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 20]

A DISTRIBUTION METHOD FOR THE DETERMINATION OF THE DISSOCIATION PRESSURES OF SALT AMMONIATES

BY RALPH P. SEWARD

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The difficulties attending the measurement of the dissociation pressures of hydrates by static and dynamic methods have been discussed by various investigators.[1] The same difficulties are encountered in measuring the dissociation pressures of ammoniates by similar methods. It seemed, therefore, worth while to investigate the possibilities of an indirect method, analogous to the one first suggested by Linebarger and since employed by others.[1a,2] This method consists of shaking the dissociating hydrates with an inert solvent in which the solid phases are practically insoluble until equilibrium is reached. The concentration of water in the solvent is then determined and from the previously determined relation between the water content of the liquid and the vapor pressure of water in equilibrium with it the dissociation pressures of the hydrate are calculated.

Chloroform was chosen as the solvent since it combines high solvent power for ammonia with very slight solvent power toward inorganic salts and their ammoniates. The salt chosen for the investigation was zinc chloride, since it forms a well-defined series of ammoniates whose properties are quite well known and the magnitudes of their dissociation pressures lend themselves to ready measurement.

The solubility of ammonia gas in chloroform at several pressures at 25° was measured since the values are required in calculating the dissociation pressures and no direct measurements appear in the literature. Biltz and Messerknecht[3] measured, by the usual static methods, the pressures of ammonia gas in equilibrium with solid ammoniates of zinc chloride of different compositions. Since they made no measurements at 25°, which was decided on as a desirable temperature for this work, static measurements on this system have been made for comparison with those by the indirect method.

Possible advantages of the proposed method over the static method are: (1) attainment of equilibrium in a shorter time due to the shaking up of the materials; (2) the measurements unlike those by the static method should be independent of the presence of adsorbed or combined gases other than ammonia. To investigate the last question some measure-

[1] (a) R. E. Wilson, THIS JOURNAL, **43**, 704 (1921); (b) W. C. Schumb, *ibid.*, **45**, 342 (1923).

[2] Linebarger, *Z. physik. Chem.*, **13**, 500 (1894); Foote and Scholes, THIS JOURNAL, **33**, 1309 (1911); Noyes and Westbrook, *ibid.*, **43**, 726 (1921).

[3] Biltz and Messerknecht, *Z. anorg. allgem. Chem.*, **129**, 161 (1923).

ments both static and by the indirect method have been made on a hydrated ammoniate, $ZnCl_2 \cdot 4NH_3 \cdot H_2O$, prepared in aqueous solution; (3) an additional advantage, of particular value where only one or two measurements are desired, is that the indirect method does not require the construction of any special apparatus such as manometers, McLeod gage, etc., required by the static method.

Solubility of Ammonia in Chloroform

The chloroform used in the measurements was prepared from U. S. P. chloroform. This material contains from five to seven tenths of one per cent. by weight of alcohol, which is the principal impurity. The alcohol may be removed readily by shaking with concentrated sulfuric acid or allowing it to stand over anhydrous zinc chloride. After removing the alcohol, the chloroform was washed with water and allowed to stand over anhydrous potassium carbonate for two days to dry it. Pure chloroform decomposes, or is oxidized readily, on standing even in a dark glass bottle. A white precipitate appears on the addition of ammonia gas to the contaminated product. No consistent values for the solubility could be obtained with this material. For this reason it was considered desirable to have a small amount of alcohol present as recommended by Baskerville and Hamor.[4] The measurements reported were made on chloroform to which one tenth of one per cent. of alcohol had been added. It is essential that the alcohol content be known as experiments with chloroform containing varying amounts of alcohol showed that the addition of one per cent. of alcohol increases the solubility of ammonia in chloroform by about twenty per cent.

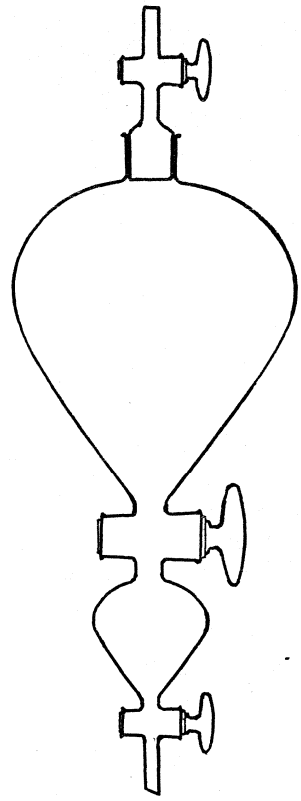

Fig. 1.

The solubilities were measured by determining the ammonia content of chloroform solutions and of the vapor phases in equilibrium with them. The apparatus used is shown in Fig. 1. The upper bulb is of about one liter volume and the lower one 50 cc. In making the measurements about 25 cc. of a saturated chloroform–ammonia solution was poured into the apparatus, which was then placed in a thermostat at 25° with the upper and lower stopcocks closed and the middle one open. After standing awhile to reach the temperature of the thermostat, the bulbs were inverted several times, allowing the liquid to flow back and forth between the two compartments, to ensure uniform distribution of the ammonia throughout the gaseous phase. The apparatus was then allowed to stand upright in the thermostat for a half hour to ensure complete draining of the liquid into the smaller bulb. The connecting stopcock was then closed and the apparatus removed from the thermostat. The ammonia in the upper bulb of known volume was then determined by allowing an excess of standardized sulfuric acid to flow in to neutralize all the ammonia and the excess acid determined

[4] Baskerville and Hamor, *J. Ind. Eng. Chem.*, **4**, 364 (1912).

by titration. The ammonia content of the liquid was determined by allowing it to flow out into excess acid and the excess determined by titration, without removing the chloroform, using methyl orange as the indicator. The volume of the liquid was calculated from its weight and known density.

Table I gives the results obtained using a series of solutions of varying concentration, produced by diluting the original saturated solution, C_1 is the concentration of ammonia in the liquid phase in moles per liter of solution, C_2 the concentration of ammonia in the vapor phase, $R = C_1/C_2$ is the distribution ratio, and p is the partial pressure of ammonia, in millimeters of mercury, calculated from C_2 assuming Dalton's law to hold in the gaseous phase and neglecting the deviations of ammonia gas from the perfect gas law. The decomposition pressures calculated on this basis will be in error to the amounts neglected here, but they are probably not great for decomposition pressures well below one atmosphere. It is seen that the distribution ratio R increases as the concentrations decrease but apparently approaches a constant value 52.0 ± 0.3, within the limits of experimental error, at lower concentrations.

TABLE I

SOLUBILITY OF AMMONIA IN CHLOROFORM AT 25°

C_1	C_2	R	p	C_1	C_2	R	p
1.105	0.0244	45.2	453.5	0.246	0.00474	51.9	88.1
0.851	.0175	48.7	325.4	.1157	.002215	52.3	41.2
.661	.0132	50.1	245.4	.0888	.001716	51.8	31.9
.423	.00814	52.0	151.3	.0393	.000756	52.0	14.0
.392	.00749	52.3	139.2				

The specific gravity of the chloroform used was determined at 25°, using a pycnometer, as 1.480 ± 0.002. The specific gravity of the solutions required in calculating the concentrations does not differ greatly from that of the pure solvent. The specific gravity of a solution containing 1.315 moles of ammonia per liter was found to be 1.450 and the small corrections required were obtained by assuming a linear relation between the specific gravity and ammonia concentration.

Pressure Measurements on the System $ZnCl_2$–NH_3.—Since the object of these measurements was to compare the results obtained by the static and indirect methods, "C. P." anhydrous zinc chloride was used without further purification.

In making the static measurements a weighed amount of the anhydrous zinc chloride was placed in a small glass-stoppered flask and ammonia gas passed in while the flask was kept cool until no further gain in weight was observed. Approximately six moles of ammonia per mole of zinc chloride are absorbed in this way. The flask was then placed in the thermostat and connected through a ground glass joint to a mercury manometer and vacuum pump. After pumping off ammonia, which was

absorbed in concentrated sulfuric acid, from the solid for a short time the tube leading to the pump was closed and the flask allowed to stand until the manometer indicated that equilibrium was reached. The other side of the manometer was connected to the pump and the thoroughness of evacuation of this arm checked by a McLeod gage. After making a pressure reading the flask was detached and weighed. The composition of the solid could then be calculated. By pumping off more ammonia and repeating the above procedure a series of pressure measurements for solid ammoniates of different composition was obtained.

The pressures found and the composition of the corresponding ammoniates are given in Table II.

TABLE II

DECOMPOSITION PRESSURES OF ZINC CHLORIDE AMMONIATES BY THE STATIC METHOD

No.	p, mm.	moles NH_3/moles $ZnCl_2$	No.	p, mm.	moles NH_3/moles $ZnCl_2$
1	122.5	5.85	9	17.8	3.60
2	121.0	5.65	10	17.7	3.40
3	118.3	5.40	11	17.2	2.62
4	118.3	4.95	12	17.2	2.21
5	116.5	4.40	13	16.0	2.05
6	114.5	4.05	14	11.5	1.90
7	17.5	3.95	15	6.0	1.88
8	17.8	3.87	16	1.2	1.82

A similar series of measurements was made by the indirect method. The procedure followed consisted of first making up a zinc ammoniate of known composition by adding ammonia gas to a known weight of solid anhydrous zinc chloride and weighing the product. Equilibrium was secured by adding a measured volume of chloroform to the solid in a glass-stoppered Erlenmeyer flask, placing in the thermostat at 25° and shaking at frequent intervals for one to two hours. Experiment showed that this time was sufficient. A sample of the liquid in the flask was then forced through a filter into a 25-cc. pipet by means of air pressure and the ammonia content determined by titrating with sulfuric acid of suitable strength. The equilibrium pressure was then calculated by means of the previously determined relation between the ammonia content of the solutions and the partial pressures of ammonia in equilibrium with them. The composition of the remaining solid was calculated by subtracting the weight of ammonia extracted by the several additions of chloroform from the amount present at the start. This calculation is not as exact as that possible in the static method through direct weighing of the solid since a small but unknown amount (probably not more than 2% of that extracted) of ammonia was lost in the vapor phase on each addition of fresh chloroform to the solid.

The results obtained from a series of measurements are given in Table III.

TABLE III

DECOMPOSITION PRESSURES OF ZINC CHLORIDE AMMONIATES AT 25° BY THE INDIRECT METHOD

No.	Concn. of NH_3 in liquid, moles/liter	p, mm. calcd.	Moles NH_3/moles $ZnCl_2$	No.	Concn. of NH_3 in liquid, moles/liter	p, mm. (calcd.)	Moles NH_3/moles $ZnCl_2$
1	0.338	121.0	5.25	10	0.0504	18.0	4.01
2	.331	118.5	5.09	11	.0479	17.2	3.03
3	.321	115.0	4.92	12	.0476	17.1	2.89
4	.325	116.3	4.74	13	.0462	16.6	2.74
5	.331	118.5	4.57	14	.0475	17.1	2.69
6	.324	116.0	4.40	15	.0421	15.2	2.45
7	.312	111.5	4.23	16	.0402	14.9	2.30
8	.274	97.3	4.02	17	.0180	6.6	2.07
9	.180	63.9	4.02				

Determination No. 10 in Table III is the mean of six consecutive determinations none of the values varying from the mean by more than one

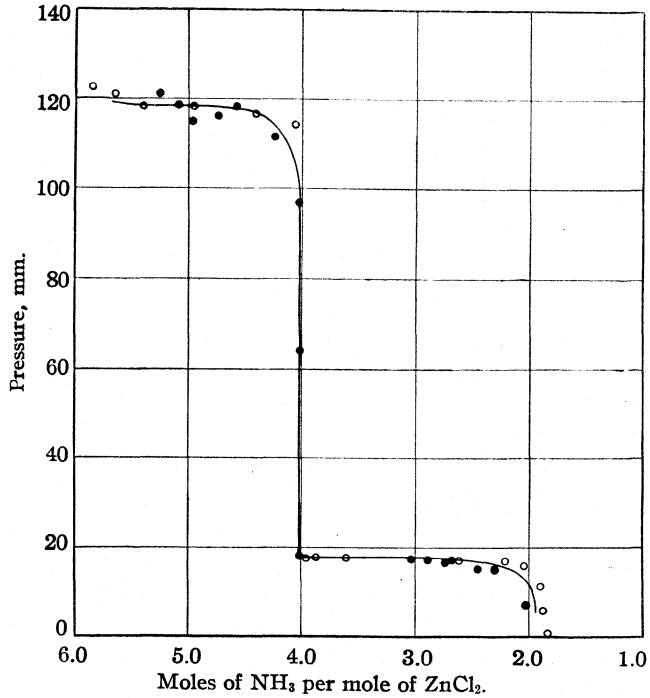

Fig. 2.—Dissociation pressures of zinc chloride ammoniates: ○, static; ●, indirect.

millimeter. Since the amount of ammonia extracted at the lower pressure is small, the composition of the solid did not change much during these determinations. For the following values another sample of ammoniate of smaller weight was used.

For ready comparison of the results obtained by the two methods the pressures and corresponding compositions have been plotted in Fig. 2. Inspection of the figure shows that the results obtained by the two methods are in good agreement and indicate an equilibrium pressure for the reaction $ZnCl_2 \cdot 6NH_3 \rightleftharpoons ZnCl_2 \cdot 4NH_3 + 2NH_3$ of about 118 mm. at 25° and for the reaction $ZnCl_2 \cdot 4NH_3 \rightleftharpoons ZnCl_2 \cdot 2NH_3 + 2NH_3$ a pressure of approximately 17.5 mm.

Time Required to Reach Equilibrium.—In many cases, especially at low pressures, the time required in reaching equilibrium by the static method is many hours. Since in the indirect method the sample can be continuously shaken, it was thought that it might be possible to reach equilibrium in a shorter time. The time required by the two methods was compared in the following manner. After pumping off ammonia for several minutes from a sample of a solid ammoniate on which several pressure measurements had already been made with the apparatus previously described, the stopcock to the pump was closed and the pressure in the manometer read at intervals. The values are recorded in Table IV. The composition of the ammoniate at this point was $ZnCl_2 \cdot 3.75NH_3$.

TABLE IV

TIME REQUIRED TO REACH EQUILIBRIUM BY THE STATIC METHOD

Time	p, mm.
20 minutes	11.5
45 minutes	13.0
2 hrs., 45 minutes	15.5
3 hrs., 45 minutes	15.6
5 hrs., 15 minutes	15.8
7 hrs., 45 minutes	15.9
24 hrs.	17.7
28 hrs.	17.7

TABLE V

TIME REQUIRED TO REACH EQUILIBRIUM BY THE INDIRECT METHOD

Time of rotation	p, mm.
15 minutes	16.65
30 minutes	17.00
45 minutes	17.45
60 minutes	17.61
90 minutes	17.42

It may be seen that more than eight hours was required to reach equilibrium. Indirect measurements were then made on the same sample; it was removed to a glass-stoppered bottle, chloroform added, and rotated in the thermostat for fifteen minutes. The chloroform was then removed and its ammonia content found. Fresh chloroform was then added and the rotation continued for a longer time. Table V gives the pressures found for different times of rotation.

These values indicate that equilibrium was reached in less than one hour of rotation.

Effect of Gases Other than Ammonia.—The values obtained by the indirect method should, unlike the static method, be independent of the presence of other gases, either adsorbed or combined, except for the amounts which their presence may affect the solubility of ammonia in chloroform. Measurements were made on a hydrated ammoniate, pre-

pared in aqueous solution, to test this question. This product was prepared according to the method of Divers[5] by adding solid zinc chloride to 14 *N* ammonium hydroxide, the solution being kept cool and fresh additions of solid made until the solution was nearly saturated. Ammonia gas was then passed through the solution until a considerable amount of solid appeared. This was redissolved by warming and when the solution was cooled well-defined crystals appeared. The liquid was drained from the crystals and they were washed with alcohol and ether. Part of the crystals were then used for the static measurements and the rest for the indirect measurements.

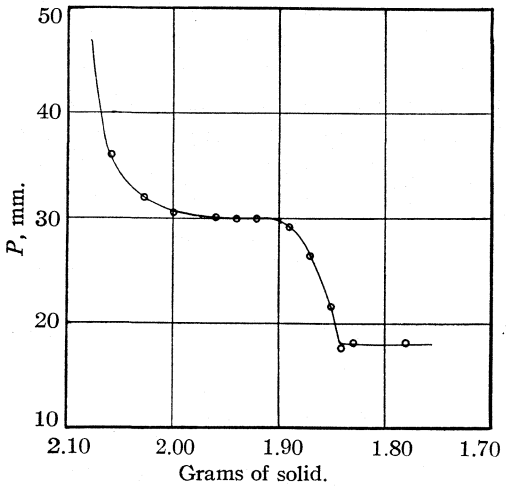

Fig. 3.—Dissociation pressures of hydrated ammoniates.

Table VI gives the pressure measurements recorded by the manometer as the solid decomposed. Since the composition of the solid was unknown the weight of the sample remaining is given so the decomposition may be shown graphically. This is done in Fig. 3.

TABLE VI

DISSOCIATION PRESSURES OF A HYDRATED ZINC CHLORIDE AMMONIATE BY THE STATIC METHOD

No.	*p*, mm.	Solid, g.	No.	*p*, mm.	Solid, g.
1	167	2.19	8	30.0	1.92
2	68.5	2.09	9	29.1	1.89
3	36.0	2.06	10	26.5	1.87
4	32.0	2.03	11	21.7	1.85
5	30.5	2.00	12	17.6	1.84
6	30.1	1.96	13	18.2	1.83
7	30.0	1.94	14	18.2	1.78

Several extractions were made with chloroform for the hydrated ammoniate. The values obtained are given in Table VII.

TABLE VII

DECOMPOSITION PRESSURES OF A HYDRATED ZINC CHLORIDE AMMONIATE BY THE INDIRECT METHOD

No.	1	2	3	4	5	6	7
p, mm.	23.3	20.6	19.6	19.2	18.7	18.6	18.7

[5] Divers, *Chem. News*, **18**, 13 (1868).

Figure 3 shows that by the static method a well-defined region of constant pressure, about 30 mm., exists as the decomposition progresses. This does not appear in Fig. 2 as the unhydrated ammoniate is decomposed.

This apparently monovariant system may be explained by assuming decomposition to proceed according to the equations

$$ZnCl_2 \cdot 4NH_3 \cdot H_2O \rightleftharpoons ZnCl_2 \cdot 4NH_3 + H_2O$$
$$ZnCl_2 \cdot 4NH_3 \rightleftharpoons ZnCl_2 \cdot 2NH_3 + 2NH_3$$

and the 30 mm. pressure to be the sum of the ammonia and water vapor partial pressures. It may also be noted that in the last points the pressure has fallen to the normal value for the decomposition of the unhydrated $ZnCl_2 \cdot 4NH_3$, approximately 18 mm. This apparently corresponds to the disappearance of the hydrated ammoniate. Table VII shows that by the indirect method the values fall off at once to a value in good agreement with the dissociation pressure of the anhydrous $ZnCl_2 \cdot 4NH_3$. The value is slightly high, however, perhaps due to an increase in the solubility of ammonia in the chloroform caused by the presence of water or alcohol from the solid. It seems reasonable, therefore, to attribute the difference between 30 mm. and 18 mm., or approximately 12 mm., to the partial pressure of water vapor produced by decomposition of the hydrated ammoniate.

Divers gives the formula $ZnCl_2 \cdot 5NH_3 \cdot H_2O$ to the product obtained by the method described. The fact that the ammonia pressure measured by the indirect method is in good agreement with that of $ZnCl_2 \cdot 4NH_3$ and not a much higher value seems good evidence that the formula $ZnCl_2 \cdot 4NH_3 \cdot H_2O$ as given by other investigators for the compound prepared by similar methods is more likely.[6]

Summary

1. An indirect method for the measurement of the dissociation pressures of ammoniates analogous to that of Linebarger for hydrates has been developed.

2. Dissociation pressures of salt ammoniates in good agreement with those obtained by the static method may be obtained by shaking the solid ammoniates with chloroform and determining the ammonia content of the chloroform solution obtained.

3. The solubility of ammonia in chloroform at 25° has been measured.

4. Measurements on a hydrated ammoniate indicate that a dissociation pressure of ammonia can be measured by the indirect method in the presence of another volatile dissociation product.

CAMBRIDGE, MASSACHUSETTS

[6] Thomas, *Ber.*, **20**, 743 (1887); Kane, *Ann. chim. phys.*, [2] **72**, 290 (1839).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RATE OF REACTION BETWEEN CHLORATE AND SULFUR DIOXIDE IN ACID SOLUTION

BY A. C. NIXON AND K. B. KRAUSKOPF

RECEIVED JULY 8, 1932 PUBLISHED DECEMBER 13, 1932

The rate of reaction between sulfurous acid and iodate has been the subject of extensive investigations.[1] At the suggestion of Professor William C. Bray, we undertook a study of the analogous reaction

$$ClO_3^- + 3H_2SO_3 \longrightarrow Cl^- + 3SO_4^= + 6H^+$$

Experimental

Rate determinations were made at three different acid concentrations, and the concentration of each reactant was varied four-fold at each acid strength. In all experiments the reaction mixture was kept at 0°.

All reagents used were standard C. P. chemicals. The potassium chlorate had been previously recrystallized to free it from all traces of bromate and iodate. The sulfurous acid solutions were made by diluting a saturated solution of sulfur dioxide. Different acid strengths were obtained by adding sulfuric acid.

The reaction was followed by pipetting samples at appropriate intervals into excess of 0.1 *N* iodine solution. The iodine stopped the reaction by removing sulfur dioxide, and the excess was titrated with 0.025 *N* thiosulfate. In order to find the original concentration of sulfur dioxide, a blank determination was made concurrently with each run on a solution containing no chlorate but otherwise identical with the reaction mixture. Titrations made on the blanks at the beginning and end of each run indicate that the experimental error due to volatility of sulfur dioxide cannot amount to more than 0.5%. Chlorate concentrations were determined from end-point titrations in runs with excess sulfur dioxide. Preliminary experiments showed that ClO_3^- did not interfere with the thiosulfate titrations at the acid concentrations used.

Results and Discussion.—Values of k for the assumed rate law

$$-\frac{d(ClO_3^-)}{dt} = k(H_2SO_3)(ClO_3^-) \qquad (1)$$

were obtained by the usual method of plotting against time the logarithm of the concentration of the reactant present in smaller amount. At any time the slope of this curve multiplied by 2.303 and divided by the concentration of the reactant in excess gave the value of k. For the plots of log ΣSO_2 against time it was necessary further to divide the observed slope by 3 and to multiply by the ratio $H_2SO_3/\Sigma SO_2$. The concentrations of

[1] (a) Skrabal, *Z. Electrochem.*, **28**, 224 (1922); this reference contains a complete bibliography of previous work; (b) Skrabal, *ibid.*, **30**, 109 (1924); (c) Skrabal and Zahorka, *ibid.*, **33**, 42 (1927).

sulfurous acid were calculated from the equilibrium constants of H_2SO_3 and HSO_4^-, which were found by interpolation from the data of Noyes and Sherrill.[2] A typical calculation for a single run is summarized in Table I, and in Table II the average k's for all runs are tabulated. All values of k are given in liters per mole per minute.

TABLE I

MEASUREMENTS IN 0.2 *N* SULFURIC ACID AT $\mu = 0.165$

Time, min.	ΣSO_2, *M*	ClO_3^-, *M*	$H_2SO_3/\Sigma SO_2$	Slope	*k*
0	0.01310	0.0160	0.878		
2	.00902	.0146	.880	0.056	2.59
3.5	.00735	.0141	.881	.054	2.59
5	.00600	.0136	.883	.0525	2.62
7.5	.00443	.0131	.882	.050	2.58
10	.00343	.0127	.882	.048	2.56
12.5	.00262	.0125	.881	.0465	2.51
15	.00200	.0123	.881	.046	2.53
17.5	.00151	.0121	.880	.0455	2.54
				Mean	2.57

TABLE II

ClO_3^-, *M*	ΣSO_2, *M*	$\frac{(HSO_3^-)(H^+)}{(H_2SO_3)}$	H_2SO_4, *M*	$\frac{(SO_4^{--})(H^+)}{(HSO_4^-)}$	Mean μ	Mean *k*	
0.0160	0.0135					2.73	
.0160	.00673	0.017	0.25	0.04	0.033	2.82	2.81
.0040	.0505					2.89	
.0160	.0131					2.57	
		.017	.1	.03	.165		2.57
.0040	.0522					2.57	
.0260	.0149					2.19	
		.016	...	...	.04		2.21
.0065	.0595					2.23	

$\Sigma SO_2 = H_2SO_3 + HSO_3^- =$ total titratable SO_2.

The constancy of the k's is ample evidence for the correctness of the above bimolecular rate law (equation 1): the largest deviation of any individual k from the average at the same ionic strength is 0.12.

The values of k obtained in the solutions containing sulfuric acid differ from the values obtained in the runs without acid by an amount greater than experimental error will account for. If the difference between the two higher values of k is assumed to be the variation with ionic strength which, according to Brönsted's theory, is allowable for reactions of this type, then extrapolation to zero ionic strength gives 2.5 ± 0.1 as the value of k. For the runs without acid an average value is 2.2 ± 0.1. It appears impossible at present to decide between these two figures. The latter value could be raised to 2.5 by a 30% increase in the dissociation constant

[2] Noyes and Sherrill, THIS JOURNAL, **48**, 1861 (1926).

of sulfurous acid; the former could be lowered either by the assumption of a third order side reaction involving H^+ or by the assumption of some specific effect of HSO_4^-, such as Livingston postulates in a recent paper.[3]

If the activity coefficient of sulfurous acid in these dilute solutions is assumed to be one, and if γ_{H^+} is assumed equal to $\gamma_{HSO_3^-}$, then

$$\frac{(H^+)(HSO_3^-)}{(H_2SO_3)} = K_c = \frac{K_c\gamma^2}{\gamma^2} = \frac{K_0}{\gamma^2}$$

and the rate law (eq. 1) can be expressed

$$-\frac{d(ClO_3^-)}{dt} = \frac{\gamma^2 k}{K_0}(H^+)(HSO_3^-)(ClO_3^-) \qquad (2)$$

This expression, which is experimentally indistinguishable from (1), is exactly similar to the rate law established by Skrabal and Zahorka[1c] for the iodate reaction in acid solution

$$-\frac{d(IO_3^-)}{dt} = k_1(H^+)(HSO_3^-)(IO_3^-)$$

The value of k_1 at 25° and low values of μ is given as 0.53×10^6. On the assumption of a normal increase of reaction rate with temperature, this indicates that the iodate reaction is about a thousand times as fast as the chlorate reaction. Skrabal and Zahorka noted that k_1 increases rapidly with ionic strength, and found a second independent reaction in alkaline solution.

Summary

The rate of the reaction between chlorate and sulfur dioxide in acid solution at 0° was found to follow the law

$$-\frac{d(ClO_3^-)}{dt} = 2.4 \pm 0.3(H_2SO_3)(ClO_3^-)$$

BERKELEY, CALIFORNIA

[3] Livingston, THIS JOURNAL, **54**, 2393 (1932).

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

THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF GOLD AND SILVER

BY A. WACHTER[1]

RECEIVED JULY 13, 1932 PUBLISHED DECEMBER 13, 1932

In a study of the thermal equilibrium relationships of alloy systems it is frequently found that the customary thermometric methods employed are not sufficiently sensitive to detect transformations of a physical or chemical nature in the solid state when the thermal changes involved are small. When it is suspected that such a change has escaped observation it becomes necessary to complete the investigation by a study of other properties of the alloys. Of the properties suitable for this purpose the electric potential assumed by an alloy in contact with an electrolyte has been promiscuously employed. The disagreement between individual observers and the lack of a critical observance of the limitations of this method have cast it into disrepute as a precise research tool in this field.

In order to obtain electromotive force measurements which will permit of reliable thermodynamic calculations the following very important factors must be considered in determining the choice of materials and in planning the procedure. The alloy electrode must consist of a homogeneous solid solution. If the alloy be heterogeneous in structure local electrolytic actions take place between the micrographic constituents at the surface, resulting in an alteration of the effective composition of the alloy and consequently in a variation of the potential. Unless the precaution is taken of annealing the solid solution for a sufficiently long time just below its melting point, the fractional crystallization which accompanies the solidification of a molten solution will result in an electrode with a surface richer in the higher melting constituent. In this connection it is important to remember that the greater the separation of the liquidus and solidus curves in the equilibrium diagram the longer and more careful an annealing process is required. Perhaps the first effect of annealing is to remove strains produced by unequal velocities of cooling at different parts of the specimen, causing contraction to take place unequally. This factor is of major importance when potential measurements are to be made at room temperature. Even in the case of pure metal electrodes errors of the order of several centivolts may occur.[2] Due to the extremely small diffusion coefficients of metals at low temperatures, e. m. f. measurements must be made by means of small capacity electrostatic instruments such as the quadrant or string electrometer in order to avoid serious polarization effects. An electrolyte should be chosen which will not react with the

[1] National Research Fellow in Chemistry.

[2] Lewis, THIS JOURNAL, **28**, 158 (1906).

electrodes and containing a sufficiently large concentration of ions of the more electropositive metal. If these precautions are taken and a cell is set up containing a metallic solid solution electrode and a pure metal electrode both immersed in an electrolyte containing ions of the latter, then accurate and reliable potential measurements are possible from which precise thermodynamic calculations can be made.

In this research solid solutions of gold and silver were investigated electrochemically by means of the cell Ag(s)/AgCl(s)/Ag + Au(s. soln.) in the temperature range from 200 to 400° and at mole fractions of silver varying from 1.000 to 0.150. There have been three earlier electrochemical investigations of the gold–silver solid solutions. Tammann[3] studied these alloys in aqueous and molten silver nitrate. His methods are open to criticism on many of the points mentioned above. Ölander[4] made a careful investigation of the cell Ag(s)/AgCl + KCl(l)/Ag + Au(s. soln.) from 400 to 625° over a wide composition range. Wagner and Englehardt,[5] employing the experimental technique described by Ölander, have measured the potentials of the same cells from mole fraction 1.000 to 0.0825 of silver and from 410 to 1085°. Reference will be made later to the results of these last two investigations.

Experimental Part

In the preliminary experimental work the electrodes were immersed in several different electrolytes at widely different temperatures. Among those tried were silver nitrate in aqueous and alcoholic solution at room temperature, pure fused silver nitrate, molten solutions of silver nitrate in a mixture of potassium and sodium nitrates, and pure fused silver chloride. The nitrate electrolytes were especially unsatisfactory, probably due to their reaction with the electrodes. While fused silver chloride was much better it was found that the e. m. f. of the cells changed slowly with time. This can be ascribed to the formation of a pyrosol of silver in the fused salt since a gradual darkening of the melt was noticed.[6] Solid silver chloride proved to be most satisfactory and permitted reproducible measurements to be made down to 200° over a long period of time. Previous use of solid silver chloride has proved it to be entirely satisfactory in galvanic cells at these temperatures.[7]

Silver and gold of the highest purity obtainable from commercial sources were employed, no attempt at further purification being made. Silver chloride was prepared as previously described. Weighed quantities of the two metals were melted together in a small graphite crucible. The button

[3] Tammann, *Z. anorg. allgem. Chem.*, **107**, 1 (1919).

[4] Ölander, THIS JOURNAL, **53**, 3577 (1931).

[5] Wagner and Englehardt, *Z. physik. Chem.*, [A] **159**, 241 (1932).

[6] *Cf.* Lorenz and Helfenstein, *Z. anorg. allgem. Chem.*, **23**, 255 (1900).

[7] Wachter, THIS JOURNAL, **54**, 919, 2271 (1932).

thus obtained was hammered into the form of a rod about 2 cm. long and 2 mm. in diameter. The rods were then annealed for at least twenty-four hours at 850°. The electrodes, both alloy and pure silver, having been spot-welded to 25 cm. lengths of nichrome wire, were dipped into the electrolyte of molten silver chloride contained in a large Pyrex test-tube. When the fused salt had solidified the cell was put into an air-stirred electric furnace the temperature of which was hand-controlled with suitable rheostats. Since the nichrome lead-wires went deeply within the furnace no trouble was experienced with thermopotentials. With the electrolyte always kept in the solid state no creeping along the electrodes occurred. Temperatures were measured by means of a chromel–alumel thermocouple calibrated at the freezing points of tin, zinc and lead. The potentials of the cells were measured by a Leeds and Northrup type K potentiometer in conjunction with a sensitive galvanometer. With this apparatus the e. m. f. of a cell could be read to 0.1 mv. at 200°. Whatever polarization was produced during a measurement must have been negligible since the cells remained constant and reproducible over a period of several days. One cell was short-circuited for several minutes with the result that its e. m. f. immediately dropped; however, within a few hours the cell potential returned to its normal value. This would indicate that at these temperatures diffusion processes are quite rapid in gold–silver alloys.[8]

The cells responded very rapidly to changes in temperature. In general, however, care was taken to avoid changes greater than 5° an hour at the higher and much less at the lower temperatures. No attempt was made to thermostat the furnace, simultaneous readings of temperature and e. m. f. proving very satisfactory. Occasionally the furnace was left with a given rheostat setting for ten or more hours during which the fluctuations in temperature did not exceed 1 or 2° and the e. m. f. of the cells remained constant. No trouble was experienced with gold, in the alloys richer in that constituent, reducing silver from silver chloride.

A few alloys, especially those at the lower concentrations of gold, gave potential readings at first which were very much higher than could reasonably be expected. These were removed, re-annealed, and then replaced in the cells. Their e. m. f. readings after the additional heat treatment were very much lower. Further heat treatment produced no further changes in potential. Two silver wires immersed in an electrolyte of solid silver chloride did not differ by more than ±0.01 millivolt at the furnace temperatures employed in this research. Obviously the difficulties of reproducibility and unstable phases which are so frequently encountered in low temperature work with bulk metal electrodes become negligibly small at elevated temperatures.

[8] Braune, *Z. physik. Chem.*, **110**, 147 (1924), gives the diffusion coefficient of gold into silver the value of 0.0002 sq. cm./day at 847°.

Results

The electromotive force readings with their corresponding temperatures for the seven cells measured are given in Table I and plotted in Fig. 1. The data for all of the cells can be plotted as straight lines within the limits of the experimental error of ±0.3 millivolt. From a very large scale plot of Fig. 1 the potentials corresponding to the temperatures of 200 and 400° were read off for each cell. The isothermal curves at these two temperatures of e. m. f. against composition were plotted from these values and are reproduced in Fig. 2. The manner in which the points fall along smooth curves in Figs. 1 and 2 predisposes one toward confidence in the validity of these measurements.

TABLE I

E. M. F. IN VOLTS OF CELLS CONTAINING SILVER OF VARIOUS MOLE FRACTIONS, N_1, DILUTED WITH GOLD

t, °C.	E. m. f.
N_1 = 0.863	
199.2	0.0120
213.0	.0124
233.5	.0128
238.3	.0123
244.1	.0130
248.6	.0131
271.7	.0132
277.0	.0128
292.9	.0143
303.3	.0148
332.0	.0152
369.0	.0152
384.3	.0151
N_1 = 0.650	
208.5	0.0356
229.9	.0372
238.0	.0371
268.4	.0388
283.0	.0379
290.2	.0387
300.0	0.0393
304.2	.0393
321.6	.0403
327.4	.0415
358.3	.0417
368.1	.0413
376.7	.0415
N_1 = 0.605	
192.4	0.0468
208.5	.0473
229.8	.0482
271.3	.0489
275.0	.0499
322.0	.0515
325.6	.0520
359.9	.0525
376.2	.0533
N_1 = 0.526	
194.0	0.0576
195.9	.0581
208.3	.0582
218.2	.0584
236.5	0.0598
267.3	.0618
281.0	.0614
290.0	.0623
308.7	.0634
334.1	.0650
	.0666
359.2	.0673
373.3	.0675
420.9	.0692
438.3	.0702
N_1 = 0.414	
210.0	0.0822
224.5	.0835
229.3	.0838
252.6	.0844
269.7	.0853
294.4	.0865
309.2	.0871
327.0	.0879
343.3	.0885
395.6	.0907
407.0	.0913
N_1 = 0.285	
189.3	0.1205
197.3	.1208
228.2	.1235
238.0	.1242
254.8	.1255
309.0	.1290
337.0	.1311
360.2	.1324
381.3	.1340
407.2	.1358
417.6	.1366
N_1 = 0.150	
193.7	0.1836
224.1	.1867
253.0	.1902
275.5	.1935
315.8	.1983
346.3	.2029
374.4	.2064
415.1	.2121

In order to facilitate the thermodynamic calculations and to make their results more useful, the e. m. f.'s at the two temperatures mentioned above were taken at equal intervals of 10 mole per cent. from mole fraction 1.000 to 0.200 of silver. In all which follows the subscript 1 refers to silver and 2 to gold.

The partial molal free energy of dilution, $\Delta\bar{F}_1$, was calculated by means of the relation $\Delta\bar{F}_1 = -23{,}074\ \Delta\mathbf{E}$, where $\mathbf{E}$ is the electromotive force in volts. The partial molal entropy of dilution, $\Delta\bar{S}_1$, was obtained from the

expression 23,074 $d\mathbf{E}/dT = \Delta\bar{S}_1$. From these two the partial molal heat of dilution, $\Delta\bar{H}_1$, was easily calculated from the equation $\Delta\bar{H}_1 = \Delta\bar{F}_1 + T\Delta\bar{S}_1$. The activity, a_1, is given by $\Delta\mathbf{E} = -RT/23{,}074 \ln a_1$. In all of the above calculations pure silver was taken as the standard state. In order to calculate the corresponding partial molal quantities for gold in these solid solutions, the Duhem equation was employed in the integrated

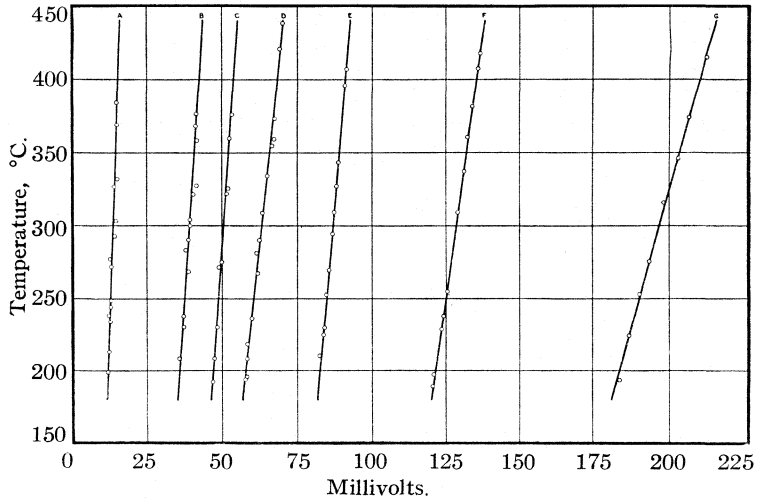

Fig. 1.—Temperature variation of e. m. f. of cells containing different gold–silver solid solutions. Mole fraction of silver in A is 0.863, B is 0.650, C is 0.605, D is 0.526, E is 0.414, F is 0.285 and G is 0.150.

form, performing a graphical integration and taking pure gold as the standard state. For a_2, the equation was $\log a_2/N_2 = -\int_0^{N_1} N_1/N_2 \, d \log a_1/N_1$; for $\Delta\bar{S}_2$ it took the form $\Delta\bar{S}_2 = -\int_0^{N_1} N_1/N_2 \, d \, \Delta\bar{S}_1$; and for $\Delta\bar{H}_2$ it was $\Delta\bar{H}_2 = -\int_0^{N_1} N_1/N_2 \, d \, \Delta\bar{H}_1$. The partial molal free energy of dilution for gold, $\Delta\bar{F}_2$, was obtained from a_2 by means of the equation $\Delta\bar{F}_2 = RT \ln a_2$. The total thermodynamic quantities, ΔF, ΔH, and ΔS, for the process of solution as represented by the equation

$$N_1Ag(s) + N_2Au(s) = N_1Ag \cdot N_2Au(s.\ soln.)$$

were easily obtained from the corresponding partial molal quantities. For example, for the total free energy change of dilution, $\Delta\bar{F} = N_1\Delta\bar{F}_1 + N_2\Delta\bar{F}_2$, and similarly for the others. The results of all these computations are given in Table II.

Discussion of Results

For the purpose of comparison the observed e. m. f.'s at 400° of Ölander[4] are plotted as triangles and of Wagner and Englehardt[5] as squares in Fig. 2.

TABLE II

THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF GOLD IN SILVER

N_1	dE/dT mv./deg.	$\Delta\bar{S}_1$ cal./deg.	$\Delta\bar{S}_2$ cal./deg.	$-\Delta\bar{H}_1$ cal.	$-\Delta\bar{H}_2$ cal.
1.000	0	0		0	
0.900	0.0100	0.231	3.794	98	2895
.800	.0215	.496	2.130	199	2339
.700	.0305	.704	1.471	373	1793
.600	.0405	.935	1.036	587	1391
.500	.0475	1.096	0.832	935	958
.400	.0495	1.142	.793	1453	540
.300	.0665	1.534	.589	1948	263
.200	.109	2.515	.282	2418	96

200°

N_1	E volts	$-\Delta\bar{F}_1$ cal.	$-\Delta\bar{F}_2$ cal.	a_1	a_2
1.000	0	0		1.000	0
0.900	0.0090	208	4733	0.802	0.0065
.800	.0188	434	3386	.631	.0273
.700	.0306	706	2570	.472	.0649
.600	.0446	1029	1980	.335	.122
.500	.0639	1453	1459	.213	.212
.400	.0864	1993	1024	.120	.337
.300	.1159	2674	654	.058	.499
.200	.1564	3608	342	.022	.696

400° 200°

N_1 Ag(s) + N_2 Au(s) = N_1Ag·N_2Au (s. soln.)

N_1	E volts	$-\Delta\bar{F}_1$ cal.	$-\Delta F$ cal.	$-\Delta H$ cal.	Δs cal.
1.000	0	0	0	0	0
0.900	0.0110	254	660	377	0.587
.800	.0231	533	1024	627	.823
.700	.0367	847	1266	799	.934
.600	.0527	1216	1409	909	.975
.500	.0725	1673	1456	947	.964
.400	.0963	2222	1412	905	.933
.300	.1292	2981	1260	769	.873
.200	.1782	4112	995	561	.729

In his thermodynamic calculations and conclusions therefrom Ölander has apparently placed too much stress on the minor variations from the regular smooth curve which may be drawn through his points. It is highly improbable that so many abrupt thermodynamic discontinuities would present themselves in this simple series of solid solutions. The thermal equilibrium diagram gives no indication of them, the micrographic and x-ray analyses do not reveal them, and the chemical as well as physical similarities of the two constituents would not lead us to expect them. It is not sufficient to establish the reproducibility with temperature of the individual cells employed. They must also be reproducible with respect

to composition. There are two serious sources of error in Ölander's experimental methods. It is highly probable that his alloys were insufficiently annealed. He allowed only two hours at 930° for this important treatment which should have been especially prolonged since the alloys were in the form of rather long wires 1 mm. in diameter. The fractional crystallization which would occur upon solidification of the molten alloy would result in a casting whose outer portion would be richer in gold.

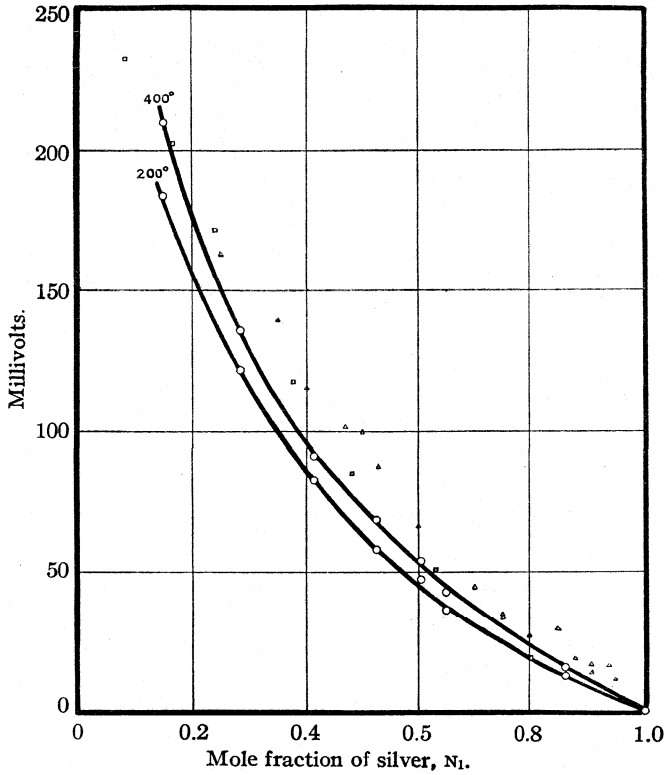

Fig. 2.—Change in e. m. f. of cells with composition at 200 and 400°. The circles are by Wachter, the triangles by Ölander, and the squares by Wagner and Englehardt.

This would explain the higher potentials which Ölander as well as Wagner and Englehardt have obtained. Then, the uncertainty which was introduced by the drop in potential with time of their gold-rich alloys when immersed in the electrolyte leaves us with still less confidence in the reliability of their thermodynamic results. Wagner and Englehardt claim no greater accuracy than ±2 mv. and find no evidence for the existence of abrupt changes in thermodynamic properties for these alloys.

Of especial interest to us are the activity curves given in Fig. 3. Both

the gold and silver show large negative deviations from Raoult's law. The addition of one to the other therefore results in an abnormally large decrease in escaping tendency of each. The formation of an intermetallic compound or a regular arrangement of both kinds of atoms in the lattice of the solid solution would give rise to this pronounced inhibition.

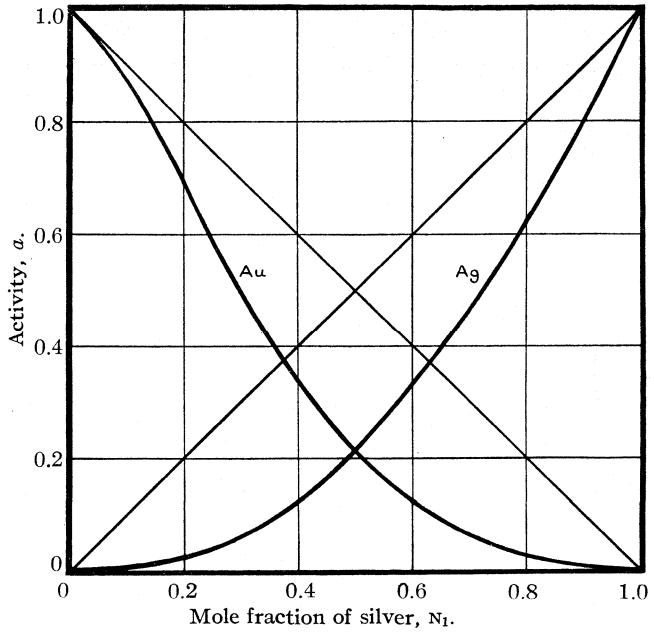

Fig. 3.—Activity curves for silver–gold solid solutions at 200°.

Tammann[3] has long supported the view which originated with him that the atomic or ionic arrangement in solid solutions is regular and that its composition can be represented by multiples of one-eighth mole of the two constituents for cubic crystals. For the gold–silver alloys, which are face-centered cubic, he has postulated, from numerous experiments on their chemical resistance limits, that the regular arrangement has the composition four-eighths mole of silver and four-eighths mole of gold. Although numerous x-ray studies of these alloys have been made,[9] no supporting evidence has been obtained from this quarter.

From a thermodynamic point of view, for any arrangement to be more probable than any of the others it must be the most stable. An examination of the data tabulated in Table II immediately shows that not only the total free energy change of solution but also the corresponding heat content and entropy changes attain a maximum value at about mole fraction 0.5.

[9] (a) Bain, *Chem. Met. Eng.*, **28**, 65 (1923); (b) McKeehan, *Phys. Rev.*, **21**, 380 (1923); (c) Sachs and Weerts, *Z. Physik*, **60**, 481 (1930).

The heat of solution is small and negative with a maximum value of −947 calories for the equi-molal solution.

The interaction between the gold and silver atoms in their solid solutions which can result in negative deviations from Raoult's law and in appreciable heats of solution can only consist of a force of attraction. If Vegard's rule[10] of the additivity of lattice constants in solid solutions is rigidly obeyed it is difficult to understand how any regular arrangement could exist. However, it has been demonstrated many times that the rule is an approximate one only. For the gold–silver alloys we have the very accurate lattice constant determinations of Sachs and Weerts,[9c] which show that the inter-atomic distances are smaller than those predicted by the linear relation. This is in agreement with the experimental fact that the hardness of this alloy series increases from both pure metals to a maximum at the equi-molal mixture.[11]

It is interesting to compare this system with the structurally and chemically similar gold–copper alloys. It has been shown by Johansson and Linde[12] that in the solid solution series of gold and copper at 0.25 and 0.50 mole fraction of gold the atoms in the crystal lattice are regularly arranged when the alloys are annealed for a sufficiently long time at 370°. The regular arrangements were recognized by the existence of extra lines in the x-ray analysis. Rapidly cooled specimens did not show this phenomenon. This latter serves to emphasize the importance of a careful annealing process if measurements are to be made of any other than accidental properties of alloys. Careless heat treatment of these systems in which the more stable regular arrangement differs so little in energy content from the statistically random one may easily result in an unstable frozen-in state which may persist indefinitely.

Summary

1. The energy changes of solid silver upon dilution with gold have been determined at mole fractions of silver varying from 1.000 to 0.150, between the temperatures of 200 and 400°.

2. The solid solution containing 0.500 mole of silver is shown to be the most stable.

3. The thermodynamic properties of these solid solutions are considered compatible with the existence of a regular arrangement of gold atoms in the silver crystal lattice.

BALTIMORE, MARYLAND

[10] Vegard, *Z. Physik*, **5**, 17 (1921).

[11] Kurnakoff and Schemtschuschny, *Z. anorg. allgem. Chem.*, **60**, 1 (1908).

[12] Johansson and Linde, *Ann. Physik*, **78**, 439 (1925).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 102]

THE FREE ENERGIES OF FORMATION OF VARIOUS FORMS OF LEAD MONOXIDE

BY HUGH M. SPENCER AND JOHN H. MOTE[1]

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Introduction

The free energies of formation of the various forms of lead monoxide are necessary links in the calculations of those of many other lead compounds. Smith and Woods[2] measured the potential of the cell

$$H_2(g),\ \text{dil. } Ba(OH)_2,\ PbO(\text{red}),\ Pb \qquad (1)$$

and thus with the $\Delta F^{\circ}_{298.1}$ of formation of water, $-56{,}560$ cal., found for that of the red lead monoxide, $-45{,}050$ cal.

Randall and Spencer[3] measured the solubility of the various forms of lead monoxide in dilute aqueous potassium hydroxide solutions and thus the free energies of formation of plumbite ion from the various forms. From the differences in free energies of formation of plumbite ion and Smith and Woods' evaluation of the ΔF of formation of the red form, one may derive that of the others.

In addition to determining the solubilities Glasstone[4] measured the electromotive forces of cells of the type

$$Pb,\ PbO,\ NaOH(1N),\ HgO,\ Hg \qquad (2)$$

using the eight different preparations of lead monoxide which he had used in the solubility measurements. The solubility measurements were interpreted as proving the identity except as to size of particles of the various preparations. The measurements were made at room temperatures, which were presumably around 20°, and the values for the cells are given to only three figures. He made no attempt to avoid diffusion potentials by placing lead monoxide in the mercuric oxide side of the cell. Glasstone assumed that the measurements of all the cells checked one another, in conformity with his solubility measurements, and gave 0.673 v. as the mean potential. In order to get the temperature coefficient he attempted some cells at 0 and 25° which he measured to one-tenth of a millivolt. For this purpose red and yellowish-green oxides were used. Only the electrode potentials are given, the value for the mercuric oxide

[1] Du Pont Fellow in Chemistry 1928–29.

[2] D. F. Smith and H. K. Woods, THIS JOURNAL, **45**, 2632 (1923).

[3] M. Randall and H. M. Spencer, *ibid.*, **50**, 1572 (1928). The results of the earlier solubility measurements are briefly discussed in this paper. Two papers including similar measurements have since appeared, by H. Töpelmann, *J. prakt. Chem.*, **121**, 320 (1929), and M. P. Applebey and H. M. Powell, *J. Chem. Soc.*, 2831 (1931).

[4] S. Glasstone, *J. Chem. Soc.*, **119**, 1914 (1921).

electrode by which he calculated the electrode potential from the cell potential being omitted. It seems likely that he used the value −0.1135 v. of Donnan and Allmand. He obtained for the red oxide an electrode potential of 0.5621 at 25° and for the yellow at the same temperature 0.5598 v. By combination with −0.1135 for the mercuric oxide electrode, the electromotive forces of the cells are 0.6756 and 0.6733 v., respectively, when the cells contain the red and yellow oxides.

Applebey and Reid[5] repeated the work of Glasstone and found $E_{293.1}$ = 0.6808 and 0.6734 v. Fried[6] measured similar cells in order to test the Nernst heat theorem. He used a lead-plated electrode and a Kahlbaum preparation of lead monoxide. The potentials varied considerably over two millivolts and since his measurements of the hydrogen–mercuric oxide cell showed much more satisfactory reproducibility, the fault seems to lie in the lead–lead monoxide electrodes. One may attribute the lack of reproducibility to inequalities in the completeness of saturation of the alkaline solutions by the lead oxide. At any rate the results cannot lead to significant free energy values since the lead oxide used was not a pure form.

In spite of the discrepancies in the potentials cited it appeared that potential measurements, in which the same care should be taken in the preparation of materials and the establishment of equilibrium by preshaking as was observed by Randall and Spencer, promised more definitive values of the differences of the free energies of formation of the oxides than were available from the solubility measurements. Moreover, since the free energy of formation of mercuric oxide is known to a fairly high degree of accuracy, measurements of cells of the type

Pb(in het. amalg.) PbO(red, yellow or hydrate), dil. $Ba(OH)_2$, HgO(red) + PbO(red, yellow or hydrate), Hg(l) (3)

afford a method of calculation of the free energies of formation of the lead monoxides independent of the one derived by Smith and Woods for the red form except in that both are dependent on the free energy of formation of water. Accordingly measurements of such cells are here presented.

Experimental Procedure

All reagents used in this investigation were of C. P. quality, and in most cases were further purified before they were used.

Mercury.—The mercury used in the cells and that used in the preparation of the lead amalgams, after the usual washing with mercurous nitrate, was thrice distilled at low pressure and was preserved in closed containers. No film was present on the surface of the mercury used in the experiments.

Lead.—The lead used was a chemically pure commercial variety designated as "Test Lead" and was silver-free.

[5] M. P. Applebey and R. D. Reid, *J. Chem. Soc.*, **121**, 2129 (1922).

[6] F. Fried, *Z. physik. Chem.*, **123**, 406 (1926).

Lead Amalgam.—The two-phase lead amalgam was prepared by heating together the lead and purified mercury in such proportion as to give a five per cent. amalgam.

Barium Hydroxide.—The barium hydroxide solution used as electrolyte and in the preparation of the hydrated oxide was made from a recrystallized C. P. product. It was made up and preserved out of contact with carbon dioxide.

Mercuric Oxide.—The mercuric oxide used was the red form.[7] It was prepared by letting chemically pure nitric acid react with distilled mercury and heating the nitrate thus formed until it had entirely decomposed, leaving mercuric oxide. The oxide was washed numerous times with conductivity water to remove the last traces of mercuric nitrate. It was stored under conductivity water.

Sodium Hydroxide.—Carbonate-free sodium hydroxide was prepared by the action of water vapor on metallic sodium in an atmosphere of hydrogen under a bell jar. The metallic sodium was suspended in a nickel gauze cone and the hydroxide formed was caught in a nickel crucible and preserved out of contact with air until ready for use.

Lead Monoxides.—The red and yellow lead monoxides[8] were prepared by a modification of the method of Geuther and of Ruer described by Randall and Spencer.[3] In the preparation of the red form usually the yellow modification formed first but on further heating changed over into the red. It was possible to form the red modification with the sodium hydroxide used in the preparation of the yellow. Dilution of the solution immediately after the yellow had formed and rapid cooling prevented the further change to the red. The homogeneity of the samples was proved by microscopic examination.

Hydrated Lead Monoxide.—The white hydrated lead monoxide was prepared by the method of Pleissner.[9]

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[7] The identity of the red and yellow forms of mercuric oxide has been established by means of x-ray analysis (powder method) [G. R. Levi, *Gazz. chim. ital.*, **54,** 709 (1924); W. Zachariasen, *Z. physik. Chem.*, **128,** 421 (1927)]. The two oxides give slightly different electromotive forces but the difference may be accounted for on the basis of difference in solubility due to difference in size of particles.

[8] The individuality and allotropy of these two forms of lead monoxide have been the subject of numerous papers in addition to the solubility measurements referred to above. V. Kohlschütter and P. Scherrer [*Helv. Chim. Acta,* **7,** 337 (1924)] proved them to be different by x-ray analysis and their ultimate structures have been determined by further use of the same methods. The results, except those of M. LeBlanc and E. Eberius [*Z. physik. Chem.*, **160A,** 69 (1932)], are summarized by J. A. Darbyshire [*J. Chem. Soc.*, 211 (1932)]. It appears certain that there are only two polymorphic forms of lead monoxide and the authors believe the variations in color are caused (1) by varying size of particles, (2) by varying amounts of the two forms and (3) by the presence of varying amounts of metallic lead.

[9] M. Pleissner, *Arb. kais. Gesundh.*, **26,** 384 (1907). The same method was used by Randall and Spencer,[3] whose analysis gave 89.8% Pb. H. Töpelmann[3] using two other methods of analysis, found for the Pleissner preparation 89.75 and 89.84% lead and 89.82 and 89.73% lead for a preparation following the directions of E. Müller, in which 2 *N* sodium hydroxide was used in place of the barium hydroxide in the Pleissner preparation. Randall and Spencer dried the hydrate in a vacuum desiccator over sulfuric acid (30–40%), whereas Töpelmann's products were dried with alcohol and ether and finally over calcium chloride in a vacuum desiccator. G. F. Hüttig and B. Steiner [*Z. anorg. allgem. Chem.*, **197,** 258 (1931)] prepared the hydrated oxide by two other methods and subjected the products to isobaric dehydration and x-ray analysis. Their hydrate No. 1 ($PbO \cdot 0.504H_2O$) was prepared by the addition at 0° of a lead acetate solution (185 g. in 1000 cc. of water) in a jet to 1000 cc. of 14 *N* ammonia. After shaking, the white crystalline precipitate was washed with water, filtered and dried over 30%

Preparation of the Cells.—The vessels used as cells were modifications of the usual H-type vessels. They consisted of two sets of three electrodes connected by a cross arm, thus nine combinations could be obtained with the six electrodes. The mercury, amalgams and mercuric oxide were first put into place. The barium hydroxide solution, saturated by shaking with the lead monoxide, along with excess of the monoxide was then added and nitrogen was bubbled alternately through the various arms of the vessel to displace the air. After this process the tubes were sealed off and the stoppers coated with de Khotinsky wax. The strength of the barium hydroxide electrolyte was determined by titration at the end of the measurements.

The cells were immersed in an oil-bath thermostat regulated to 25 ± 0.05°. The temperature was determined by a sensitive thermometer which had been checked against a Bureau of Standards thermometer. The electromotive force measurements were made with a Leeds and Northrup Type K potentiometer and Type R (2500-c) galvanometer. The standard cell was frequently checked against a Standard Weston cell with a Bureau of Standards certificate.

Results and Discussion

After five or six hours the cells were generally within several tenths of a millivolt of their equilibrium values, and values which proved to be the final ones were attained in one or two days. Table I, a, b and c presents the measured values of the potentials of cells of Type 3 where the lead monoxide was the hydrate, red and yellow forms, respectively. Cells 1 and 2 consisted of one pair of electrodes only. Where fewer than nine combinations for a given concentration are given, one or more of the electrodes proved insensitive or yielded constantly drifting values.

potash in a vacuum desiccator for one day. Their hydrate No. 10 ($PbO \cdot 0.470H_2O$), white without recognizable crystalline structure, was precipitated from potassium plumbite solutions by 33% acetic acid. After washing and filtering it was dried for three days over soda lime. There remained in the product 0.64% K_2O. Other preparations differed from No. 1 in later treatment and showed different proportions of water. One is left with the impression that the analysis, except for K_2O, etc., consisted in the determination of water content. Hydrate No. 5 ($PbO \cdot 1.218H_2O$) (same as No. 1 except that it was not dried after filtration) when subjected to isobaric dehydration at 10 mm. gave a flat in the water %–time curve corresponding to 0.5 mole of water per mole of lead monoxide. The loss of water below 0.5 mole they describe as "zeolithic" in character. They consider that both their dehydration experiments and x-ray analysis offer no indications of hydrates other than $2PbO \cdot H_2O$. Those of lower water content show tinges of color and in addition to the well-marked x-ray pattern of the semi-hydrate (No. 1), show weakly but nevertheless plainly the most important lead monoxide lines. If in the dehydration experiments the temperature rises to 100° the product is mainly the red form.

The theoretical percentages of lead in the hydrates $2PbO \cdot H_2O$, $2.5PbO \cdot H_2O$, $3PbO \cdot H_2O$ are 89.22, 89.93 and 90.39, respectively. The early papers reported the first and third of these. Glasstone[3,4] and Töpelmann[3] write the formula of the compound in the second form. Though the analysis of Randall and Spencer agrees exactly with that of Töpelmann, they write the formula in the form used by Pleissner and others, $3PbO \cdot H_2O$, and we shall also use this form in the present paper. It is unfortunate that the interesting experiments of Hüttig and Steiner were not carried out also with Pleissner's preparation and that their method of analysis is not stated. It seems highly probable that the composition of all the forms is the same.

Assuming the cell reactions indicated in the equations

$$Pb(\text{in het. amalg.}) + HgO(\text{red}) + 1/3H_2O(\text{in } xM\ Ba(OH)_2) = PbO\cdot 1/3H_2O(s) + Hg(l);\ \Delta F_{298.1} = -30{,}752 \text{ cal.} \quad (3a)$$

$$Pb(\text{in het. amalg.}) + HgO(\text{red}) = PbO(\text{red}) + Hg(l);\ \Delta F^\circ_{298.1} = -30{,}985 \text{ cal.} \quad (3b)$$

$$Pb(\text{in het. amalg.}) + HgO(\text{red}) = PbO(\text{yellow}) + Hg(l);\ \Delta F^\circ_{298.1} = -30{,}840 \text{ cal.} \quad (3c)$$

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Pb(in het. amalg.), PbO(red, yellow, or hydrate), $Ba(OH)_2(xM)$, HgO(red) + PbO(red, yellow or hydrate), Hg(l)

(a) Solid Phase, $PbO\cdot 1/3H_2O$

No.	Molality $Ba(OH)_2$	$E_{298.1}$
1	0.1054	0.66647
2	.1160	.66660
4	.1018	.66635
5	.1018	.66635
6	.1018	.66636
7	.1018	.66626
8	.1018	.66626
9	.1018	.66626
10	.1018	.66651
11	.1018	.66651
12	.1018	.66652
14	.05	.66632
15	.05	.66642
16	.05	.66619
	Average	.66638

(b) Solid Phase, PbO (red)

No.	Molality $Ba(OH)_2$	$E_{298.1}$
31	0.1540	0.67165
32	.1540	.67154
34	.1540	.67156
35	.1540	.67143
37	.1944	.67130
38	.1944	.67138
39	.1944	.67144
40	.1944	.67114
41	.1944	.67120
42	.1944	.67127
43	.1944	.67138
44	.1944	.67147
45	.1944	.67154
	Average	.67141

(c) Solid Phase, PbO (yellow)

No.	Molality $Ba(OH)_2$	$E_{298.1}$
49	0.1650	0.66834
50	.1650	.66834
51	.1650	.66845
52	.1650	.66833
53	.1650	.66835
54	.1650	.66843
55	.2122	.66820
56	.2122	.66835
58	.2122	.66815
59	.2122	.66828
61	.2122	.66826
62	.2122	.66839
	Average	.66832

The free energy of formation of mercuric oxide was calculated by Lewis and Randall[10] from data of Brönsted, Ming Chow and Buehrer on the cell

$$H_2(g),\ \text{dil. NaOH or KOH, HgO, Hg} \quad (4)$$

for which the standard electromotive force is 0.9265, 0.9264 and 0.9264 v., respectively. The free energy of formation of water necessary to obtain that of the mercuric oxide is partially dependent on the potential of this cell since Lewis and Randall's final value for water, −56,560 cal., is based on four sets of determinations, one involving the above cell and the less accurate value for the free energy of formation of mercuric oxide from direct dissociation measurements. This leads to

$$Hg(l) + 1/2O_2(g) = HgO;\ \Delta F^\circ_{298.1} = -13{,}808 \text{ cal. (prelim.)} \quad (5)$$

Ishikawa and Kimura[11] measured cells of Type 4 with 1.027 N sodium hydroxide as electrolyte at 0, 15, 25, 35 and 40°. They find after correction for the lower activity of water (0.33 to 0.42 mv.), E° = 0.92565 −

[10] G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 408, 477–485.

[11] F. Ishikawa and G. Kimura, *Sexagint, Y. Osaka, Chem. Inst. Dept. Science Kyoto Imp. Univ.*, 255 (1927).

$0.0002948\,(t-25) + 0.0000004991\,(t-25)^2$, where the mercuric oxide is the red form, a Kahlbaum product prepared from mercuric nitrate. Ishikawa and Kimura also used the yellow form (Merck product) and found after several days $E^\circ_{298.1} = 0.9263$ v. One of these cells was followed for fifteen days, by which time its potential had fallen to 0.9260 v., and was thus approaching the value gotten immediately with the red form. They point out that Brönsted and Miyamoto gave no description of the oxides used, that Ming Chow's was described as a "chemically pure commercial preparation," and that Fried[6] used a yellow precipitated oxide. The five cells at 25° gave values differing from the mean 0.92565 by 0.05 mv. Their equation leads to $\Delta S_{298.1}$ for the cell reaction equal to −13.60 E. U. A more significant check by the third law of thermodynamics can now be made. Using the following entropies: Hg, 18.3 (Rodebush and Rodebush), H_2O, 15.92 (Latimer and Greensfelder), H_2, 31.23 (Giauque), and HgO, S = 16.6 (Rodebush and Rodebush),[12] $\Delta S_{298.1}$ for the cell reaction is equal to −13.61 E. U. The check is closer than the uncertainty in the entropy values. ΔH of formation of mercuric oxide from the cell measurements and that of water, −68,313 cal., by Rossini[13] is −21,540, and is thus within the range of thermochemical values −20,700 by Nernst, −22,000, Thomsen, and −21,500 cal., Varet. We shall therefore accept the value of Ishikawa and Kimura, $\Delta F_{298.1} = -42{,}717$ cal., for cell 4 and combine it with the free energy of formation of water by Lewis and Randall (since their final value, the mean of all four values, is also the mean of those excluding that determined through mercuric oxide). Thus for Reaction 5, $\Delta F^\circ_{298.1} = -13{,}846$ cal.

Spencer and Randall[14] from a study of the data of Gerke, Hulett, Obata and others take

$$\text{Pb} = \text{Pb(in het. amalg.)};\ E_{298.1} = 0.00586 \text{ v.},\ \Delta F_{298.1} = -270 \text{ cal.} \qquad (6)$$

Combination of Reactions 3a, 5(Ishikawa and Kimura), and 6 yields for the white hydrate of lead monoxide[15]

$$\text{Pb(s)} + 1/2\text{O}_2\text{(g)} + 1/3\text{H}_2\text{O(l)} = \text{PbO}\cdot 1/3\text{H}_2\text{O(s)};\ \Delta F^\circ_{298.1} = -44{,}868 \text{ cal.} \quad (7)$$

With less certainty, due to the problematical status of the formula of the hydrate, one may obtain the standard free energy of formation from the elements by combining Equation 7 with one-third the free energy of formation of water, *i. e.*, −18,853 cal. Thus

$$\text{Pb(s)} + 2/3\text{O}_2\text{(g)} + 1/3\text{H}_2\text{(g)} = \text{PbO}\cdot 1/3\text{H}_2\text{O(s)};\ \Delta F^\circ_{298.1} = -63{,}721 \text{ cal.} \quad (8)$$

[12] W. H. Rodebush and E. Rodebush, "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, pp. 88, 90; W. M. Latimer and B. S. Greensfelder, THIS JOURNAL, **50**, 2202 (1928); W. F. Giauque, *ibid.*, **52**, 4816 (1930).

[13] F. D. Rossini, *Proc. Nat. Acad. Sci.*, **16**, 694 (1930).

[14] H. M. Spencer and M. Randall, unpublished data.

[15] The correction for the lower activity of water in the more concentrated barium hydroxide solutions has been estimated from freezing point measurements. Since its value, five calories, is less than the experimental error it has not been applied.

Combinations of Reactions 3b and 3c with 5 and 6 yield for the red and yellow forms of the monoxide

$$Pb(s) + 1/2O_2(g) = PbO(red); \quad \Delta F^\circ_{298.1} = -45{,}101 \text{ cal.} \qquad (9)$$

$$Pb(s) + 1/2O_2(g) = PbO(yellow; \quad \Delta F^\circ_{298.1} = -44{,}956 \text{ cal.} \qquad (10)$$

If $-13{,}808$ cal., the value for Reaction 5 by Lewis and Randall, is used, the values for Reactions 7, 9 and 10 are, respectively, $-44{,}830$, $-45{,}063$ and $-44{,}918$ cal.

The result of Reaction 9 is to be compared to $-45{,}050$ cal., from Smith and Woods' cell 1. Ishikawa and Shibata[16] have found for a similar cell, $\Delta F^\circ_{298.1} = -44{,}921$ cal. Unfortunately the nature of the lead monoxide used is not stated in the abstracts. Neither yields values of $\Delta S_{298.1}$ (-14.76, Smith and Woods and -18.46 E. U., Ishikawa and Shibata) in good agreement with the third law value, -17.06 E. U., based on the entropies at 25°, Pb, 15.55 (Ulich and Stackelberg),[17] PbO, 17.3 E. U. (Rodebush and Rodebush)[12] and those of hydrogen and water cited above. The modification involved in the specific heat measurements and the homogeneity of the samples are in doubt. Smith and Woods' cells do yield a value for the ΔH of formation of lead monoxide, $-52{,}403$ cal., using Rossini's[13] value for water, in good agreement with that of Werth and Eucken,[18] $-52{,}700 \pm 500$, whereas Ishikawa and Shibata's cells yield $-51{,}296$ cal.

The free energy contents of the white hydrate (aside from the water involved) and yellow anhydrous forms are greater than that of the red modification by 233 and 45 cal., respectively, whereas Randall and Spencer[3] found greater differences, 391 and 238 cal.

Summary

The free energies of formation at 25° of the various forms of lead monoxide, red and yellow, and the white hydrate, as they are based on that of mercuric oxide, have been determined from measurements of cells of the type

Pb(in het. amalg.) PbO(red, yellow or hydrate), dil. $Ba(OH)_2$, HgO(red) + PbO(red, yellow or hydrate), Hg(l)

The free energy of formation of the red modification is compared with that obtained through the hydrogen–mercuric oxide cells and the differences in free energy content of the various forms are compared with those derived from solubility measurements.

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[16] F. Ishikawa and E. Shibata, *J. Chem. Soc. Japan*, **48**, 59 (1927), and *Science Repts., Tohôku Imp. Univ.*, [1] **18**, 109 (1929).

[17] H. Ulich and M. v. Stackelberg, Landolt–Börnstein "Tabellen," Erg. II, p. 1605, newly calculated with the results of Keesom and van den Ende.

[18] H. Werth and A. Eucken, Landolt–Börnstein, "Tabellen," Erg I, p. 837.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

DETERMINATION OF FLUORINE BY PRECIPITATION AS TRIPHENYLTIN FLUORIDE

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Introduction

Batchelder and Meloche[2] have recently given a survey of the gravimetric methods for fluorine in their paper on the determination of fluorine by titration with cerous nitrate. Treadwell and Köhl[3] have made critical studies of the various gravimetric procedures that have been proposed and other reviews have been published by Hawley, Adolph, and Wagner and Ross.[4] Hillebrand and Lundell treat the determination of fluorine extensively in their "Applied Inorganic Analysis."[5] The conclusion reached by these reviewers is that the gravimetric determination of fluorine is fraught with many difficulties and uncertainties. Especially is this true when small quantities of fluorine are being dealt with and in fact gravimetric methods are precluded in such cases and recourse must be had to the colorimetric methods of de Boer and Steiger-Merwin.[6] Such colorimetric methods cannot be expected to show a high degree of accuracy.

In 1920 Krause and Becker[7] reported the preparation of triphenyltin fluoride and recorded the observation that the substance "was so difficultly soluble in cold alcohol, ether and water that fluorine can be quantitatively precipitated with triphenyltin chloride." They prepared the fluoride by treating a boiling-hot water–alcohol solution of potassium fluoride with a hot dilute alcoholic solution of triphenyltin chloride. A search of the literature subsequent to the appearance of the above paper failed to reveal that any effort had been made to apply the formation of the triphenyltin fluoride to the determination of fluorine. In view of the reported low solubility of the substance and of the very small conversion factor to fluorine (0.05153) it was deemed worth while to make an exhaustive investigation of the possibilities of the compound in the gravimetric determination of fluorine.

[1] J. T. Baker Chemical Company Fellow in Analytical Chemistry for 1931–1932, Eastern Division.

[2] Batchelder and Meloche, THIS JOURNAL, **53**, 2131 (1931).

[3] Treadwell and Köhl, *Helv. Chim. Acta*, **9**, 470 (1926).

[4] Hawley, *Ind. Eng. Chem.*, **18**, 573 (1926); Adolph, THIS JOURNAL, **37**, 2500 (1915); Wagner and Ross, *J. Ind. Eng. Chem.*, **9**, 1116 (1917).

[5] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929.

[6] De Boer, *Chem. Weekblad*, **21**, 404 (1924); Steiger, THIS JOURNAL, **30**, 219 (1908); Merwin, *Am. J. Sci.*, **28**, 119 (1909).

[7] Krause and Becker, *Ber.*, **53**, 183 (1920).

Experimental

Preparation of Materials.—Krause and Becker[7] used triphenyltin chloride as the precipitant in the preparation of the fluoride. This substance is not available commercially so it was prepared from tetraphenyltin. Two lots of the tetraphenyltin were prepared by Mr. R. E. Pflaumer of this Laboratory, using the zinc diphenyl method of Chambers and Scherer[8] for one lot, and the Grignard method proposed by Pfeiffer and Schnurmann for the other.[9] Mr. Pflaumer regards the latter method as the more satisfactory of the two, both in regard to the ease of execution and to the yield secured. A third lot of tetraphenyltin was procured from the Eastman Kodak Company. Identical results were secured with the three separate lots.

Krause prepared triphenyltin chloride by first making the bromide by treating tetraphenyltin in pyridine solution with bromine dissolved in pyridine while cooling with solid carbon dioxide.[10] The bromide was dissolved in ether, converted to the hydroxide and then to the chloride by shaking with 12 *N* hydrochloric acid. A less difficult method has been proposed by Chambers and Scherer[11] and this method was used in the present work. On account of a few minor changes, the procedure will be briefly outlined. Triphenyltin iodide is prepared by refluxing tetraphenyltin in chloroform solution with iodine, the chloroform and iodobenzene are distilled off, the iodide dissolved in ether and converted to the hydroxide by shaking with a cold 30% solution of sodium hydroxide. The hydroxide was found to be only slightly soluble in ether and it is liable to separate out at this stage as a pasty mass. The ether solution and any hydroxide that has separated are thoroughly washed with cold water by shaking in a separatory funnel. This point is not mentioned by Chambers and Scherer but is rather important because the sodium iodide if not removed is converted in part to hydriodic acid on treatment with hydrochloric acid and the former acid, being somewhat soluble in ether, is very difficult to remove from the crystals of triphenyltin chloride. The ether solution of the chloride is also washed with water to remove excess hydrochloric acid. It is then dried over anhydrous sodium sulfate, evaporated down to separate out the crystals of the chloride and the compound recrystallized from ether and dried in air at room temperature.

A few attempts were made to use the iodide as a precipitant but it was found to be less soluble in alcohol than the chloride and the solution showed some decomposition on standing, turning brown after a few days. Twenty grams of the pure chloride was weighed out and shaken vigorously with one liter of 95% ethyl alcohol and any small residue left undissolved was filtered off. Twenty grams of chloride per liter apparently represents the limit of solubility at room temperature; the solubility increases with rising temperature. This solution containing approximately 0.02 g. of triphenyltin chloride per ml. was used for all of the precipitations.

Various methods of preparing standard solutions of fluoride have been proposed. Batchelder and Meloche[12] prepared sodium fluoride from sodium bicarbonate and redistilled hydrofluoric acid; Clarke and Bradshaw[13] prepared the standard fluoride from solutions of potassium fluoride and sodium chloride; Kurtenacker and Jurenka[14] titrated hydrofluoric acid with standard carbonate-free sodium hydroxide and Hawley[15] used

[8] Chambers and Scherer, THIS JOURNAL, **48**, 1054 (1926).

[9] Pfeiffer and Schnurmann, *Ber.*, **37**, 319 (1904).

[10] Krause, *ibid.*, **51**, 913 (1918).

[11] Chambers and Scherer, Ref. 8, p. 1055.

[12] Batchelder and Meloche, Ref. 2, p. 2132.

[13] Clarke and Bradshaw, *Analyst*, **57**, 138 (1932).

[14] Kurtenacker and Jurenka, *Z. anal. Chem.*, **82**, 210 (1930).

[15] Hawley, Ref. 4, p. 574.

sodium carbonate and hydrofluoric acid. An adaptation of Hawley's method was used in this investigation. Sodium carbonate, C. P., was treated with an excess of C. P. hydrofluoric acid in a platinum dish and allowed to stand for several hours. The excess acid was then driven off by heating and after cooling, the mass was again treated with an excess of acid. After thorough mixing and stirring the dish was heated gently at first and then intensely until the sodium fluoride was entirely fused. The fused salt was cooled in a desiccator over calcium chloride and then pulverized in an agate mortar. The powder was dried in a platinum dish at 110° for three days and stored in platinum over calcium chloride. That this salt was relatively pure was shown by converting samples to sodium sulfate; the results are recorded in Table I.

TABLE I

Trial	NaF, g.	Calcd. wt. Na_2SO_4, g.	Found wt. Na_2SO_4, g.	Variation, %
1	0.5749	0.9723	0.9699	−0.25
2	.4932	.8341	.8330	− .13
3	.2199	.3719	.3709	− .27

For the preparation of a standard solution, enough salt for a 0.1 *N* solution was weighed out, dissolved in distilled water and diluted up to a known volume in an accurately calibrated flask. The solution was at once transferred to a paraffin-lined bottle and portions of this solution measured out by calibrated pipets as used. For the smaller amounts of fluorine a 0.005 *N* solution was prepared from the 0.1 *N* one by dilution as needed. It was found, however, that the dilute solution could be kept in glass without undergoing any change that could be detected.

Procedure for Precipitation.—Some thirty precipitations were made in order to find out the optimum conditions for a quantitative formation of pure triphenyltin fluoride. In the course of these experiments it was observed that the precipitant came down with the fluoride if the water content of the sodium fluoride solution was too high, this, of course, being due to the insolubility of triphenyltin chloride in water. On the other hand, a too high concentration of alcohol in the solution caused low results and it was found that the fluoride was relatively soluble in 95% ethyl alcohol. In a number of trials the precipitate was washed on a Jena sintered-glass crucible with 50 ml. of alcohol and approximately 2.5 mg. of the substance was dissolved. This points to a solubility of about 0.05 g. per liter; obviously then pure alcohol cannot be used for washing nor can water. By holding the alcohol concentration between 60 and 70% by volume and washing with 95% alcohol saturated with the triphenyltin fluoride, checking results were secured. No loss in weight of the fluoride was observed on washing with ether but any triphenyltin chloride precipitated with the fluoride could not be washed out with ether or with the alcohol wash solution. It appears that in the case of precipitant coming down with the fluoride there is co-precipitation of a type so often met with in gravimetric analysis where the impurity cannot be removed by washing. The fluoride is so insoluble in water that the precipitate is not even wetted by it. Triphenyltin chloride melts at 106° but the fluoride does not melt when heated in the open; it sublimes with partial decomposition around 300°. Krause reports that it melts in a sealed tube at 357°. The pure fluoride is stable at 110° and is quickly dried at that temperature. Precipitates dried in glass crucibles overnight at 110° changed their weight less than 0.2 mg., this being the maximum change observed for precipitates weighing about 0.4 g. If the precipitate is contaminated with chloride, heating at 110° produces a garlic-like odor but the loss in weight on continued heating is not appreciable.

The proper procedure for precipitation follows: 95% ethyl alcohol is added to the aqueous solution of the fluoride so that it comprises 60 to 70% of the final volume and the solution is heated to boiling. About twice the calculated amount of the triphenyltin

chloride solution containing 0.02 g. per ml. is diluted with an equal volume of 95% alcohol and also heated to boiling; this solution is then slowly run into the hot fluoride solution with rapid stirring and the whole again heated to boiling. The heat is then removed and the stirring continued until the solution has cooled down somewhat. The beaker is covered and allowed to stand overnight to complete precipitation as the reaction is a slow one. If the quantity of fluoride is large the precipitate begins to form in about a minute after the addition of the reagent as large white crystals, but with small amounts it does not appear until the solution has cooled down to room temperature and the crystals are much smaller. After standing overnight the beaker containing the precipitate is packed in ice and allowed to stand for about an hour to lower the solubility of the fluoride in the solution. If the amount of fluoride is large and the total volume of solution is small this step is not necessary as the solubility of the precipitate in the solution containing about 40% water and an excess of the precipitant is very slight. The precipitate is filtered off through a Jena sintered-glass crucible or other similar type crucible and washed with 95% ethyl alcohol saturated with triphenyltin fluoride, the washing solution being at room temperature and about 50 ml. being used. The precipitate is dried for 30 minutes at 110°, cooled in a desiccator and then weighed. Triphenyltin fluoride shows no tendency to take up moisture.

Using the above procedure the results listed in Table II were obtained. This table gives a summary of all of the determinations made in order to show the variations that were encountered. The low gravimetric factor justifies the calculation of the weight of fluorine to the fifth place. The volumes of sodium fluoride and of reagent used are shown in Table III.

TABLE II

DETERMINATION OF FLUORINE AS TRIPHENYLTIN FLUORIDE

Factor $(C_6H_5)_3$ SnF to F = 0.05153

Trials	F pres., mg.	Range wt. prec., mg.	Range wt. F found, mg.	Av. error, mg.
1– 2	47.46	920.4–917.7	47.43–47.29	0.10
3– 7	18.96	368.9–366.1	19.01–18.87	.03
8–11	9.48	186.1–183.5	9.59– 9.46	.035
12–17	3.84	76.5– 75.1	3.94– 3.87	.07
18–21	0.96	20.1– 19.9	1.04– 1.03	.075
22–26	.95	19.5– 18.1	1.00– 0.93	.02
27–34	.47	10.4– 8.3	0.54– .43	.03
35–40	.19	4.0– 3.2	.21– .16	.01

TABLE III

Trials	NaF, ml.	*N* NaF	H_2O, ml.	Alcohol, ml.	Total vol., ml.	Reagent, ml.
1– 2	24.98	0.1000	5	60	90	60
3– 7	9.98	.1000	10	40	60	25
8–11	4.99	.1000	15	40	60	15
12–17	2.02	.1000	8	20	30	6
18–21	10.06	.00500	0	20	30	2
22–26	9.98	.00500	0	20	30	2
27–34	4.99	.00500	2	14	21	1
35–40	2.02	.00500	3	10	15	1

In Table IV are given results with very minute amounts of fluorine. In the first ten trials 1 ml. of 0.005 *N* sodium fluoride was measured from a

calibrated micro-buret and in the last five trials 0.5 ml. was used. Enough water was added to bring the volume up to 5 ml. and then 10 ml. of 95% alcohol, making the solution about 63% alcohol by volume. One ml. of the precipitant was used in each one of the trials. No precipitate could be detected until after standing overnight and then it was quite evident. Blanks treated in exactly the same manner as the fluoride solutions showed no signs of precipitates even after standing for several days. The weight of fluorine is calculated to the sixth place for the purpose of comparison; only the fifth place is justified by the data.

TABLE IV

DETERMINATION OF MINUTE QUANTITIES OF FLUORINE

Trials	Range wt. prec., mg.	Range wt. F found, mg.	F present, mg.	Av. error, mg.
1–10	2.0–1.4	0.103–0.072	0.095	0.0076
11–15	1.2–0.6	.062– .031	.048	.0081

If the last five trials in Table IV represent the limit of sensitivity of the method it is evident that the procedure may be successfully applied to quantities of fluorine down to 0.05 mg. Since the volume of solution used in these trials was 15 ml., this is a concentration of fluoride of one part in 300,000. On the other hand, the method does not lend itself so well to the determination of large quantities, both because of the large volume of reagent required and the bulk of the precipitate secured in such cases. With a weight of precipitate approaching one gram the results are erratic, hence the upper limit of fluorine that may be precipitated accurately is about 0.04 g.

Effect of Other Salts.—The solution of the fluoride to be precipitated should be at a P_H of 7 to 9; if acid some fluorine will be lost on heating to boiling and if too basic triphenyltin hydroxide will be precipitated along with the fluoride. The hydroxide is readily soluble in the wash solution but if too much comes down with the fluoride it is difficult to wash out. Adolph[16] has pointed out that very little, if any, fluorine is lost on evaporating or boiling neutral or alkaline solutions of sodium fluoride. A large number of inorganic salts are only slightly soluble in 60–70% alcohol and if present in high concentrations they will separate out when the solution cools down. In some work on the application of the method to the determination of fluorine in rocks, the solution to be precipitated contained a very large amount of sodium and potassium nitrates which crystallized out on cooling. It was found possible, however, to remove these salts by first washing the precipitate several times with the alcohol wash solution to remove the excess of precipitant and then with cold water to remove the salts. It has already been pointed out that the triphenyltin fluoride is extremely insoluble in water. A large amount of foreign salts appears to

[16] Adolph, *Z. anal. Chem.*, **55**, 395 (1916).

cause some of the chloride to come down with the precipitate, as the results tend to run high in such cases. If present in only moderate quantities nitrate, chloride, bromide, iodide and sulfate do not interfere. Carbonate should be removed by bringing to neutrality with dilute acid and boiling out the carbon dioxide. This is best done by neutralizing to phenolphthalein in the hot. Silicic acid and phosphate must be eliminated by prior treatment of the fluoride solution by the method of Berzelius or of Hoffman and Lundell.[17] These methods effect the complete removal of silicic acid through the use of ammoniacal zinc oxide.

A study of the influence of substances met with in the analysis of fluorspar and of rocks was made by preparing solutions of fluoride from the Bureau of Standards standard sample of fluorspar, No. 79. This sample contains 94.83% calcium fluoride or 46.20% fluorine.[18] Three samples of the fluorspar were treated by the method of Berzelius, all of the residues being fused a second time with sodium and potassium carbonates. The phosphate and a large part of the carbonate were removed by silver nitrate and the excess silver by potassium chloride; the carbonate was then completely removed by neutralizing with dilute nitric acid and boiling out the carbon dioxide. The resulting solutions were cooled and diluted up to 250 ml. in calibrated volumetric flasks; 10.06 ml. of each solution was pipetted out, 15 ml. of water and 50 ml. of 95% ethyl alcohol added and the fluoride precipitated in the regular manner. The results obtained appear in Table V.

TABLE V

RECOVERY OF FLUORINE FROM FLUORSPAR

Trials	Range wt. prec., mg.	Range wt. F found, mg.	F calcd., mg.	Av. error mg.
1–4	89.8– 89.0	4.63–4.59	4.51	0.10
5–8	113.5–110.8	5.85–5.71	5.75	.06
9–12	134.1–131.7	6.91–6.79	6.79	.08

The fluoride is recovered as triphenyltin fluoride to about 0.1 mg., but the accuracy is not as great as with solutions of pure fluoride and the variations are larger. The results run high as has been mentioned before. Further work on applications of the method to fluorspar and to rock analysis is now being carried out.

Disadvantages of the Method.—1. An uncommon and expensive reagent is used.

2. The sample must be of such a size that the amount of fluorine is below 0.04 g.

3. Care must be exercised to prevent precipitation of the reagent due to its insolubility in water.

[17] Hillebrand and Lundell, Ref. 5, pp. 800–807.

[18] Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, Inc., New York, 1931, pp. 562–572.

4. The precipitate is slightly soluble in alcohol and this necessitates washing with a saturated alcoholic solution of the precipitate.

5. Large amounts of foreign salts cause co-precipitation of the reagent and give high results.

Advantages of the Method.—1. It is particularly adapted to small amounts of fluorine due to the low conversion factor.

2. The precipitate is crystalline and is easily filtered and quickly washed.

3. The precipitate is stable and no ignitions have to be made.

4. Not counting the standing overnight, the time required for precipitation and further treatment of the precipitate to the final weighing is less than in any other gravimetric method for fluorine.

Acknowledgment.—This work was done under a fellowship grant in analytical chemistry from the J. T. Baker Chemical Company of Phillipsburg, N. J. Gratitude is here expressed for the aid given.

Summary

Fluorine may be quantitatively precipitated as triphenyltin fluoride as reported by Krause and Becker in 1920. The method is advantageous for small quantities of fluorine. The procedure for the precipitation and treatment of the fluoride is given.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

DIPOLE ROTATION IN CRYSTALLINE SOLIDS

BY C. P. SMYTH AND C. S. HITCHCOCK

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Another paper[1] has presented the results of a preliminary investigation of the possibility of contribution to the dielectric constant of a crystalline solid through the rotation of a polar group in a molecule fixed in the crystal lattice or through the rotation of the entire molecule in the lattice. It was found that heptyl bromide, hydroquinone dimethyl ether, and anisole showed no such contribution, while the apparent small contribution in phenol and benzoyl chloride was attributed to the effect of impurities. As it is the purpose of the present paper to extend this investigation with an improved apparatus, it is desirable to give some consideration of the factors involved.

It is evident that, if freezing fixes the molecules in the space lattice, dipoles fixed in the molecules cannot orient in an externally applied field and their contribution to the dielectric constant becomes zero. Accord-

[1] Kamerling and Smyth, unpublished.

ingly, on solidification the dielectric constant of a polar substance ordinarily drops sharply to a value arising from induced polarization alone, this polarization being usually but slightly higher than and sometimes indistinguishable from the molar refraction for visible light.

Debye[2] has shown how the dielectric constant of a polar liquid may decrease with increasing viscosity, decreasing temperature, and increasing frequency of the alternating field used in the measurement because of the increasing difficulty of the molecules orienting in the externally applied field. He has even found that this theory of anomalous dispersion gives an adequate explanation of the results of Errera and other investigators upon ice.[3] Errera found a more or less similar anomalous dispersion in a number of polar organic substances in the solid state, which made it appear that the molecules of these substances could turn in the solid state as if in a viscous liquid.

Pauling[4] used the quantum mechanics and specific heat data to show the rotation of molecules with small moments of inertia in the space lattice. The hydrogen, oxygen, nitrogen, carbon monoxide, methane and hydrogen halide molecules were shown to rotate at temperatures between the freezing points and certain regions of transition, and it was predicted that the dielectric constants of the solid hydrogen halides at temperatures just below the melting points would be very high and dependent upon the temperature, the values being given by Debye's theory of the orientation of dipole molecules, while the low-temperature forms would have low dielectric constants nearly independent of the temperature. This prediction was strikingly confirmed for hydrogen chloride by the measurements of Cone, Denison and Kemp,[5] who, using the high frequency of 3000 kilocycles, found that the dielectric constant of the solid just below the melting point was actually higher than that of the liquid although the polarization was slightly lower. The dielectric constant–temperature curve does not conform to the simple Debye equation, but gives evidence of some anomalous dispersion before it finally drops sharply at a transition temperature to a low value for the dielectric constant. Pauling further concluded that heat capacity measurements on the ammonium halides showed transitions corresponding to the transition from oscillation to rotation of the ammonium ions and that the ammonia molecules in $Ni(NH_3)_6Cl_2$, the water molecules in alum, and the aliphatic carbon chains in mono-alkyl substituted ammonium halides showed symmetry, when examined with x-rays, arising from the rotation of the molecule or group in the space lattice.

[2] See Debye, "Polar Molecules," The Chemical Catalog Company, Inc., New York, 1929, Chap. V.

[3] Errera, *J. phys. radium*, [6] **5**, 304 (1924); Granier, *Compt. rend.*, **179**, 1314 (1924); "International Critical Tables," 1929, Vol. VI.

[4] Pauling, *Phys. Rev.*, **36**, 430 (1930).

[5] Cone, Denison and Kemp, THIS JOURNAL, **53**, 1278 (1931).

All of these rotations involve moments of inertia small in comparison with those involved in the possible rotations of the molecules of the organic substances investigated by Errera, for even a zig-zag carbon chain has a surprisingly low moment of inertia around its long axis. The rotation of the molecule or group depends not only upon its moment of inertia but also upon a potential function representing the averaged interaction of the molecule with surrounding molecules. This function may be calculated roughly from specific heat data, but, in the absence of such data for most of the substances to be considered and in view of the very approximate character of the theoretical treatment, the magnitude of the moment of inertia may be regarded as a rough criterion of the improbability of rotation. Evidently, only such molecular or group rotations should occur in a crystalline solid as involve small moments of inertia and internal fields and these may be studied by means of the dielectric constant when the molecule or group contains a dipole. Since the apparent conductance of a material may give quantitative evidence of anomalous dispersion, the conductance of the solids has been measured simultaneously with the dielectric constants at frequencies from 300 to 60,000 cycles.

Apparatus.—The capacity bridge used in the measurements was a slight modification of the instrument previously described.[1,6] The resistance in series with the condenser in each of the two capacity arms was replaced by a parallel resistance in the other capacity arm. Each of these resistances was a non-inductively wound 10,000-ohm General Radio Company Type 102-J decade box. The bridge could now be balanced much more accurately than formerly when a material of some conductance was in the measuring condenser. The resistance R of the condenser filled with the substance under investigation was calculated simply from the values of the two parallel resistances and the specific conductance k (ohm^{-1} cm.$^{-1}$) of the material was calculated by means of the equation[7]

$$k = \frac{0.0885}{C_0 R}$$

in which C_0 is the geometrical capacity in micromicrofarads of the condenser as obtained in the calibration for the calculation of the dielectric constant. The condensers used were the cylindrical type described previously,[8] a very small one being employed for ice and two large cells, one with gold cylinders, being used on the other substances. A platinum resistance thermometer was used to measure the temperature of the bath surrounding the cell and, in the measurements upon ethylene chloride, phenol and benzene, a second thermometer was placed in the center of the

[6] Smyth and Kamerling, THIS JOURNAL, **53**, 2988 (1931).

[7] Debye, "Polar Molecules," The Chemical Catalog Co., Inc., New York, 1929, p. 99; Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

[8] Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).

cell. The general procedure and technique was similar to that previously outlined.[1,6]

Purification of Materials

Nitrobenzene.—Merck "Pure" nitrobenzene was three times crystallized, twice dried with phosphorus pentoxide and fractionally distilled under reduced pressure; m. p. 5.67°; n_D^{20} 1.55261.

Aniline.—Merck C. P. aniline was twice fractionally distilled and once recrystallized from its own melt; b. p. 183.7° (754.5 mm.); m. p. −6.15°; n_D^{20} 1.58610.

Phenol.—The best sample was obtained by fractional distillation of Merck C. P. phenol and two recrystallizations of the material from its own melt; b. p. 181.9° (761 mm.); m. p. 40.7°.

Ethylene Chloride.—The same material used in earlier work;[9] b. p. 83.5–83.7°; n_D^{20} 1.44476.

Water.—Conductivity water of specific conductance 2×10^{-6} ohm^{-1} cm.$^{-1}$ was used.

Benzene.—Purified as in earlier work.[10]

Dimethyl Sulfate.—Eastman "Practical" dimethyl sulfate was fractionally distilled five times under reduced pressure, the last two times from over calcium oxide; b. p. 72.5–72.7° (13 mm.); m. p. −31.4°; n_D^{20} 1.38738. A cooling curve showed that solidification occurred within a range of 0.3°.

Diethyl Sulfate.—Eastman "Practical" ethyl sulfate was fractionally distilled three times under reduced pressure, the third time from over calcium oxide; b. p. 93.0–93.2° (13 mm.); m. p. −25.2°; n_D^{20} 1.40010. A cooling curve showed that solidification occurred within a range of 1°.

Experimental Results

A large number of determinations have been made at frequencies from 300 to 60,000 cycles over a wide range of temperature upon substances in both the solid and the liquid state, in different stages of purification, and, in some cases, at different intervals of time after solidification. Only such determinations are included in this paper as are needed to show the dependence of the dielectric constant and, at times, the conductance upon the different variables. For example, the dielectric constant of nitrobenzene is so nearly independent of frequency in the range studied that the values are given at 60,000 and at 500 cycles only, and, similarly, the conductance is not followed throughout its entire course. As the dielectric constant is determined for a large aggregate of crystals, it represents a roughly weighted mean of the values for the different crystal axes. Also its value may be low because of the presence of pockets and interstices between the crystals, which, of course, cause errors in the conductance also. These errors do not, however, impair the value of the data for the purposes of the present investigation.

The dielectric constants ϵ and the specific conductances k (ohm^{-1} cm.$^{-1}$) are given in Table I, the temperatures being given in the first column and the frequencies in kilocycles across the top of each group of data.

[9] Smyth, Dornte and Wilson, THIS JOURNAL, **53**, 4242 (1931).

[10] Smyth and Rogers, *ibid.*, **52**, 2227 (1930).

TABLE I

DIELECTRIC CONSTANTS AND SPECIFIC CONDUCTANCES

Nitrobenzene (m. p. 5.67°)

k.c. = t, °C.	60 ϵ	0.5 ϵ	60 k(× 10⁹)	0.5 k(× 10⁹)
−10	3.14	3.23	<0.1 throughout	
0	3.25	3.38		
4	3.34	3.51		
5	3.62	3.96		0.085
5.5	4.2	4.6	0.9	.21
	Liquid			
5	36.0	36.2		8.3
6	35.8	35.9		8.4
8	35.5	35.6		8.6
10	35.2	35.3		8.9
20	33.3	33.4		10.8
30	31.6	31.8		12.9

Ethylene Chloride (m. p. −35.3°)

t, °C.	60 ϵ	5 ϵ	1 ϵ	0.5 ϵ	60−0.5 k (× 10⁹)
−60	2.56	2.56	2.57	2.58	<0.1 throughout
−50	2.57	2.57	2.59	2.61	
−40	2.63	2.63	2.65	2.66	
−38	2.85	2.85	2.88	2.90	
−36	3.26	3.27	3.33	3.39	

Aniline (m. p. −6.15°)

k.c. = t, °C.	60 ϵ	5 ϵ	1 ϵ	0.5 ϵ	0.3 ϵ	60 k(× 10⁹)	5 k(× 10⁹)	1 k(× 10⁹)	0.5 k(× 10⁹)	0.3 k(× 10⁹)
−70	3.32	3.32	3.33	3.33	3.33		<0.1 throughout			
−50	3.44	3.44	3.45	3.46	3.46		<0.1 throughout			
−30	3.60	3.63	3.66	3.68	3.69	0.34	0.09	0.025	0.02	0.02
−20	3.69	3.70	3.72	3.74	3.76	.43	.15	.05	.03	.025
−10	3.82	3.90	4.06	4.15	4.23	.68	.34	.17	.13	.10
− 8	3.88	3.97	4.20	4.42	4.49	.85	.6	.29	.14	.10
− 7	3.94	4.04	4.38	4.61	4.81	1.1	.68	.31	.21	.15
				Liquid						
− 5	7.51	7.51	7.60	7.66	7.76	4.75	4.9	4.9	4.85	4.85
0	7.35	7.37	7.47	7.56	7.64	6.3	5.9	5.8	5.8	5.8
20	6.78	6.80	6.97	7.07	7.17	10.5	10.2	10.0	9.95	9.95

Phenol (m. p. 40.7°)

k.c. = t, °C.	60 ϵ	5 ϵ	1 ϵ	0.5 ϵ	0.3 ϵ	60 k(× 10⁹)	5 k(× 10⁹)	1 k(× 10⁹)	0.5 k(× 10⁹)	0.3 k(× 10⁹)
−60	2.68	2.68	2.66	2.66	2.66					
−40	2.69	2.70	2.69	2.69	2.69	0.85				
−20	2.70	2.73	2.75	2.77	2.79	0.85	0.06	0.03	0.03	
−10	2.71	2.75	2.79	2.83	2.88	1	.15	.06	.03	0.03
0	2.73	2.78	2.84	2.88	2.94	1.7	.21	.09	.06	.03
10	2.74	2.80	2.90	2.96	3.01	2	.30	.15	.09	.09
20	2.75	2.81	2.92	2.98	3.04	2.5	.32	.15	.09	.09
30	2.79	2.84	3.00	3.09	3.16	2.5	.42	.21	.15	.15
35	2.80	2.86	2.96	3.02	3.12	2.5	.36	.15	.12	.12
38	2.84	2.92	3.05	3.13	3.20	3.4	.33	.15	.09	.09
40	3.02	3.14	3.27	3.37	3.48	3.9	.45	.18	.15	.12
40.5	3.23	3.52	3.82	3.99	4.13	6.5	.86	.38	.30	.27
				Liquid						
45	10.30	10.59	11.06	11.55	11.91	45.5	40.4	40.1	40.1	40.1

Ice (m. p. 0°)

k.c. = t, °C.	60 ϵ	20 ϵ	5 ϵ	1 ϵ	0.5 ϵ	0.3 ϵ	60 k(× 10⁸)	20 k(× 10⁸)	5 k(× 10⁸)	1 k(× 10⁸)	0.5 k(× 10⁸)	0.3 k(× 10⁸)
−70	2.98	2.97	2.99	3.33	3.59	4.00	1.1	0.11	0.11	0.069	0.052	0.052
−60	3.00	3.00	3.12	3.50	3.92	4.35	1.2	.24	.16	.11	.086	.086
−50	3.02	3.04	3.21	3.82	4.65	6.17	1.37	.43	.29	.24	.21	.21
−40	3.03	3.06	3.32	5.37	8.78	16.3	2.58	.89	.69	.58	.55	.48
−30	3.04	3.15	4.06	14.6	31.3	46.2	3.33	2.06	1.84	1.48	1.18	.62
−20	3.12	3.57	7.60	45.2	65.9	71.9	6.7	5.5	4.55	2.14	0.86	.31
−10	3.33	5.46	24.4	69.4	73.6	74.8	15.6	12.7	9.0	1.25	.40	.10
− 5	3.71	8.34	40.2	72.5	73.8	73.6	23.7	19.7	9.86	0.81	.20	.07
− 3	4.2	10.4	46.3	72.4	73.5	74.2	27.5	23.3	9.62	.65	.17	.052
− 1	4.3	12.3	51.6	72.5	73.6	73.7	29.9	25.6	8.85	.57	.17	.086

TABLE I (*Continued*)

0.0002 *M* KCl Solution (−0.0007°; eutectic point, −10.8°)

k.c. = *t*, °C.	60	20	5	1	0.5	0.3	60	20	5	1	0.5	0.3
			ε (Falling temperature)						k (× 10^8)			
−70	3.04	3.24	4.32	9.06	11.5	15.6	2.6	1.29	0.86	0.51	0.41	0.33
−60	3.15	3.68	5.41	11.4	17.0	23.2	3.78	2.27	1.32	.74	.57	.43
−50	3.35	4.21	6.72	15.5	24.5	32.0	4.98	3.26	1.89	1.05	.74	.57
−40	3.64	4.80	8.12	22.2	37.4	50.1	7.12	4.36	2.74	1.57	1.13	.76
−30	3.93	5.32	10.4	39.0	63.4	75.7	9.35	6.35	4.46	2.32	1.34	.76
−20	4.08	6.13	17.3	62.5	84.4	93.2	14.2	10.5	7.4	2.4	1.24	.67
−10	4.20	8.27	34.5	90.8	112	121	23.7	19.2	12.0	2.74	1.49	.95
− 5	4.55	11.3	47.8	102	123	134	31.0	26.9	13.5	3.26	1.8	1.17
− 3	4.98	13.0	53.3	111	136	149	37.8	30.0	14.9	3.78	2.24	1.41
− 1	5.3	15.2	61.5	128	158	176	44.6	37.8	17.2	4.8	2.98	1.89
			(Rising temperature)									
−40	3.64	4.78	8.11	22.4	37.1	51.5	6.7	4.3	2.7	1.5	1.1	0.69
−20	4.07	5.98	17.3	64.0	82.9	89.9	14.2	9.8	7.4	2.35	1.03	.55
−10	4.36	8.90	36.2	84.9	96.5	103	23.7	19.4	11.0	1.85	1.05	.62
− 3	5.53	15.2	55.6	91.1	102	107	36.0	29.2	11.2	1.9	1.03	.69
− 1	6.05	17.0	61.6	93.2	103	110	41.2	32.6	11.2	1.99	1.12	.79

Benzene (m. p. 5.4°)

k.c. = *t*, °C.	60	5	1	0.3
		ε		
0	2.307	2.307	2.309	2.306
5	2.316	2.313	2.319	2.319
		Liquid		
5	2.341	2.344	2.347	2.344

Benzene saturated with water (0.01–5%) (f. p. 5.4°)

t, °C.	60	5	1	0.3
		ε		
−50	2.318	2.322	2.321	2.327
−30	2.335	2.340	2.346	2.354
−10	2.352	2.362	2.381	2.404
0	2.362	2.376	2.401	2.437
5	2.372	2.389	2.418	2.455
		Liquid		
25	2.310	2.312	2.319	2.332

Dimethyl Sulfate (m. p. −31.4°)

k.c. = *t*, °C.	60	20	5	1	0.5	0.3	60	20	5	1	0.5	0.3
			ε						k (× 10^8)			
−90	2.98	2.99	3.03	3.06	3.09	3.14			< 0.01			
−80	3.02	3.02	3.10	3.16	3.21	3.26			< .01			
−75	3.06	3.06	3.12	3.21	3.25	3.28			< .01			
−72	3.07	3.09	3.13	3.21	3.28	3.35			< .01			
−70 (Rising temp.)	3.09	3.10	3.17	3.22	3.27	3.38			< .01			
−70 (Falling temp.)	8.25	8.22	8.17	8.32	8.50	8.57		0.089	0.053	0.018	0.018	
−65 (1 hr. after transition)	9.29	9.28	9.42	10.39	10.97	11.47	0.35	.35	.18	.09	.05	0.035
−65 (5 hrs. after transition)	7.50	7.60	7.85	8.78	9.55	10.20	.71	.35	.27	.14	.12	.11
−60	8.02	7.97	8.06	8.40	8.69	9.00	.36	.18	.089	.036	.036	.018
−50	7.88	7.90	8.09	8.76	9.29	9.87	.36	.36	.20	.089	.071	.053
−40	7.89	7.98	8.32	9.35	10.21	10.98	.89	.53	.34	.18	.14	.12
−35	8.01	8.13	8.60	10.03	11.04	11.90	.89	.71	.50	.32	.27	.25
−33	8.34	8.51	9.19	11.15	12.52	13.55	1.8	1.1	.71	.46	.41	.37
−32	8.62	8.86	9.70	11.95	13.45	14.70	1.8	1.4	.93	.62	.57	.53
						Liquid						
−30	60.2	60.1	60.3	61.5	62.6	64.0			10			
−20	55.8	55.8	56.0	57.8	59.4	61.3			14			
0	48.3	48.3	48.9	51.4	53.5	55.9			25			
20	42.6	42.7	43.8	47.2	50.6	55.8			37			

TABLE I (*Concluded*)

Diethyl Sulfate (m. p. −25.2°)

k.c. =	60	5	1	0.5	0.3	60	5	1	0.5	0.3
t, °C.			ϵ					k (× 10^8)		
−70	2.91	2.91	2.96	3.15	3.24		0.035	0.018	0.018	
−50	3.24	3.30	3.60	3.98	4.24		.089	.053	.035	0.035
−40	3.44	3.54	4.01	4.47	4.87		.14	.071	.053	.053
−30	4.06	4.18	4.93	5.63	6.33	0.18	.18	.12	.09	.09
−28	4.65	4.79	5.63	6.54	7.24	.35	.25	.18	.14	.12
								Liquid		
−25	37.5	37.5	37.6	38.1	38.6			2.3		
−20	36.4	36.4	36.7	37.4	37.8			2.7		
0	32.7	32.7	33.2	33.8	34.4			3.6		
20	29.2	29.4	31.0	32.4	33.6			7.4		

Discussion of Results

The behavior of nitrobenzene, which has a moment 3.9×10^{-18}, is typical of the normal pure polar substance, the difference between the values at 60 and at 0.5 kilocycles being too small to be evident in Fig. 1. The dielectric constant rises with falling temperature as required by the Debye equation until solidification occurs, when it drops sharply. There is no abnormality in the curve for the liquid just above the freezing point or supercooled a little below it, which argues strongly against any suddenly increased formation of aggregates in this region, as such formation would almost certainly alter greatly the effect of the large dipoles in the molecules and change the course of the curve. The considerable decrease in the dielectric constant and in the conductance of the solid as the temperature falls just below the freezing point is probably due to the disappearance of a trace of liquid arising from the presence of minute quantities of impurities. The continued slow decrease as the temperature decreases further is a phenomenon observed in all of the solids in Table I. It may be due to the displacement of a very small number of ions, which becomes less as decreasing temperature renders the structure more rigid and becomes greater

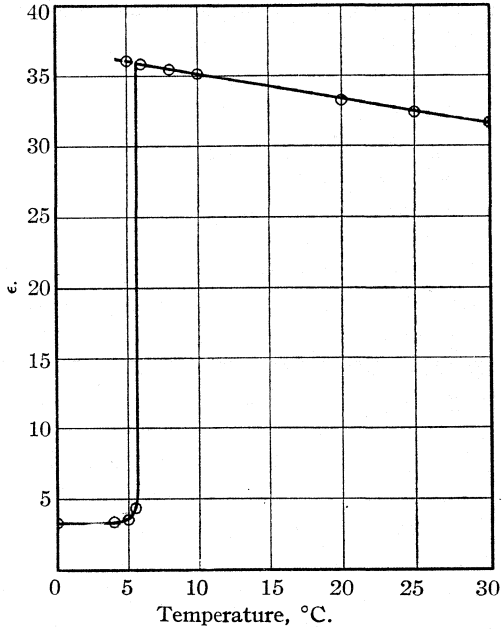


Fig. 1.—Variation of the dielectric constant of nitrobenzene with temperature (500–60,000 cycles).

as decreasing frequency of the applied field gives more time for the process of displacement to continue, thus causing a slight increase in dielectric constant with decreasing frequency as generally observed in Table I. This latter effect is just distinguishable in liquid nitrobenzene, but is very strong in liquid dimethyl sulfate, which has a much higher conductance, and to a lesser extent in diethyl sulfate. It was also very apparent in unreported measurements made upon an impure sample of acetic acid, which had a considerable conductance. It is not impossible that an occasional molecule in the solid may possess sufficient freedom of motion to orient in the field, an orientation which, of course, would be more difficult the lower the temperature and the higher the frequency. Although no great accuracy is claimed for these conductance measurements, it is interesting to note that those for the liquid lie within the range of the values given in "International Critical Tables," $2 \times 10^{-7} - < 2 \times 10^{-10}$.

The dielectric constant of the solid is much lower and shows much less variation with frequency than the values found by Errera,[3] a difference attributable to the presence of impurities in the material used in the latter's measurements. There is nothing to suggest the extraordinary behavior reported by Wolfke and Mazur,[11] whose values for the dielectric constant of liquid nitrobenzene are in excellent agreement with those in Table I above 9.5°. Below this temperature, however, their values drop rapidly to 10.973 at 6.01°, show a slight rise on solidification, 11.365 at 5.50°, and decrease only to 9.709 at −75°. It is very difficult to picture the large nitrobenzene molecules as possessing sufficient freedom of motion in the solid state to give so large a dielectric constant. Wolfke and Mazur determined an energy change of 0.14 cal. per gram as accompanying a transformation from one liquid phase to another at 9.5°. Calculation from this heat of transformation shows that only 0.00043 mole fraction of impurity would be required to lower this transition down to the freezing point, below which it would not occur. A similar calculation shows that this same amount of impurity would lower the freezing point only 0.024°. The observed melting point of our material 5.67° is in satisfactory agreement with that given in "International Critical Tables," 5.72 ± 0.10°, and higher than the value 5.5° reported by Mazur.[12] Although it is evident that there may be enough impurity in our material to prevent the occurrence of a transition, the melting point found by Mazur would seem to indicate the presence of a greater amount of impurity in his material. Other investigators[13] have failed to find discontinuities in other physical properties of liquid nitrobenzene as found by Wolfke and Mazur.

[11] Wolfke and Mazur, *Z. Physik*, **74**, 110 (1932); Mazur, *Nature*, **126**, 993 (1930).

[12] Mazur, *ibid.*, **127**, 893 (1931).

[13] Masson, *ibid.*, **128**, 726 (1931); Massy, Warren and Wolfenden, *J. Chem. Soc.*, 91 (1932); Friend, *Nature*, **129**, 471 (1932).

If the dielectric constant of solid nitrobenzene is taken as 3.1 and the density of the solid at 0° given by "International Critical Tables" as 1.2229 is used, the polarization, $P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$, is calculated as 42.1, while the molar refraction of the liquid extrapolated to infinite wave length is 31.6. The atomic polarization P_A, calculated as the difference 10.5, is slightly higher than the value 8 previously reported,[14] and is probably too high because of the effect which produces increase of dielectric constant with rising temperature and decreasing frequency. These results tell nothing as to the possible rotation of the nitro group about its bond to the ring because the moment of the group lies in the axis of possible rotation,[15] but they do show that the molecules are firmly fixed in the space lattice with certainly little and, probably, no opportunity of rotation.

Solid ethylene chloride resembles nitrobenzene in behavior. The effect of temperature and frequency upon the dielectric constant is less at temperatures well removed from the melting point. A value of 1.44 was determined for the density of the solid at the melting point, which made possible the calculation of the polarization as 23.8, and of P_A as 3.0. This shows clearly that the externally applied field does not produce rotation of the molecule as a whole or, to any extent, of the two halves of the molecule relatively to one another. The latter point is interesting in view of the fact that the temperature variation of the moment of the molecule in solution and in the gaseous state has shown that here the two halves of the molecule oscillate about the C–C line as axis.[16]

The aniline molecule has a moment, 1.56×10^{-18}, and, as the two N–H bonds lie in a different plane from the C–N, rotation around the latter bond as axis would alter the orientation of the resultant dipole. Aniline resembles nitrobenzene in behavior, showing no abnormality just above the melting point, the same sharp drop in dielectric constant and conductance on freezing and the same slowing up of the decrease in the values as the temperature is lowered. However, at −70°, the decrease of dielectric constant with falling temperature is still pronounced, although the variation with frequency has almost disappeared, and the values are high for so low a temperature. This suggests that there may be some turning of the NH_2 group to effect a partial dipole orientation in the field, which would, of course, contribute to the dielectric constant. The small moment of inertia of the NH_2 group about the C–N line should make this easy, unless the internal field is strong. However, if decreasing temperature is decreasing the contribution of this dipole orientation to the dielectric con-

[14] See Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931, p. 164.

[15] Ref. 14, p. 121.

[16] Smyth, Dornte and Wilson, THIS JOURNAL, 53, 4242 (1931); Zahn, *Phys. Rev.*, 38, 521 (1931).

stant, increasing frequency should also cause it to decrease. As it does not do so to an appreciable extent at the low temperature, it appears improbable that the dielectric constant receives any contribution from dipole orientation through rotation.

The general course of the values for phenol in Table I is similar to those for aniline and nitrobenzene. The apparent anomalous dispersion just below the melting point is presumably due to water, which is very difficult to remove and is certainly present in small amount. The presence of water is also probably responsible for slight humps in the curves at low frequencies between 20 and 30°and for the fact that the curves at low frequencies obtained with rising temperature, the data for which are not given in Table I, lie slightly above those obtained with falling temperature. A difference between the curves obtained with falling and with rising temperature is commonly observed when impurities are present because of delay in the attainment of equilibrium in the solid. A difference was hardly detectable in the case of the other substances which have been discussed.

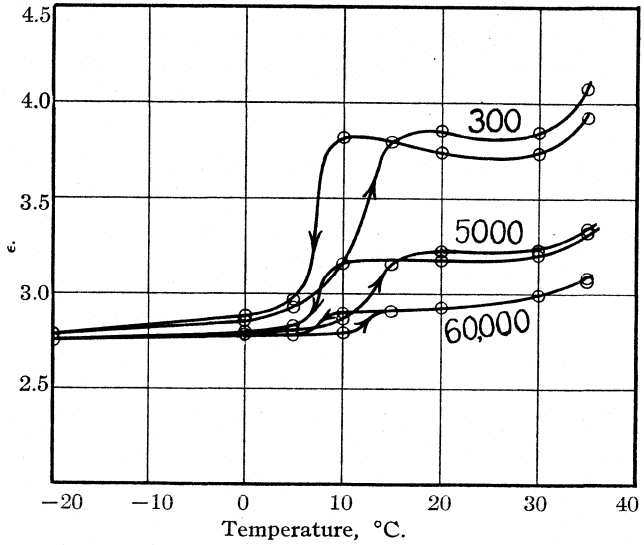


Fig. 2.—Variation with temperature and frequency of the dielectric constant of phenol containing a small quantity of water.

Another more thoroughly dried sample had the same freezing point and gave values close to those in Table I. A less pure sample of freezing point 40.5° gave the curious curves shown in Fig. 2, which are similar to those obtained for another sample of about the same purity. The curves marked with arrows pointing down along them represent values obtained with falling temperature and those with arrows pointing up values obtained with rising

temperature. The curves at each frequency form a sort of hysteresis loop starting at 15° and ending at about 5°. The conductance curves not shown have somewhat similar loops closing at 5° but clearly defined at the upper end only in the case of the higher frequencies. Rhodes and Markley,[17] investigating the system phenol–water, obtained a melting point 40.8° for carefully purified phenol and found that on adding water to phenol a eutectic point was reached at 15.9°. Below this point, however, the curve could be extended to represent a metastable equilibrium so that, in an area extending down to −1.2°, solid phenol could exist in metastable equilibrium with a solution of water in phenol. The curves in Fig. 2 indicate that the material contains liquid, a solution of water in phenol, which, as the temperature is lowered, begins to solidify rapidly at 10° and has practically all solidified at 5°. With rising temperature liquid begins to form just below 10° causing the sharp rise in dielectric constant and conductance up to the eutectic point for stable equilibrium, above which no sharp change occurs until the melting point is approached. If 40.8° is the freezing point of pure phenol, the curve obtained by Rhodes and Markley shows that our material of freezing point 40.7° contains about 0.026% water and the less pure material of f. p. 40.5° about 0.078%, all the impurity present being assumed to be water. In spite of the low moment of inertia of the O–H group about the C–O line, there is no definite evidence in Table I of a contribution to the dielectric constant through rotation of the O–H dipole, although the possibility of orientation of an occasional group or molecule in the field is not excluded.

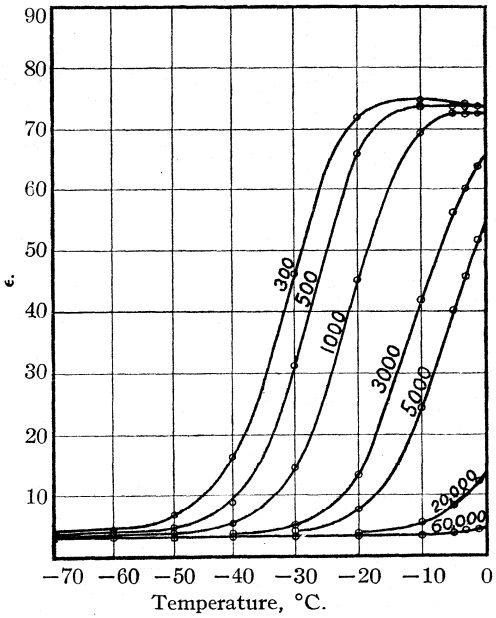


Fig. 3.—Variation of the dielectric constant of ice with temperature and frequency.

Ice was first prepared from distilled water, then from conductivity water, which gave somewhat lower values of the dielectric constant, and finally from conductivity water after long soaking and rinsing of the cell. This last ice had a slightly lower dielectric constant than that made from

[17] Rhodes and Markley, *J. Phys. Chem.*, **25**, 527 (1921).

the first conductivity water and no change was effected by further soaking and rinsing of the cell. The values in Table I and Fig. 3 are for a very pure ice.

The curves for ice are like those for a very viscous liquid. At the lowest frequencies, the dielectric constant is close to that of liquid water, and, for the first few degrees of temperature decrease, actually rises as the lessened thermal motion interferes less with the orientation of the polar molecules in the external field. As the temperature is further lowered, the increasing rigidity of the structure reduces molecular orientation until,

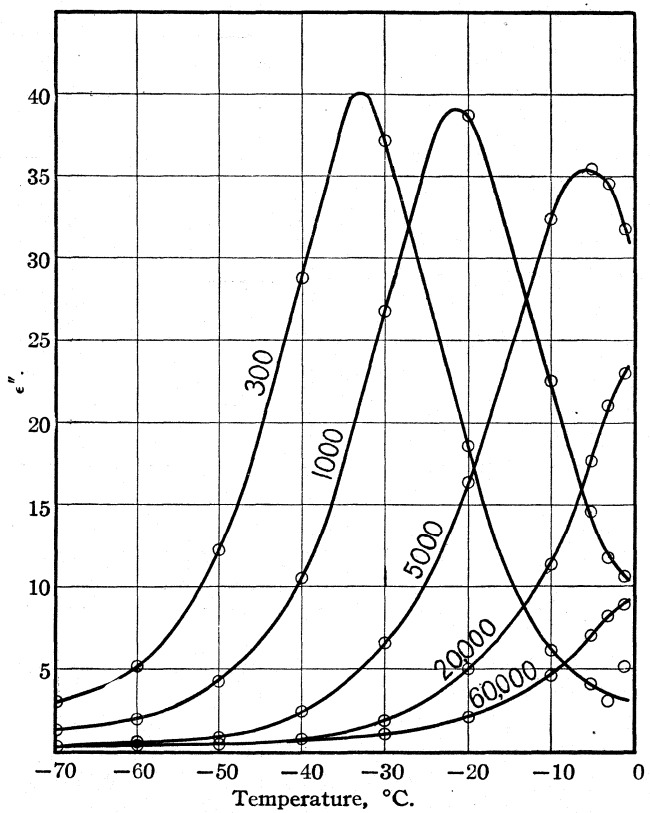


Fig. 4.—Variation of ϵ'' for ice with temperature and frequency.

at $-70°$, the dipole of moment 1.85×10^{-18} contributes little to the dielectric constant even at low frequency. At 60,000 cycles even just below the melting point, so little time is given the molecule to turn that the dipole contributes little more to the dielectric constant than at $-70°$ and 300 cycles. The anomalous dispersion is best shown by plotting the values of ϵ'' for each frequency against temperature (Fig. 4). ϵ'' is shown in the

equation $\epsilon = \epsilon' - i\epsilon''$, in which the first term on the right is the real part and the second the imaginary part of the dielectric constant.[18] It is calculated by means of the equation[19] $\epsilon'' = 9 \times 10^{11}(2k/f)$, in which k is the conductance and f the frequency in cycles. These curves make clear the fact that we are dealing with a typical anomalous dispersion, the maximum moving to lower temperature as the frequency decreases. Evidently the molecules possess a certain freedom of rotation which diminishes gradually as the temperature is lowered. There is no abrupt disappearance of this freedom of rotation as in the case of hydrogen chloride. The existence of rotation at these temperatures is consistent with the small moment of inertia of the molecule.

In view of the evident influence of small quantities of impurities upon the results, it seemed desirable to investigate ice with a known quantity of impurity. A 0.0002 M solution of potassium chloride in some of the same conductivity water, containing one potassium chloride to every 278,000 water molecules, was, therefore, frozen in the cell. The calculated freezing point, $-0.0007°$, was indistinguishable in these measurements from that of pure water. The rather high eutectic point, $-10.8°$, assured the absence of liquid throughout most of the range of the measurements. The dielectric constant curves obtained at four frequencies are plotted in Fig. 5 as broken lines, arrows pointing down along the curves indicating measurements taken with falling temperature. The solid lines are similar curves for pure ice given for comparison, the values obtained with falling and with rising temperature being approximately the same. The minute amount of potassium chloride increases the dielectric constant to a surprising extent at the low frequencies, but has relatively little effect at 60,000 cycles. No alteration in the trend of the curves is apparent at the

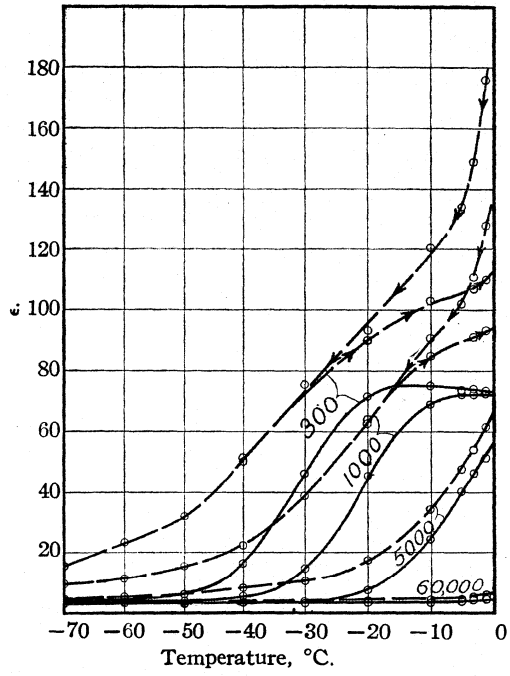


Fig. 5.—Variation of the dielectric constant of frozen 0.0002 M KCl solution.

[18] Ref. 2, p. 94.

[19] *Cf.* Ref. 2, p. 99.

eutectic point and the lower curves obtained with rising temperature at the low frequencies show that a long time is required for the attainment of equilibrium in the solid. At frequencies of 5000 and more the rising and falling curves are too close together to be distinguishable from each other. It appears that the increase in dielectric constant is due to the displacement of the ionic charges by the field, which is greater the longer the time in which the field acts in one direction. The conductance is increased by the potassium chloride ten-fold in the liquid to 2.2×10^{-5} and to a smaller extent in the solid.

When water saturated with benzene (0.15%) at 0° was frozen and measured, the dielectric constant and conductance values obtained were the same as those of pure ice and the conductance of the liquid was also indistinguishable from that of pure water. This is to be expected as the amount of benzene present is insufficient to dilute the water enough to alter these properties by a detectable amount and as no ions or dipoles are introduced by it. The effect of saturating benzene with water is shown by the data in Table I. As the benzene, saturated with water at room temperature, was slightly cloudy with separated water at the freezing point, the total water content was probably about 0.05%, although the solubility at 5.4° obtained by extrapolation is 0.008%.[20] Pure benzene shows practically no change of dielectric constant with frequency either in the solid or in the liquid and a conductance too small to measure, but the benzene saturated with water shows a markedly higher dielectric constant,[21] a conductance of the order of 2×10^{-10}, and variation with frequency particularly just below the freezing point, as would be expected. It is easy to see, therefore, how a substance containing a small amount of water as impurity, particularly, a substance which may hydrolyze to give ionic impurities, may show a considerable apparent anomalous dispersion when the pure substance would show none.

Four different samples of methyl sulfate were studied, the third and fourth of which were moderately pure as indicated by the freezing point curve. The results for the third sample, which were in good agreement with those for the fourth, are given in Table I with values for the second sample at the lowest temperatures, where impurities caused but little error. The two sets of values at −65° were determined for the fourth sample during five hours' standing at −65° and are not directly comparable with the other values. Although, as previously remarked, the high dielectric constant curves for the liquid (moment = 3.3×10^{-18}) at different frequencies (Fig. 6) are somewhat separated from one another, probably because of the displacement of ionic impurities, they rise with falling temperature in accordance with the Debye equation. The sharp drop on

[20] See Seidell, "Solubilities," New York, D. Van Nostrand Company, Inc., 1928.

[21] *Cf.* Williams, *Physik. Z.*, **29**, 204 (1928).

solidification does not extend as low as with the other polar substances and the dielectric constant is obviously too large to arise from an ordinary induced polarization, which suggests the occurrence of some dipole orientation. The values are much lower than those found by Errera for the solid, which must have contained considerable quantities of impurities. The separation of the curves and downward slope of those for low frequencies below the freezing point is probably due to displacement of ionic impurities

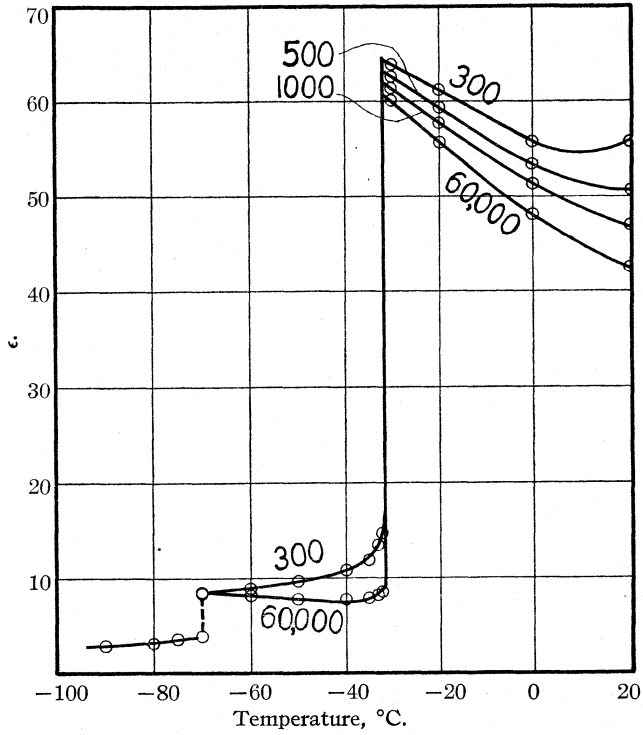
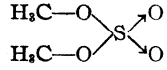


Fig. 6.—Variation of the dielectric constant of dimethyl sulfate with temperature and frequency.

as in cases previously discussed. At frequencies of 60,000 and 20,000 (not shown) cycles, where the effect of ions has been shown to be small, the curves rise with falling temperature in such a way as to support the indication of dipole orientation given by the high values of the dielectric constant. At −70° the curves drop sharply to values like those obtained for the other solids at low temperatures and, below −70°, resemble these other curves. Cooling curves run on two samples of the solid show a transition beginning at −71.0° and heating curves on the same samples a transition at −68.0°. This explains the high value of the dielectric constant found at −70° with falling temperature while a low value is found with rising temperature.

The transition from the state of lower dielectric constant to that of higher brings about an abnormally high initial value of the constant which decreases somewhat on standing as shown by the values at $-65°$ one hour and five hours after the substance had been brought to the transition temperature. Possibly the transition brings about a temporary loosening of the structure which facilitates the dipole orientation apparently occurring above the transition point.

The transition appears to resemble that predicted by Pauling and found by Cone, Denison and Kemp for hydrogen chloride. However, the sharp drop on solidification and the subsequent absence of marked anomalous dispersion show that dipole orientation in the solid cannot come from turning of the molecule freely in the alternating field unless such turning is limited to certain axes. It is more natural, however, in view of the large moment of inertia of the molecule, to seek rotation in a group of small inertia within the molecule. The only rotation which can give rise to dipole orientation within the molecule  is that of the two methoxy groups around the S–O bonds as axes. Although no evidence has been obtained of rotation of the methoxy group in solid anisole and hydroquinone dimethyl ether,[1] it is quite possible that the different molecular spacing and internal field in dimethyl sulfate should permit the rotation of the polar CH_3–O group, the moment of inertia of which about the line of the S–O bond is not large.

The remote possibility had been considered that the sharp drop in dielectric constant and conductance at $-70°$ might be due to the solidification here of a small quantity of a liquid phase containing sulfuric acid, but the complete absence of any such effect in the less pure diethyl sulfate eliminated this possibility. The curves for the latter substance drop sharply on solidification to values like those usually found for solids and, presumably, containing no contribution from dipole orientation. This is not surprising as the rotation of the ethoxy group is less probable than that of the methoxy because of its greater moment of inertia and the greater possibility of the larger groups' interfering with one another's rotation.

The results of this investigation show that there is no suddenly increased formation of molecular aggregates in the liquids here studied as the freezing point is approached. They show the tremendous effect that very small quantities of impurities may have upon the dielectric constant of a solid measured at low frequencies and thus give warning of the care which must be used in interpreting the results of such measurements. They also suggest the dielectric constant as a very sensitive instrument for the investigation of some equilibria and transitions in solids. No evidence has been found of the free rotation of large polar molecules in solids, although it is not impossible that the methyl sulfate molecules should rotate around

certain axes. The high dielectric constants found by Errera for such solids must be attributed to the presence of impurities. However, the occasional rotation of a large molecule in a solid, particularly just below the melting point, cannot be positively excluded by the results. The rotation found for the molecule in ice and presumably for the small polar group in solid dimethyl sulfate and the absence of rotation of the large molecules give further confirmation of Pauling's conclusions as to the rotation in the solid of molecules and groups having small moments of inertia.

Summary

Dielectric constants and specific conductances have been measured over a wide range of temperature and frequency for nitrobenzene, ethylene chloride, aniline, phenol, ice, benzene, dimethyl sulfate and diethyl sulfate in the solid state, and for certain of them as liquids near the melting point.

It is shown that no suddenly increased formation of molecular aggregates occurs in the liquids as the freezing point is approached. No evidence has been obtained of the second liquid phase in nitrobenzene reported by Wolfke and Mazur.

It is found that a very small quantity of impurity may have a very large effect upon the dielectric constant of a solid measured at low frequencies and the dielectric constant is suggested as a means for the investigation of some equilibria and transitions in solids. No evidence has been found of the rotation of large polar molecules in solids, although the possibility of an occasional rotation of a large molecule, particularly just below the melting point, is not excluded and it is not impossible that the methyl sulfate molecules should rotate around certain axes. As indicated by the results of previous investigators, molecules rotate in ice, which, in this respect, behaves like a very viscous liquid. No rotation of small polar groups in the molecules was found except in dimethyl sulfate, where, apparently, the methoxy group gives dipole orientation down to a transition point at $-70°$.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 341]

THE PHOTOCHLORINATION OF TETRACHLOROETHYLENE IN CARBON TETRACHLORIDE SOLUTION

BY JOHN A. LEERMAKERS AND ROSCOE G. DICKINSON

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When a carbon tetrachloride solution of chlorine and tetrachloroethylene which has been made up without the exclusion of dissolved oxygen is illuminated with radiation absorbable by only the chlorine, oxidation of the tetrachloroethylene to trichloroacetyl chloride and phosgene occurs[1] while the chlorine concentration remains sensibly constant. The rate of this oxidation is fairly low, the quantum yield at 20° and tetrachloroethylene concentrations of 0.02 to 1.5 molal being from 1 to 2.5 moles of tetrachloroethylene oxidized per einstein absorbed. We have found that if the experiment is carried out in such a way that the liquid has no access to additional oxygen, then after a period of illumination which varies with the amount of oxygen originally present, the chlorine concentration suddenly begins to decrease. The rate of the chlorination is then comparatively high; a solution originally 0.05 molal in chlorine and 0.002 molal in oxygen and containing an excess of tetrachloroethylene may, with a certain illumination, require an hour for the reaction of the oxygen before chlorination sets in, and then only a few additional minutes to bleach.[2]

The present paper deals with some aspects of the kinetics of the photochlorination.

Materials.—The carbon tetrachloride, tetrachloroethylene and chlorine solution in carbon tetrachloride were prepared as previously described.[1] In the course of the present work several different preparations of each have been employed with concordant results.

Apparatus and Procedure.—The reaction cell is shown in Fig. 1. It was a cylindrical Pyrex vessel 2.0 cm. in diameter and 3.05 cm. long with plane ends. The side tubes were of small bore; the cell was filled with liquid well into these tubes to eliminate access of oxygen to the main body of solution. The cell was then mounted between a 500-watt lamp and a thermopile and given a preliminary illumination to remove oxygen; the light was filtered through blue glass and copper sulfate solution. Suitable stirring to keep the solution homogeneous was regarded as important; without it the oxygen might be used up at the front end of the cell and chlorination proceed there before chlorination had started at the rear end. Stirring without further admission of oxygen was accomplished with the aid of a glass bead which normally remained out of the light beam in a depression from which it could be shaken when needed; tests with permanganate showed the stirring to be efficient.

[1] R. G. Dickinson and J. A. Leermakers, THIS JOURNAL, **54**, 3852 (1932).

[2] This phenomenon affords a possible explanation of Faraday's observation [*Ann. chim. phys.*, [2] **18**, 55 (1821)] that the chlorination did not occur in ordinary daylight but did occur in sunlight: the exposure to diffuse light was probably insufficient to remove oxygen; once the chlorination starts its rate is appreciable even in comparatively weak light.

The preliminary illumination was continued with occasional stirring until the thermopile deflections began suddenly to increase; then with very frequent stirring a short additional exposure was made which reduced the chlorine concentration by about one-third of its original value. The cell was then transferred to a two-thermopile photometer which furnished both a monochromatic source for the chlorination and a means of following the chlorine concentration.

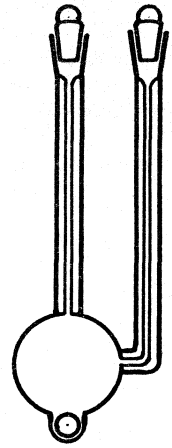

Fig. 1.—Cross section of cylindrical reaction cell.

This apparatus is shown in Fig. 2.[3] Light from a mercury arc H passed through a hole 1.0 cm. in diameter fitted with a shutter S, and then through a compartment containing the light filters immersed in running water; the radiation selected was λ4358. The light was rendered approximately parallel by the lenses L and then fell at about 45° on two thin plane plates of glass M; a portion of the light was reflected by M to the thermopile T_2 (*two* plates were used in order to secure sufficient reflection). The beam transmitted by M was considerably stronger than that which was reflected, and in it was interposed the cell B containing the reacting solution. A second thermopile T_1 was carefully adjusted to be the mirror image of T_2 across the plane of M and this second thermopile received light transmitted by the solution. The absorption cell B was immersed in a glass-walled tank of xylene (this liquid was chosen because it is reasonably non-volatile and has about the same refractive index as carbon tetrachloride); a similar tank X_2 of just the same thickness was placed in the other beam. The thermopiles were connected to two high-sensitivity galvanometers G_1 and G_2 which could be read simultaneously.

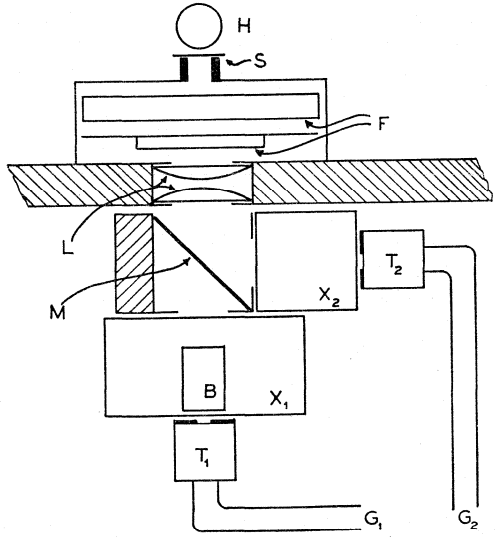

Fig. 2.—Photometer in which the chlorination was conducted and the chlorine concentration followed.

The apparatus was calibrated for chlorine concentration measurements simply by measuring the ratio of the two galvanometer deflections with pure carbon tetrachloride in the cell and again with a chlorine solution of known concentration. The value of αl, defined by the equation $\ln_e \tau = -\alpha l(Cl_2)$ where τ is the transmission, was found to be 14.7 liters per mole.

The apparatus was calibrated for quantum yield determination as follows. The thermopile T_1 was calibrated against a Bureau of Standards carbon filament lamp. T_1 was placed in the position normally occupied by the reaction vessel and the ratio of the readings of T_1 and T_2 determined. Making a small allowance for reflection and for the slight non-uniformity of the beam, it was found that a deflection of 1 cm. given

[3] The development of this apparatus was carried out mainly with the aid of Dr. E. P. Jeffreys.

by T_2 corresponded to an intensity of 6.4×10^2 ergs per cm.^{2} per sec. at the reacting solution.

At the end of the experiment, the solution was usually analyzed as previously described[1] to determine the amount of oxidation of tetrachloroethylene which had occurred in the preliminary illumination.

Sample Run.—The data of a typical run are given in some detail in Table I. In this table, the times of exposure in each successive interval of illumination are given under Δt. In the next three columns are given the transmission τ of the solution, the deflection d_2 given by the thermopile T_2, and the chlorine concentration; in each case the values are those prevailing at the beginning of the interval.

TABLE I

DETAILS OF A SINGLE EXPERIMENT (NO. 11)

(Cl_2) before preliminary illumination, 0.1 mole per liter
(C_2Cl_4) before preliminary illumination, 0.461 mole per liter

Δt, sec.	τ	d_2, cm.	(Cl_2) mole/liter	$(Cl_2)^{1/2}$	$\Delta t(1-\sqrt{\tau})\sqrt{d_2} \times 7.2 \times 10^{-5}$	Σ
	0.490	1.77	0.0485	0.220	0	0
225	.585	1.73	.0364	.191	5.73×10^{-3}	5.73×10^{-3}
292	.680	1.73	.0262	.162	5.70	11.43
360	.761	1.70	.0186	.136	5.13	16.56
352	.818	1.75	.0137	.117	3.69	20.25

Decrease in (C_2Cl_4) due to oxidation, 0.0029 mole per liter.
Slope of $(Cl_2)^{1/2}$ *vs.* $\Sigma = -kf = -5.10$.

Dark Reaction.—When a solution in which photochlorination had been started was allowed to stand in the dark, a slow chlorination was found to occur. For example, in a solution having (C_2Cl_4) = 0.83 *m*, the concentration of chlorine dropped in the dark from 0.0504 to 0.0487 in fifty-five minutes; from 0.0474 to 0.0451 in sixty minutes; and from 0.0380 to 0.0369 in thirty-three minutes. In the average photochemical run which consumed thirty minutes, the chlorine concentration fell from 0.05 to 0.01 molal. Thermal reaction was thus accountable for perhaps 3% of the total change. Since a correction for thermal rate would be small and, at present, uncertain of application, we have made none.

Treatment of Measurements.—A preliminary examination of measurements similar to those of Table I showed that the rate of disappearance of chlorine could be approximately represented by the equation

$$-\frac{d(Cl_2)}{dt} = \text{const.} \times (I_{abs.})^{1/2}(Cl_2) \qquad (I)$$

We shall assume that the local rate prevailing at any point in the solution can be represented by

$$-\frac{d(Cl_2)}{dt} = k(I_{abs.})^{1/2}(Cl_2)f \qquad (II)$$

where ($I_{abs.}$) is the rate of absorption of radiation in einsteins per liter per second at that point and f is a function of the concentrations. We may then derive an expression for the (volume) average rate for the case where the absorption is too large to permit regarding ($I_{abs.}$) as the same throughout the solution. For this purpose it may reasonably be supposed that: (1) the concentration of chlorine is kept uniform; (2) Beer's law applies;

(3) the rate at a given point is independent of the intensity prevailing at neighboring points (*i. e.*, the rate of diffusion of intermediate reactants is small); (4) the solution occupies a cylindrical space illuminated by light parallel to its axis and uniformly distributed over one end of the cylinder. Making use of Beer's law, we obtain from (II) the local rate in a layer at distance x from the front of the cylinder

$$-\left(\frac{d(Cl_2)}{dt}\right)_x = kI_0^{1/2}\, e^{-\alpha(Cl_2)x/2}\,(1000\alpha)^{1/2}(Cl_2)^{3/2} f \qquad \text{(III)}$$

where I_0 is the intensity of the incident radiation in einsteins per sq. cm. per sec. The volume average of this rate is obtained by integration over the length, l, of the cell

$$-\left(\frac{d(Cl_2)}{dt}\right)_{av.} = \frac{1}{l}\int_0^l kI_0^{1/2}\, e^{-\alpha(Cl_2)x/2}\, 10^{3/2}\alpha^{1/2}(Cl_2)^{3/2} f\, dx$$
$$= 2 \times 10^{3/2} l^{-1}\, \alpha^{-1/2} kI_0^{1/2}\,(Cl_2)^{1/2} f\,[1 - \sqrt{\tau}] \qquad \text{(IV)}$$

where $\sqrt{\tau}$ is written for $e^{-\alpha(Cl_2)l/2}$. Since (Cl_2) is uniform throughout the solution, we may drop the subscript av. and write

$$-\frac{d(Cl_2)^{1/2}}{dt} = -1/2\,(Cl_2)^{-1/2}\frac{d(Cl_2)}{dt} = kf10^{3/2}\,\alpha^{-1/2} l^{-1} I_0^{1/2}\,[1 - \sqrt{\tau}] \qquad \text{(V)}$$

From this it appears that if $(Cl_2)^{1/2}$ be plotted against $\int_0^t 10^{3/2}\alpha^{-1/2} l^{-1} I_0^{1/2}\cdot[1 - \sqrt{\tau}]dt$, the slope of the curve at any point will give $-kf$; and if f be only slightly dependent on the concentrations, the plot will be a nearly straight line.

The integral was approximated by the summation $\Sigma 10^{3/2}\alpha^{-1/2} l^{-1} I_0^{1/2}\,[1 - \sqrt{\tau}]\Delta t$ taken over all intervals from the beginning of the measurements; I_0 and τ were given mean values prevailing in each short interval, Δt, of illumination. For numerical purposes we have taken $l = 3.05$ cm., $\alpha = 4.81$ liters moles^{-1}cm.$^{-1}$ and $I_0 = 6.4 \times 10^2 \times 3.66 \times 10^{-13} d_2$ einsteins cm.$^{-2}$sec.$^{-1}$, and have accordingly plotted $(Cl_2)^{1/2}$ against $\Sigma 7.2 \times 10^{-5} \times d_2^{1/2}(1 - \sqrt{\tau})\,\Delta t$. A sample of this treatment of the data is given in Table I; plots obtained in this way are shown in Figs. 3 and 4; values of kf obtained from these slopes are given under $kf_{obs.}$ in Table II.

Discussion of Results.—The plots in Fig. 3, which involve the higher values of (C_2Cl_4), may be seen to be practically straight lines of substantially equal slope. This method of plotting has been developed on the assumption that the rate is everywhere proportional to the one-half power of the intensity. Justification of this is found in Expts. 7, 8, 9 and 10. During the intervals shown dotted on the plots a calibrated absorber was interposed before the reaction vessel; the absorber transmitted 45% in Expt. 7 and 10.5% in Expts. 8, 9 and 10. Were the rates proportional, for example, to the first power of the intensity, these plots would appear as broken lines with slopes in the dotted portions less than one-third (in 8,

TABLE II

SUMMARY OF SPECIFIC REACTION RATE DETERMINATIONS

Expt.	Composition of soln. before prelim. illum. $(C_2Cl_4)_0$ mole/liter	$(Cl_2)_0$ mole/liter	Concentration of Cl_2 during rate meas. $(Cl_2)_{initial}$ mole/liter	$(Cl_2)_{final}$ mole/liter	(C_2Cl_4) oxidized mole/liter	$\left(\frac{(Cl_2)}{(C_2Cl_4)}\right)_{Av.}$	$kf_{obs.}$	$kf_{calcd.}$
3	0.882	0.080	0.0406	0.0150	0.0024	0.033	4.77	5.09
4	.882	.080	.0302	.0110	.0027	.025	4.81	5.09
6	.882	.108	.0782	.0138	.0031	.054	5.07	5.06
7	.882	.108	.0739	.0143	.0029	.052	4.97	5.06
8	.882	.108	.0605	.0128	.0029	.045	5.10	5.08
9	.882	.108	.0582	.0137	.0031	.044	5.40	5.08
10	.882	.108	.0561	.0141	...	.044	5.47	5.08
18	.882	.108	.0466	.0160	.0005	.039	5.32	5.09
20	.882	.101	.0358	.0123	.0029	.030	4.80	5.09
21	.882	.108	.0268	.0122	.0720	.027	5.35	5.09
22	.882	.108	.0450	.0149	.0118	.039	5.23	5.09
26	.676	.100	.0525	.0142	...	.055	5.06	5.06
11	.461	.114	.0485	.0137	0029	.081	5.10	5.03
17	.251	.110	.0629	.0150	...	.21	4.53	4.90
25	.180	.100	.0439	.0143	...	.26	4.35	4.85
12	.0989	.110	.0679	.0540	0030	1.37	4.06	4.10
13	.0989	.109	.0540	.0433	...	1.66	3.83	3.96
13*						4.51	3.0	3.04
24	.0799	.097	.0524	.0400	.0032	1.94	3.60	3.84
24*						6.95	2.6	2.63

Temperature of all experiments, 22 ± 1°.

Expt. 18; solution shaken with N_2 and cell first filled with N_2.

Expt. 22; solution shaken with O_2 and cell first filled with O_2.

Expt. 21; solution shaken with air to replenish O_2 several times during preliminary illumination.

Expt. 20; solution made 0.716 molal in C_2Cl_6 at start.

Expt. 7; intensity was dropped 55% in some of the intervals of illumination.

Expts. 8, 9, 10; intensity was dropped 90% in some of the intervals of illumination.

Expts. 13*, 24*; k's determined from later part of run.

9 and 10) of the slopes in the adjacent solid portions. There are, however, no indications of breaks in these plots.

Since the reacting solutions contained small amounts of the products of oxidation (corresponding to (C_2Cl_4) oxidized = 0.003 molal) experiments were made to see whether their quantity affected the rate. In Expt. 18 the solution as made up was shaken with nitrogen to remove most of the oxygen at the outset, and the reaction cell was filled with nitrogen before introducing the solution; the (C_2Cl_4) oxidized was only 0.0005 *m* but the rate of chlorination was not appreciably changed. In Expt. 22 a similar treatment was given with oxygen and the (C_2Cl_4) oxidized became 0.0118 *m*. In Expt. 21 the solution was frequently shaken with air during the preliminary illumination, so that the (C_2Cl_4) oxidized was 0.0720 *m;* the use of these larger amounts of oxygen did not, however, appear to affect the subsequent chlorination rates.

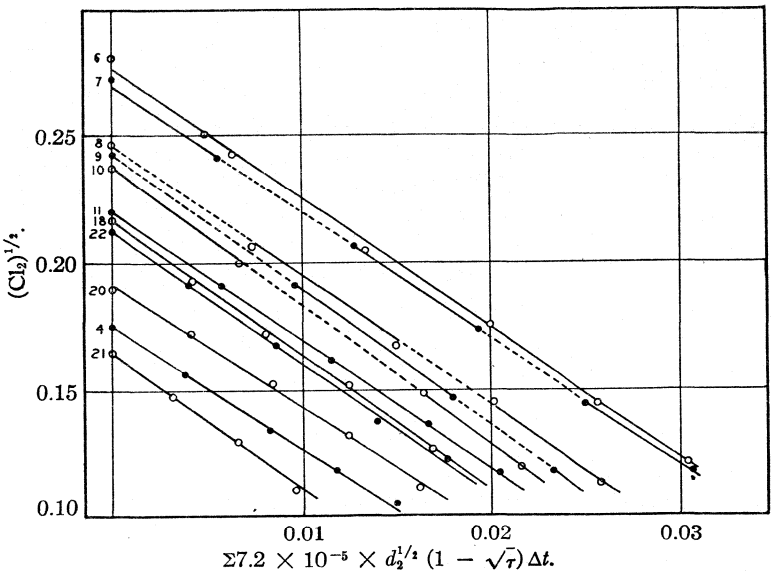

Fig. 3.—Results of runs at the higher tetrachloroethylene concentrations.

In Expt. 20 enough resublimed hexachloroethane was dissolved to make the solution 0.716 molal in hexachloroethane at the start; this was several

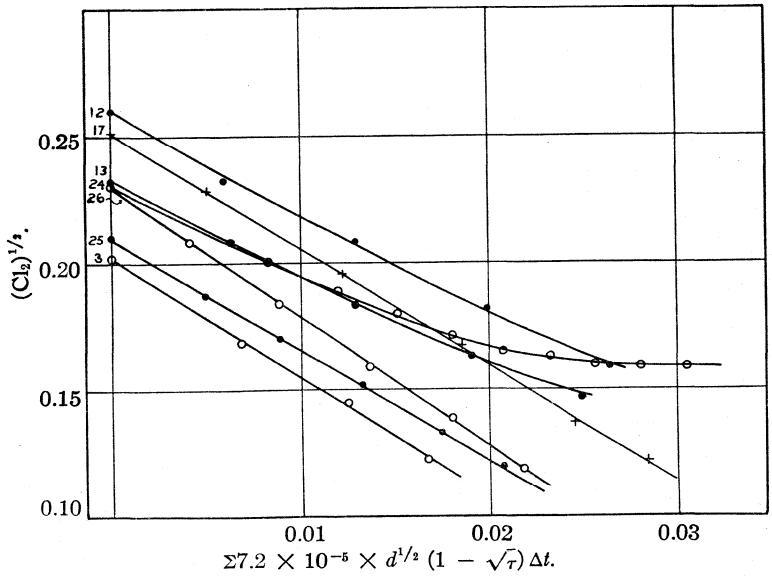

Fig. 4.—Results of runs at various tetrachloroethylene concentrations; the original tetrachloroethylene concentrations decrease in the order 3, 26, 17, 25, 12, 13, 24.

times the concentration ever built up in the ordinary runs, but had little if any effect on the rate.

Figure 4 shows plots for experiments with lower tetrachloroethylene concentrations (Nos. 3 and 26 with high (C_2Cl_4) are included here for comparison). At the lower values of (C_2Cl_4) the slopes, *i. e.*, the values of kf, are somewhat smaller; and in those experiments (for example, 24 and 13) where (C_2Cl_4) undergoes a considerable percentage change during the run the plotted lines show curvature. Thus f is to some extent dependent on concentrations; the nature of the dependence is discussed below.

Quantum Yield.—From Equation (II) it immediately follows that the local quantum yield expressed in moles of chlorine reacting per einstein absorbed is, for a given intensity and composition of solution

$$\text{Quantum yield} = -\frac{1}{(I_{\text{abs.}})}\frac{\mathrm{d}(Cl_2)}{\mathrm{d}t} = k(I_{\text{abs.}})^{-1/2}(Cl_2)f \qquad \text{(VI)}$$

At the beginning of sample Expt. 11 (Table I), the quantum yield was then 790, and at the end 430. The extreme variations in quantum yield occurring in the measurements made are from 2500 in the early part of Expt. 7 to about 300 near the end of Expt. 24.

Temperature Coefficient.—With a separate apparatus, we have measured rates at 0, 10, 20 and 30°. These measurements have not been sufficiently satisfactory to give in detail, but they make it possible to say that the temperature coefficient is not large; our present best value of the 10° multiplication of the specific rate constant is 1.16 ± 0.08.

Products of the Reaction.—In several experiments carried out with low tetrachloroethylene concentration and a slight excess of chlorine, the illumination was prolonged until the chlorination ceased. It was found that about 9% less chlorine disappeared than would correspond to complete reaction according to the equation: $Cl_2 + C_2Cl_4 = C_2Cl_6$. (Correction for oxidation of tetrachloroethylene in the preliminary illumination was applied but was small, usually about 3%, except in one case where 12% of the tetrachloroethylene was purposely oxidized without changing the corrected result.)

A series of experiments was made to determine the constancy of the ratio of the number of mols of chlorine used up to the number of mols of tetrachloroethylene taken (corrected for oxidation). The initial ratio of (Cl_2) to (C_2Cl_4) was varied two-fold; the light intensity was varied ten-fold; three independently purified samples of tetrachloroethylene were tried; the change in chlorine was determined both by the photometer and by direct titration. In no case was a significant variation of the ratio $\Delta(C_2Cl_4)/\Delta(Cl_2)$ from 1.09 found.

Failure to use up enough chlorine could hardly be the result of a back reaction since large amounts of C_2Cl_6 did not reduce the rate of chlorination. It may indicate a side reaction resulting in, for example, C_4Cl_8 or

C_4Cl_6 (C_4Cl_{10} is not known). The residual solutions from these experiments were collected, washed with water, and the carbon tetrachloride layer allowed to evaporate. The white crystalline product gave a melting point 4° lower than a sample of resublimed hexachloroethane in the same bath (m. p. C_2Cl_6 185°). When mixed with hexachloroethane, the melting point was 2° below that of pure hexachloroethane.

If the failure to use up enough chlorine is due to the formation of some C_4Cl_8, the products must contain 4.2 mole per cent. of C_4Cl_8; if due to C_4Cl_6, they must contain 2.9 mole per cent. Whether these results are to be attributed to the formation of a small amount of product containing a smaller proportion of chlorine than does tetrachloroethylene, or to some small unsuspected source of experimental error, there is no doubt that by far the main portion of the reaction results in the formation of hexachloroethane.

Possible Mechanisms of the Chlorination.—In analogy with what is known to occur when blue light is absorbed by gaseous chlorine, it may be assumed that the primary absorption process leads to the production of chlorine atoms. Starting with this, the following simple chain reaction scheme may be written

$$Cl_2 + h\nu \longrightarrow 2Cl \qquad (1)$$

$$Cl + C_2Cl_4 \rightleftharpoons C_2Cl_5 \qquad (2' \text{ and } 2'')$$

$$C_2Cl_5 + Cl_2 \longrightarrow C_2Cl_6 + Cl \qquad (3)$$

$$2C_2Cl_5 \longrightarrow 2C_2Cl_4 + Cl_2 \text{ (or } C_2Cl_6 + C_2Cl_4) \qquad (4)$$

In 2′ the compound C_2Cl_5 is formed which may sometimes dissociate (2″) before forming the product, C_2Cl_6, according to 3; reactions 2′ and 3 constitute the chain which is finally broken by 4. The products of 4 may be those suggested or any others which do not perpetuate the chain. This reaction scheme is essentially similar to that proposed by Berthoud and Beraneck[4] for the brominations of cinnamic acid and stilbene, and leads, when the quantum yields are high, to the rate expression

$$-\frac{d(Cl_2)}{dt} = \frac{k_3}{\sqrt{k_4}}(I_{abs.})^{1/2}(Cl_2) \qquad (VII)$$

which is of the form of (II) with f constant. Since f is found to vary only moderately, the mechanism accounts for the main features of our kinetic results.

Two additional chain-breaking reactions suggest themselves whose occurrence in addition to the above reactions leads to a decrease of the rate with decreasing (C_2Cl_4); these reactions are

$$C_2Cl_5 + Cl \longrightarrow C_2Cl_4 + Cl_2 \text{ (or } C_2Cl_6) \qquad (5)$$

$$2Cl \longrightarrow Cl_2 \qquad (6)$$

Applying the usual methods of treatment, and noticing that when the quantum yields are high

$$k_2'(Cl)(C_2Cl_4) = k_2''(C_2Cl_5) + k_3(Cl_2)(C_2Cl_5) \text{ nearly}$$

[4] A. Berthoud and J. Beraneck, *J. chim. phys.*, **24**, 213 (1927).

the following rate expression may be obtained

$$-\frac{d(Cl_2)}{dt} = \frac{k_3}{\sqrt{k_4}}(I_{abs.})^{1/2}(Cl_2)\left[1 + \frac{k_5[k_3(Cl_2) + k_{2''}]}{k_4k_{2'}(C_2Cl_4)} + \frac{k_6[k_3(Cl_2) + k_{2''}]^2}{k_4k_{2'}^2(C_2Cl_4)^2}\right]^{-1/2} \quad \text{(VIII)}$$

From this, the effect of suppressing one or more of the reactions 2″, 5 and 6 may be seen by setting the corresponding k equal to zero. It is probably not possible, with our data, to attribute the decrease in f with decreasing (C_2Cl_4) to any one of these causes to the exclusion of the others; satisfactory agreement with the data may be had by setting $k_{2''}$ and k_6 equal to zero, $k_3/\sqrt{k_4}$ equal to 5.1, and $k_5k_3/k_4k_{2'} = 0.4$ so that (VIII) becomes

$$-\frac{d(Cl_2)}{dt} = 5.1(I_{abs.})^{1/2}(Cl_2)\left[1 + 0.4\frac{(Cl_2)}{(C_2Cl_4)}\right]^{-1/2} \quad \text{(IX)}$$

Values of $kf_{calcd.}$ obtained by using the above numerical values for the k's and the mean values of $(Cl_2)/(C_2Cl_4)$ prevailing in the experiment, are given in the last column of Table II. Equation (IX), then, corresponds to a mechanism made up of reactions 1, 2′, 3, 4 and 5.

It should be pointed out that another different but equally simple mechanism leads to types of rate expression similar to those obtained from the scheme just discussed. This mechanism is

$$Cl_2 + h\nu \longrightarrow 2Cl \quad (1)$$
$$Cl + Cl_2 \longrightarrow Cl_3 \quad (2)$$
$$Cl_3 + C_2Cl_4 \longrightarrow C_2Cl_6 + Cl \quad (3)$$
$$2Cl \longrightarrow Cl_2 \quad (4)$$
$$Cl + Cl_3 \longrightarrow 2Cl_2 \quad (5)$$
$$2Cl_3 \longrightarrow 3Cl_2 \quad (6)$$

Here, as before, 2 and 3 are chain carrying reactions while 4, 5 and 6 are chain breaking reactions. The scheme differs from the first in having the intermediate Cl_3 instead of C_2Cl_5 and in having (to secure agreement with the experiments) the uniting of 2 chlorine atoms instead of the reaction of $2C_2Cl_5$ as the principal chain breaking step. Rollefson and Eyring[5] have given arguments based on quantum mechanics to show that halogen molecules of the type X_3 are stable at room temperature with respect to decomposition into X_2 and X.

Reactions 1, 2, 3 and 4 lead to the rate expression (VII) but with k_2 replacing k_3. Reactions 1, 2, 3, 4 and 5 give, when the quantum yield is high

$$-\frac{d(Cl_2)}{dt} = \frac{k_2}{\sqrt{k_4}}(I_{abs.})^{1/2}(Cl_2)\left[1 + \frac{k_2k_5}{k_3k_4}\frac{(Cl_2)}{(C_2Cl_4)}\right]^{-1/2} \quad \text{(X)}$$

which again is of the form of Equation (IX), and in agreement with the experiments. The further introduction of reaction 6 and of the reversal of 2, gives a complicated expression which may be put in a form resembling (VIII); while these reactions are not necessary in order to secure agreement, our data do not wholly exclude them.

[5] G. K. Rollefson and H. Eyring, THIS JOURNAL, **54**, 176 (1932).

Summary

The photochemical chlorination of tetrachloroethylene in carbon tetrachloride solution has been studied in monochromatic light of wave length 4358 Å., and the specific rates have been expressed in absolute units. The rate has been found proportional to the square root of ($I_{abs.}$), at least approximately proportional to the first power of (Cl_2), and only moderately dependent on (C_2Cl_4); Equation (IX) summarizes these results. Under the conditions of the experiments, the quantum yield has varied from 300 to 2500. Two alternative mechanisms, one involving C_2Cl_5 and one involving Cl_3, have been discussed, and both found to account for the observations.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 331]

THE DENSITY AND MOLECULAR STATE OF RHENIUM TETRACHLORIDE AND RHENIUM HEXACHLORIDE IN THE GASEOUS STATE

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Introduction.—Previous experiments on the nature of the rhenium chlorides[1] have shown that more than one compound is formed when chlorine is passed over the heated metal. Some of the substances so formed are reported to be easily volatile. Hönigschmid,[2] in an attempt to determine the atomic weight of rhenium by the analysis of a chloride, found the best preparations to be mixtures since the proportions of rhenium and chlorine were not constant and led in the more reproducible cases to the formula $ReCl_{4.3}$. He also observed that this substance decomposed on heating in an atmosphere of nitrogen with the formation of a less volatile product, whereas similar treatment in the presence of chlorine resulted in complete volatilization without apparent change.

In the present article are presented the results of vapor density measurements made on various mixtures of rhenium and chlorine in order to determine the molecular state and composition of some of the rhenium chlorides.

Experimental Method and Preparation of Materials.—The vapor density measurements were carried out in the same manner as in a previous investigation,[3] the method consisting of heating weighed amounts of rhenium and chlorine in previously evacuated tubes until the contents were completely reacted and vaporized and then allowing the excess to escape

[1] W. Noddack, *Z. Elektrochem.*, **34**, 627 (1928).

[2] Hönigschmid and Sachtleben, *Z. anorg. Chem.*, **191**, 147 (1931).

[3] Yost and Hatcher, THIS JOURNAL, **53**, 2549 (1931).

until the pressure became atmospheric. By weighing the tubes before and after releasing the excess, and knowing the initial weights present and the volumes of the tubes, the vapor densities could be calculated.

As a source of rhenium the very pure potassium perrhenate now available was used. To obtain the metal the finely pulverized perrhenate was reduced with hydrogen. The hydrogen was passed slowly through a Pyrex tube heated almost to the softening point over about 30 cm. of its length. The gas then passed over the salt which, however, was not otherwise heated until reduction was well started. The reduction was then carried to completion with moderate heating of the salt. The resulting mixture, after cooling, was washed several times with hot water to remove the potassium hydroxide formed as well as the unreduced perrhenate. The black product obtained was dried, ground in a mortar, again washed several times with hot water, and dried. This material was placed in a silica tube and treated with hydrogen at bright red heat in order to reduce the last traces of rhenium oxides that are present after the first reduction.

Chlorine from a cylinder was purified by passing through water and then through a long drying tube containing anhydrous calcium chloride. It was condensed with liquid air in small capsules provided with easily breakable tips. The capsules were sealed and weighed, their weight empty having been previously determined.

Results of the Vapor Density Experiments.—The results of the vapor density measurements are presented in Table I. In the last column are given the values M of the apparent molecular weights calculated from the equation $M = [m\ 82.07(273.1 + t)]/pv$ in which m is the weight of material present in v cc. at the pressure p in atmospheres and the temperature t.

TABLE I

RESULTS OF THE VAPOR DENSITY MEASUREMENTS

Expt.	Atomic ratio Cl:Re	Weight of material, m, g.	Pressure p in mm.	Temp., t, °C.	Volume v, cc.	Apparent molecular wt., M
1	4	0.2742	748	670	45.1	478
2	4	.3378	748	670	58.5	476
3	4	.2796	748	670	47.2	465
4	4	.4256	748	670	69.9	478
5	4	.2671	746	567	40.4	465
7	6	.1328	738	563	37.1	253
8	6	.1205	738	616	37.1	244
9	6	.1721	738	560	48.9	248
10	6	.1587	738	609	48.9	242
15	7.540	.1220	746	565	38.5	222
16	7.540	.1186	746	618	38.5	230
11	8	.1129	741	558	42.1	188
12	8	.1044	741	618	42.1	186
13	8	.0947	741	558	34.7	191
14	8	.0874	741	618	34.7	187

The vapors are assumed to obey the law of perfect gases. Measurements were made using various atomic ratios of Cl : Re and with varying initial amounts of rhenium and chlorine.

It was necessary to work at rather high temperatures since complete vaporization of the material did not take place below these temperatures, and at temperatures much higher than the highest used the glass reaction bulbs softened.

The reaction between metallic rhenium and chlorine is very slow at room temperature but much more rapid at 650°. In order to assure complete reaction it was necessary to heat the tubes containing the rhenium and chlorine in the ratio 1:4 for fourteen hours at 620° while tubes containing larger proportions of chlorine required somewhat less time.

The vapors at and above atmospheric pressure were in all cases dark reddish-brown in color and quite opaque in layers 2.5 cm. thick. The color of the vapors was, as far as could be determined visually, independent of the ratio of rhenium to chlorine used, thus indicating that at least one constituent was present in appreciable amounts in all of the experiments. The solid condensing out at room temperature consisted principally of small crystals which, when thin, were dark red by transmitted light, and when thick practically black. When tubes containing chlorine and rhenium in the ratio 6:1 and greater were cooled with liquid air and then allowed to come again to room temperature, a small amount of yellowish-red solid was observed which volatilized readily on warming with the hands. Free chlorine could always be seen in tubes containing chlorine in excess of that necessary to form the tetrachloride.

When the tubes were opened under water the rhenium chlorides reacted with it forming a black precipitate except when the chlorine-to-rhenium ratio was 8:1, in which case a yellow solution was formed which rapidly became colorless with the formation of perrhenic acid. When the black crystals were added to 6 *N* hydrochloric acid a salmon-pink colored solution resulted which gave no precipitate even after two weeks but did gradually become green in color. These results are in agreement with those found recently by Briscoe, Robinson and Stoddart[4] in their experiments on the solid tetrachloride. They also established that the dark crystals had the composition $ReCl_4$.

Discussion of the Results

As may be seen from the results of the experiments, the maximum deviation to be expected between the apparent molecular weights is less than 4%. The mean error is somewhat less than this. It is to be observed that the variation of the apparent molecular weights with temperature is small and of the order of magnitude of the errors involved.

[4] Briscoe, Robinson and Stoddart, *J. Chem. Soc.*, **134**, 2263 (1931).

The formula weight of $ReCl_4$ is 328.14 while the average value obtained in experiments 1 to 5, in which the atomic ratio of rhenium to chlorine is 1:4, is much greater than this, namely, 472. This fact indicates that polymerization takes place but that it does not go to completion since the observed molecular weight is not a simple multiple of the formula weight. If the polymer is assumed to dissociate rapidly and reversibly in accordance with the reaction

$$Re_2Cl_8(g) = 2ReCl_4(g) \qquad (1)$$

then agreement with the observed molecular weights would result if the degree of dissociation were 0.39. That equilibrium was attained rapidly was shown by the fact that variations in the initial pressures had no effect on the values of the vapor densities although only some ten seconds were necessary for the excess material to escape before atmospheric pressure was attained.

In the experiments in which the atomic ratio of Re:Cl was 1:6 the average observed molecular weight is 247, while the formula weight of $ReCl_6$ is 399.06. Evidently the hexachloride does not exist as such to the exclusion of other substances at the temperatures of the experiments. If it is assumed that the following reactions take place

$$ReCl_6(g) = ReCl_4(g) + Cl_2(g) \qquad (2)$$
$$2ReCl_4(g) = Re_2Cl_8(g) \qquad (3)$$

and that the reactions are rapid and reversible, then a mixture could result whose apparent molecular weight would be that observed. Moreover, it is possible to calculate the equilibrium constant for reaction (2), since that for reaction (3) is known from the experiments on the tetrachloride. The following two values are found for the temperature range of the experiments, the pressures being expressed in millimeters of mercury.

$$\frac{P_{Re_2Cl_8}}{P^2_{ReCl_4}} = 1.86 \times 10^{-3} \qquad \frac{P_{ReCl_4} P_{Cl_2}}{P_{ReCl_6}} = 708$$

The assumptions made may now be tested using the results of the experiments in which the rhenium-to-chlorine ratio was 1:8 and making the assumption that no higher chlorides are formed. This latter assumption seems a reasonable one to make since the experiments on the hexachloride showed that even it undergoes extensive decomposition. Using the equilibrium constants just given, together with the pressure shown in the table for the experiments in question, an apparent molecular weight of 183 is calculated. This is in good agreement with the observed value, 188. The evidence then, both of a qualitative and quantitative nature, supports the assumptions made above regarding the nature of the rhenium chloride vapors.

It is to be noted that the calculations have been made on the assumption that all the experiments were at the same temperature, which was not

the case. The fact that the vapor densities are, within the limits of experimental error, independent of the temperature indicates that the equilibria involved are not undergoing any great changes in the temperature range employed.

There remains to be considered the possible existence of the compounds Re_2Cl_4, Re_2Cl_6 and $ReCl_7$ under the conditions of the experiments. If either of the first two or both were formed without the simultaneous presence of the tetrachloride, then the apparent molecular weights in the experiments in which the ratio of Re:Cl was 1:4 would have been 328 or less, much smaller than those found experimentally. It is necessary, therefore, that Re_2Cl_8 be present along with the Re_2Cl_4 or Re_2Cl_6. Assuming Re_2Cl_8 to be in equilibrium with either of these two lower chlorides and chlorine, the calculated molecular weights for the case in which excess chlorine is present are found not to be in agreement with those determined experimentally. The simultaneous existence of either of the two lower chlorides together with the tetrachloride, hexachloride and chlorine does not, from purely chemical considerations, seem very probable.

The possibility that $ReCl_7$ rather than $ReCl_6$ is present in the tubes with excess chlorine does not seem at all likely since it is hardly to be expected that rhenium would exhibit its maximum valence with chlorine under the conditions of the experiments. Moreover, when it is assumed that a heptachloride is present in equilibrium with the tetrachlorides and chlorine the calculated molecular weight of the 1:8 mixtures is found to be much too high. The assumption that the vapors consist of the polymerized and simple tetrachlorides and the hexachloride in addition to chlorine suffices for the explanation of the experimental results.[5]

Summary

The vapor densities of mixtures of rhenium and chlorine in various proportions have been determined in the neighborhood of 600°. The results show that a polymerized tetrachloride, Re_2Cl_8, exists in equilibrium with $ReCl_4$, and that in the presence of excess of chlorine the hexachloride is also formed and is present in equilibrium with the tetrachlorides and chlorine.

The reaction between metallic rhenium and chlorine was found to be slow at temperatures much below 650°. After completion of the reaction and cooling to room temperature black or dark red crystals are formed which consist principally of the tetrachloride.

PASADENA, CALIFORNIA

[5] The results of the experiments of Briscoe, Robinson and Stoddart indicate that some of the substances previously described as higher chlorides may be oxychlorides or related substances.

NOTE

Note on the Preparation of Pure Methane from Natural Gas[1]

By H. H. Storch and P. L. Golden

A convenient method of removing higher hydrocarbons from natural gas is to pass the gas through a layer of active charcoal. This method has been successfully used during the past year for the preparation of about 1000 cubic feet of methane containing less than 0.05% ethane and no higher hydrocarbons, from Pittsburgh natural gas which contains 8–15% of ethane and 1–3% of hydrocarbons higher than ethane. Because of the large number of inquiries concerning the preparation of pure methane, it was thought desirable to present briefly our procedure and results.

The charcoal unit consists of a section of 15-cm. pipe, 117 cm. long, fitted with reducing caps and 6.4-mm. valves at each end. On the outer surface of the 15-cm. pipe is a tight-fitting, closely wound coil of 8-mm. copper tubing. The whole unit is mounted vertically and insulated with commercial asbestos and magnesia pipe covering. About 20 pounds of coconut charcoal (8–14 mesh, forty minutes service time by accelerated chloropicrin test, obtained from Barnebey and Cheney of Columbus, Ohio) was used. Before admitting the natural gas the char was heated at 110° (high-pressure steam) for about twelve hours, the top valve being open. At the end of this period, a laboratory vacuum oil pump was connected to the char container and the gases were pumped off for about four hours. Natural gas was then passed through an oil gas meter, three drying units (two of which contained calcium chloride and the third sodium hydroxide pellets), and then through the charcoal (cooled to atmospheric temperature) at the rate of 5 cubic feet per hour. Experience showed that the 20 pounds of char would reduce the content of ethane and higher hydrocarbons to less than 0.05% in 100 cubic feet of Pittsburgh natural gas, even during the summer months when the ethane content is highest. The gas obtained in the initial part of a run is rather low in methane—that is, about 96% methane and 4% nitrogen—whereas that obtained subsequently is about 98% methane and 2% nitrogen. About 0.2% of oxygen is a constant impurity. The content of ethane and higher hydrocarbons was determined by low-temperature fractional distillation. For precise work the methane was condensed by using a bath of liquid nitrogen, the non-condensable gases were pumped off, and the methane repeatedly (about twelve times is necessary) melted and frozen with intermittent pumping off of the trapped gases which are thus released. Finally, the initial third and last third of the methane vapor obtained upon warming the apparatus were discarded.

[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

After passage of 100 cubic feet of natural gas through the 20 pounds of char, the latter was again heated at 110° and evacuated as described above.

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PITTSBURGH EXPERIMENT STATION
U. S. BUREAU OF MINES
PITTSBURGH, PENNSYLVANIA

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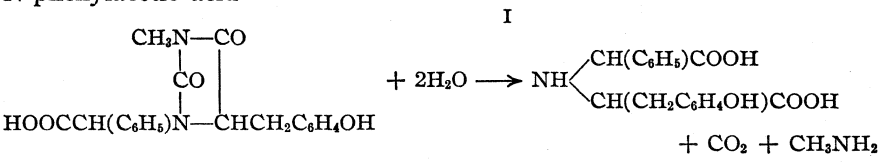
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

TYROSINE-N-ACETIC ACID: INTRODUCING A NEW GENERAL METHOD FOR PREPARING SYMMETRICAL AND ASYMMETRICAL IMINO DIBASIC ACIDS

BY DOROTHY A. HAHN AND ANNE LITZINGER

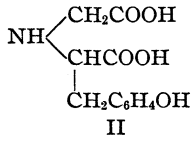
RECEIVED MAY 19, 1932 PUBLISHED DECEMBER 13, 1932

It has been shown that the N-3-methyl-5-tyrosylhydantoin-N-1-phenylacetic acid, on hydrolysis with barium hydroxide, breaks down to tyrosine-N-phenylacetic acid[1]

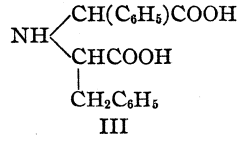


I

This reaction has now been found applicable as a new general method for preparing α-imino dibasic acids of the diacetic acid type, $HOOCCH_2NHCH_2COOH$, in which the methylene hydrogen atoms are replaced by different hydrocarbon residues. Previous to this time substances belonging to this class have been prepared almost exclusively by hydrolysis of the corresponding dinitriles.[2] In addition to the acid referred to above (I), three others have now been synthesized in this Laboratory, namely, tyrosine-N-acetic acid (II), β-phenylalanine-N-phenylacetic acid (III) and β-phenylalanine-N-acetic acid (IV)

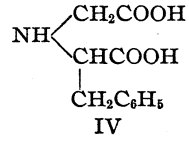


II



III

and



IV

A detailed study of the intermediate products involved in the synthesis of the hydantoins used in the preparation of III and IV is still in progress. The present report is, therefore, limited to a brief description of these acids at the end of this paper preceded by a detailed consideration of *tyrosine-N-acetic acid* and its salts.

A crystalline diethyl ester and a barium salt of the latter acid (II) have

[1] Hahn and Dyer, THIS JOURNAL, **52**, 2495 (1930).

[2] Jongkees, *Rec. trav. chim.*, **27**, 287–326 (1908).

already been prepared[3] by the hydrolysis of N-3-methyl-5-tyrosylhydantoin-N-1-acetic acid, but both of these substances were isolated with difficulty and in very small quantities. A method for the hydrolysis of the hydantoin has now been developed which provides approximately quantitative yields. The acid may be transformed into the corresponding hydrochloride by treatment with aqueous hydrochloric acid; it also furnishes the dimethyl ester hydrochloride by the standard procedure, practically quantitative yields being obtained. On treatment with aqueous alkalies it yields the mono-potassium and mono-sodium salts; these in turn may be converted into the salts of heavy metals by double decomposition. A di-potassium salt separates on treating a solution of the acid in excess of concentrated potassium hydroxide with alcohol.

Table I shows the similarity in the melting points of imino-diacetic acid and the four acids referred to above and also the solubility relationships which exist among these five substances.

TABLE I

COMPARISON OF PHYSICAL PROPERTIES OF IMINO ACIDS

Imino acid	Imino-diacetic	I	II	III	IV
M. p., °C.	225–226[4]	222–224	228–230	227–228	220–228
Solubility,[5] g.	0.3975	0.0107	0.0604	0.0024	0.0154

Experimental

Tyrosine-N-acetic Acid, $NH(CH_2COOH)CH(CH_2C_6H_4OH)COOH$.—To a solution of 57.5 g. of N-3-methyl-5-tyrosylhydantoin-N-1-acetic acid in 250 cc. of boiling water was added a hot solution of 225 g. of crystallized barium hydroxide in 500–600 cc. of water. The mixture was heated on a steam-bath under reflux for twenty to twenty-four hours and then distilled with steam (four to five hours) in order to remove the resulting methylamine. The solution was then freed of barium with exactly the necessary amount of sulfuric acid, filtered, and concentrated under reduced pressure to one liter. On standing overnight most of the free α-imino-dibasic acid separated in the form of rosets made up of small white hard well-defined prisms, which after extraction with hot alcohol and recrystallization from water melted with decomposition at 228–230°.

Anal. Calcd. for $C_{11}H_{13}O_5N \cdot H_2O$: H_2O, 7.00. Found: H_2O, 5.38, 5.34. Calcd. for $C_{11}H_{13}O_5N$: N, 5.86. Found: N, 5.88, 5.86.

The acid is very soluble in cold aqueous ammonia and alkali and in cold dilute aqueous hydrochloric acid and can be recovered in exceptionally pure condition on hydrolysis of these salts. It is fairly soluble in boiling water, 5 g. dissolving in 135 cc. It is only slightly soluble in cold water, 4.1 g. separating from the above solution on cooling. There seems to be a tendency for the acid to form supersaturated aqueous solutions since it separates very slowly, usually upon standing overnight. It is almost insoluble in hot alcohol and other neutral organic solvents. It is only slightly soluble in boiling acetic acid (2 g. in 225 cc.) except upon prolonged heating, when relatively large quantities dissolve and are recovered with difficulty.

[3] Hahn and Renfrew, THIS JOURNAL, **47**, 161, 162 (1925).

[4] Eschweiler, *Ann.*, **278**, 231 (1894).

[5] Solubility is measured by the number of grams present in 10 cc. of a saturated aqueous solution at 25°.

Further quantities of the acid were obtained on concentrating the filtrates, the final yield averaging over 90% of the theoretical. In cases where the product was slightly discolored, the color was removed with only negligible loss by extracting with boiling alcohol. The alcoholic extract was found to contain, in addition to the coloring matter, small quantities of an acid melting at 217–220°, which upon analysis showed the same composition as the main product. This acid crystallized in large hard transparent prisms and differed also in being more soluble in water and in alcohol; it was readily soluble in dilute aqueous hydrochloric acid and ammonia. It has not been investigated in greater detail owing to the difficulty of obtaining it in sufficient quantity.

Hydrochloride of Tyrosine-N-acetic Acid.—This separated on cooling a solution of 5 g. of the free acid in 35 cc. of boiling aqueous hydrochloric acid (1:1), the weight of the crop so obtained being 4.2 g. On recrystallization from the same solvent it formed hard glistening plates, m. p. 212.5–213°.

Anal. Calcd. for $C_{11}H_{13}O_5N \cdot HCl$: N, 5.08; Cl, 12.88. Found: N, 4.98, 5.18; Cl,[6] 12.98, 13.00.

The salt dissolves in about 5 parts of boiling 1:1 hydrochloric acid, but requires about 60 parts of the same solvent in the cold. It dissolves in 2 parts of cold water but within five to ten minutes separation of the free acid takes place.

The hydrochloride of dimethyl tyrosine-N-acetate was obtained by dissolving 12 g. of free acid in 75 cc. of methyl alcohol saturated with dry hydrogen chloride gas, solution being accompanied by the development of a pink color. After refluxing for half an hour the solution was concentrated to 45 cc. and treated with two to three times this volume of ether, when 13.2 g. of ester separated. The product melted at 163–165° and decomposed at 200°. It was analyzed without further purification.

Anal. Calcd. for $C_{13}H_{18}O_5NCl$: N, 4.61; Cl, 11.69. Found: N, 4.87, 4.92. Cl,[6] 11.67, 11.63.

This salt is fairly soluble in cold methyl alcohol (8 g. in 30 cc.), not quite so soluble in cold water (5 g. in 25 cc.) and insoluble in ether.

Metallic Salts.—The mono-alkali salts were prepared in good yield by dissolving the free acid in cold aqueous solutions containing somewhat more than an equivalent weight of the corresponding hydroxide; and a dipotassium salt when two equivalents was used. The salts of the heavy metals (6, 9, 10 and 11) were obtained by treating aqueous solutions of the mono-potassium salt with 2.2 equivalents of the corresponding nitrates. Two different barium salts were obtained with 2 equivalents of the hydroxide[3] and the chloride, respectively, and a silver salt with 1.2 equivalents of nitrate.[7] The salts 1, 4, 6 and 10 were transformed quantitatively into the free acid, m. p. 228–230°, by the action of dilute hydrochloric acid, carbon dioxide and dilute sulfuric acid, respectively.

β-Phenylalanine-N-phenylacetic acid, III, m. p. 224–226° with decomposition and **β-phenylalanine-N-acetic acid,** IV, m. p. 220–228° with decomposition, were obtained by hydrolyzing N-3-methyl-5-benzylhydantoin-N-1-phenylacetic acid and N-3-methyl-5-benzylhydantoin-N-1-acetic acid, respectively, under the action of barium hydroxide in the same manner as has been described in the preparation of tyrosine-N-acetic acid. The crude products obtained in each case were purified both by extraction with alcohol and subsequent recrystallization from water and also by conversion into their respective hydrochlorides and subsequent hydrolysis of the latter in boiling water.

Anal. III. Calcd. for $C_{17}H_{17}O_4N \cdot H_2O$: H_2O, 5.68. Found: H_2O, 5.68. Calcd. for $C_{17}H_{17}O_4N$: N, 4.68. Found: N, 4.90, 4.99.

[6] The halogen was determined by direct precipitation with aqueous silver nitrate.

[7] Salts 2 and 6 separated in crystalline condition when the oil obtained from evaporating their aqueous solutions was warmed with alcohol.

TABLE II

ANALYSES[8] OF METALLIC SALTS

	Salt	Formula	H_2O, %[9] Calcd.	H_2O, %[9] Found	N, % Calcd.	N, % Found	Met., % Calcd.	Met., % Found
1	K	$C_{11}H_{12}O_5NK \cdot 2H_2O$	11.50	11.56	5.05	5.26		
2	K	$C_{11}H_{11}O_5NK_2 \cdot 1.5H_2O$	7.89	8.30	4.44	4.65		
3	Na	$C_{11}H_{12}O_5NNa \cdot H_2O$			5.02	4.95		
4	NH_4	$C_{11}H_{16}O_5N_2$			10.94	10.84		
5	Ag[10]	$C_{11}H_{12}O_5Ag \cdot H_2O$			3.85	4.04	29.65	29.49[11]
6	Pb	$C_{11}H_{11}O_5NPb \cdot H_2O$	3.90	3.74	3.15	3.21	46.62	46.62[12]
7	Ba	$(C_{11}H_{12}O_5N)_2Ba \cdot 3H_2O$	14.98	14.47	4.57	4.80	22.22	22.21[12]
8	Ba	$2[(C_{11}H_{11}O_5N \cdot Ba)]Ba(OH)_2 \cdot H_2O$	1.92	1.84	3.04	3.24	44.79	44.04[12]
9	Cu[10]	$2(C_{11}H_{11}O_5NCu) \cdot H_2O$	2.90	2.21	4.66	4.92	21.15	21.62[13]
10	Cd	$[(C_{11}H_{12}O_5N)_2Cd \cdot 5H_2O] \cdot 4H_2O$	9.60	9.52	4.13	3.76	16.52	16.25[14] / 16.66[12]
11	Cd[10]	$C_{11}H_{11}O_5NCd \cdot 2H_2O$	9.33	9.25	4.01	4.57		

TABLE III

PHYSICAL PROPERTIES[15] OF METALLIC SALTS

	Salt	M. p., °C.	Solubility
1	K	250–255 decomp.	1 g. in 2 cc. cold water, insol. alcohol
2	K	174–200 decomp.	V. s. water, insol. alcohol
3	Na	180–186 decomp.	1 g. in 3 cc. cold water, insol. alcohol
4	NH_4	218.5–220 decomp.	V. s. water, insol. alcohol
5	Ag	148.5–149.5 decomp.	Insol. cold water, decomp. boiling water
6	Pb	260–262 decomp.	5.3 g. in 50 cc. boiling water, 0.4 g. in 50 cc. cold water, insol. alcohol
7	Ba[17]	223–227 decomp.	2.0 g. in 6 cc. boiling water, insol. cold water[16]
8	Ba[17]	Not melted up to 315	1.5 g. in 40 cc. boiling water, insol. cold water
9	Cu	241–242.5 decomp.	1 g. in 50 cc. boiling water, insol. alcohol
10	Cd	Not melted up to 315	1.5 g. in 25 cc. boiling water, 0.01 g. in 20 cc. cold water,[16] insol. alcohol
11	Cd[18]	205–208 decomp.	0.3 g. in 30 cc. boiling water, fairly sol. cold water, insol. alcohol

[8] The figures given are the average of duplicate determinations.

[9] Salts 3 and 5 were analyzed in the hydrated form, all others were heated to constant weight at 110°. In the case of 10 only four molecules of water was lost at 110°.

[10] Salt was not recrystallized for analysis.

[11] Determined by direct precipitation as silver chloride.

[12] Determined by ignition as the sulfate.

[13] Determined by ignition as copper oxide.

[14] Determined electrolytically.

[15] Salts crystallized as follows: 1, 2 and 3 from alcohol–water as fine needles in the form of rosets; 4 and 11 from alcohol–water as crystalline powders; 5, 6, 8 and 9 from water as crystalline powders; 7 from water in the form of clumps suggesting the cauliflower; 10 from water as needles.

[16] A marked tendency to form supersaturated solutions is exhibited.

[17] The behavior of the two barium salts when heated on platinum serves to distinguish them since 7 forms a snake and 8 merely chars.

[18] Alcohol was used to precipitate this salt, while 10 separated from water.

The free acid is only slightly soluble in boiling water, 0.1 g. dissolving in 300 cc., and almost insoluble in cold water and alcohol. It separates from its aqueous solutions in the form of soft white needles appearing in the form of rosets.

Anal. IV. Calcd. for $C_{11}H_{13}O_4N$: N, 6.28. Found: N, 6.03, 6.04.

The free acid is soluble in about 50 parts of boiling water from which it separates in hard elongated white plates which grow in rosets. It shows no tendency to form supersaturated aqueous solutions and is insoluble in alcohol.

Summary

Free tyrosine-N-acetic acid, its hydrochloride, the hydrochloride of its dimethyl ester and certain of its metallic derivatives have been prepared and described.

A new general method for the synthesis of α-imino dibasic acids has been outlined. Investigations will be continued on the derivatives of the four acids referred to in this paper and on the intermediate hydantoins involved in their synthesis.

SOUTH HADLEY, MASSACHUSETTS

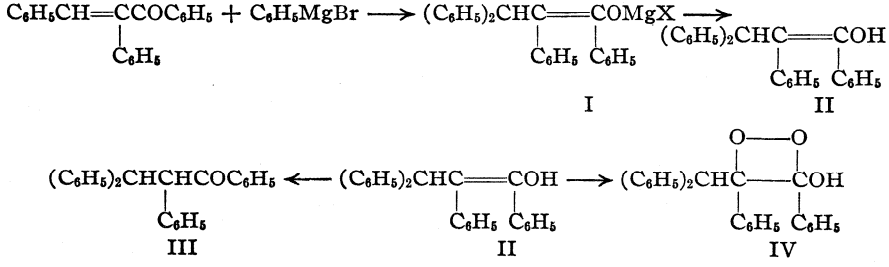
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE REACTION BETWEEN ALPHA, BETA-UNSATURATED KETONES AND ORGANIC MAGNESIUM COMPOUNDS. THE STRUCTURE OF THE ADDITION PRODUCTS

BY E. P. KOHLER AND W. E. MYDANS

RECEIVED JUNE 8, 1932 PUBLISHED DECEMBER 13, 1932

Many α,β-unsaturated ketones combine with Grignard reagents and other metallic compounds to form metallic derivatives which on hydrolysis yield saturated ketones. In some cases, notably those in which there are substituents in the alpha position, it is known that the saturated ketones are secondary products, and that the primary products of hydrolysis are enols which are capable of combining with oxygen to form peroxides. In these cases it is reasonable to infer that the metallic derivatives are enolates which are formed by 1,4-addition to the conjugated system

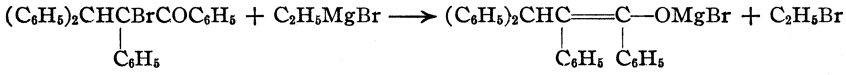


Owing to the rapidity with which most enols of mono ketones undergo rearrangement, this method of arriving at the structure of the metallic

derivatives is seldom applicable; in most cases the structure of the addition products, and consequently the mode of addition, has to be based on analogy or inferred from the course of metathetical reactions—both equally likely to lead to conclusions that are illusory. For securing evidence that is more reliable but two ways appear to be open, namely, proof of the presence of an ethylenic linkage or proof of the presence of a carbonyl group. We decided to explore the first of these possible ways.

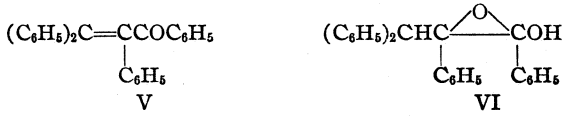
To this end we planned to treat the addition products with oxygen. It is well known that many metallic enolates and all Grignard reagents undergo spontaneous oxidation. In both cases, doubtless the primary product is a peroxide, but the final result usually is oxidative cleavage. In the case under consideration the alternative peroxides, being very different in character, would be expected to give cleavage products that are distinctive

In order to keep as close to the known as possible we selected as the first magnesium compound to study the addition product represented by I. Ethereal solutions of this compound can be obtained both by the reaction indicated in the equation, and also by the action of ethylmagnesium bromide on alpha bromo-α,β,β-triphenylpropiophenone.



When oxygen was passed into these solutions they immediately became yellow in color, then gradually changed into brown viscous liquids which, when freed from magnesium by treatment with acid or ammonium chloride, yielded a product that crystallized well and melted sharply.

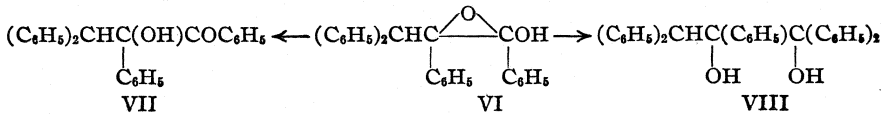
This substance proved to be composed of two compounds which cannot be separated by crystallization, namely, tetraphenylpropenone (V) and oxo tetraphenylpropanol VI



The unsaturated ketone has been known for a long time but the oxanol is new and it is the first of its type. Our formula is based mainly on the following observations: (1) chromic acid oxidizes it to benzophenone and benzil, establishing the carbon chain and the position of the phenyl groups, (2) it rapidly liberates a mole of gas from methylmagnesium iodide, therefore contains one hydroxyl group, (3) among the products that are formed when it is heated is an isomer which was described in an earlier paper and there formulated as an alpha hydroxy ketone VII;[1]

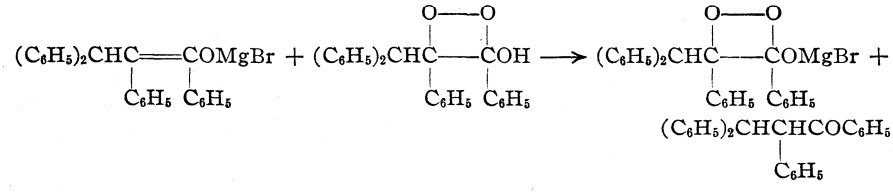
[1] Kohler, Richtmyer and Hester, THIS JOURNAL, 53, 205 (1931).

when it is heated with alkalies this isomer is formed quantitatively, and (4) phenylmagnesium bromide converts it in part into this same isomer and in part into a glycol of which the structure is certain (VIII). Assuming the formulas of the earlier paper to be correct, these transformations must be represented as follows

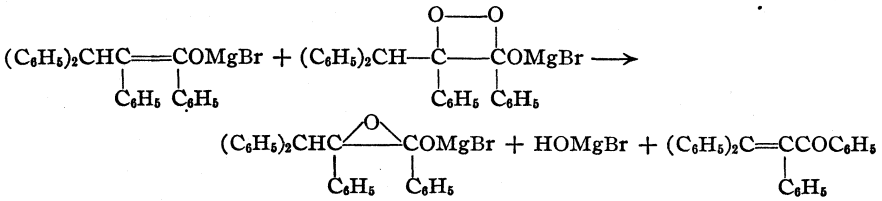


Since here for the first time an alpha hydroxy ketone and its cyclic isomer appear as two stable and independent compounds, there is, naturally, some difficulty in the allocation of the two possible formulas. The reasons for our choice are as follows. Since phenylmagnesium bromide converts both isomers into the glycol, at least one of them must be the oxanol VI; the other isomer might be either a stereoisomeric oxanol or an alpha hydroxy ketone. Of these two types of compounds the hydroxy ketone would be expected to be the more stable, both on general considerations and because most ethylene oxides are rearranged more or less readily into open-chained isomers. Ethylene oxides also generally combine with water when they are treated with bases—a process which would likewise transform an oxanol into an hydroxy ketone. For these reasons we regard our new compound as the oxanol and the isomer into which it passes on rearrangement as the hydroxy ketone but we realize that until derivatives of both isomers are available for comparison these formulas are open to revision.

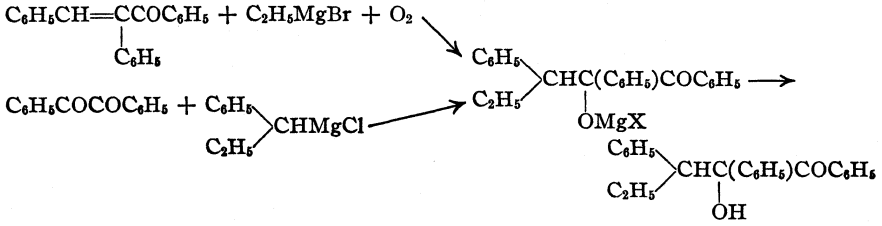
According to the foregoing account the autoxidation of the magnesium derivative appears to be much more involved than that of the enol which is formed from it by hydrolysis. It is possible, however, that the primary reaction is the same in both cases, the final products being due to the interaction of oxidized and unoxidized magnesium compounds. In order to test this possibility phenylmagnesium bromide was added to benzaldesoxybenzoin as before, but then the solution was treated with half a mole of the peroxide (IV) instead of with oxygen. The result was a mixture of magnesium derivatives which, on hydrolysis, yielded, along with some of the saturated ketone, the same crystalline product that had been obtained with oxygen. In this case, doubtless, the more acidic peroxide first reacts with one molecule of addition product to form a new magnesium derivative



The new magnesium derivative then oxidizes a second molecule of the addition product to the unsaturated ketone and is thus reduced to the magnesium derivative of the oxanol



In the case under investigation the results confirmed the conclusions which had been reached in another manner, but they held little promise that in doubtful cases oxygen might be used with success for determining the structure of magnesium derivatives. We nevertheless examined one more case, starting with the same unsaturated ketone but employing ethyl instead of phenylmagnesium bromide. Here also a product was formed which had the composition and molecular weight of an oxanol but the same substance was synthesized by a method which would be expected to yield an hydroxy ketone and it could not be isomerized with alkalies. It therefore probably is not the oxanol but the isomeric alpha hydroxy ketone



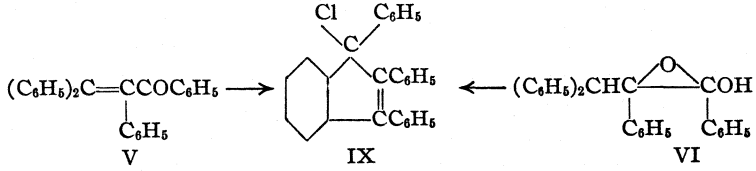
Experimental Part

As was indicated in the introduction, the solutions of the magnesium derivative were made by two completely different reactions of which one required a slight excess of phenylmagnesium bromide, and the other an excess of ethylmagnesium bromide. The action of oxygen was examined in different solvents and at different temperatures, and the reaction was allowed to proceed for various intervals of time ranging from two to eighty hours. These comparative experiments need not be described in detail because, excepting that higher temperatures and prolonged action increased the quantity of oily by-products, changes in procedure had no effect on the result.

In all experiments the principal product was a substance which melts sharply at 162°. This substance is, doubtless, a definite compound containing the unsaturated ketone and the oxanol in equimolar quantities. The former melts at 154°, the latter at 159°; all mixtures prepared from these two compounds excepting those which contain less than 10% of

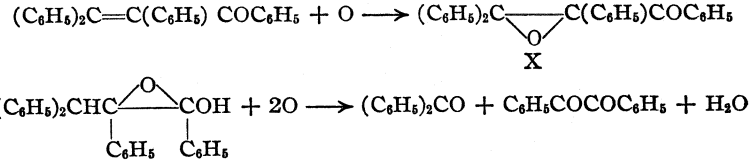
one of them melt higher than the components, the highest melting point attainable being 162°, which is reached when the components are mixed in equimolar quantities.

Inasmuch as this product cannot be separated by crystallization and contains as one component a new and entirely unexpected type of compound, it was necessary at the outset to subject it blindly to the action of a number of reagents in the hope of securing a clew to its character. In some reactions it behaves like a chemical individual because both components are converted into the same product as, for example, in the reaction with acetyl chloride which transforms both into chloro triphenyl indene



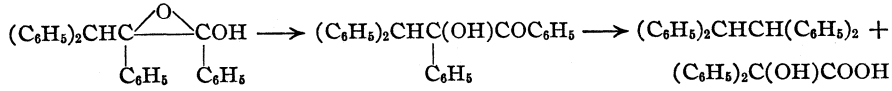
V IX VI

In other reactions both components participate but yield different products. Thus in glacial acetic acid chromic acid merely adds one atom of oxygen to the unsaturated ketone while under the same conditions it oxidizes the oxanol to benzophenone and benzil

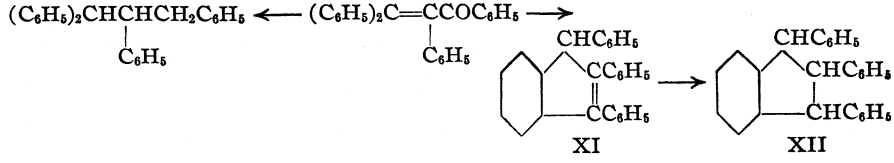


X

A few reagents, notably methyl alcoholic potassium hydroxide, transform the oxanol without affecting the ketone and leave a mixture from which the ketone can be separated by crystallization



More frequently the unsaturated ketone is altered while the remarkably insensitive oxanol is left intact; thus hydrogen bromide in glacial acetic acid converts the former into a bromo indene under conditions under which it does not attack the latter. And, similarly, zinc in glacial acetic acid reduces only the ketone; even hydrogen iodide leaves the oxanol unchanged under conditions under which the unsaturated ketone is reduced completely to hydrocarbons



XI XII

All these reactions in which the ketone alone is changed yield crystalline products from which the oxanol can be isolated by fractional crystallization but the separations are troublesome and wasteful. A more useful mixture of products was obtained with ethylmagnesium bromide, which combines with the unsaturated ketone and converts the oxanol into a magnesium derivative from which it is regenerated by acids; from the resulting mixture of products the oxanol can be separated without too great difficulty.

Most of the chemical properties of the ketone and the oxanol are inferred from the reactions of the crystalline mixture, but whenever there was any doubt with respect to the interpretation of the results, the reactions were subsequently repeated with each of the components. The procedure finally adopted for the preparation of the substance was as follows.

An ethereal solution of the magnesium derivative was prepared in the usual manner from 114 g. of benzaldesoxybenzoin and a solution of phenylmagnesium bromide containing 29 g. of magnesium. Into this solution which was chilled in a freezing mixture and stirred vigorously was passed a rapid stream of oxygen dried over phosphorus pentoxide. At the outset the gas was absorbed almost completely and a bright yellow color appeared immediately. The color gradually changed to green and finally to brown. After oxygen had been passed into the solution for three hours the viscous brown liquid was poured into iced hydrochloric acid. A crystalline solid separated in the ethereal layer. After allowing sufficient time for complete separation, the solid was collected on a filter, washed with ether and dried—yield 55 g. melting at 158–159°.

The ethereal filtrate, now almost black in color, was extracted with 10% aqueous sodium hydroxide until free from phenol; the extract by suitable manipulation yielded 14 g. of phenol, 0.7 g. of benzoic acid and a small quantity of tarry material. The ethereal layer on distillation with steam gave a distillate containing bromobenzene and diphenyl and left a residue which, after washing with ether to remove some colored resinous material, on drying melted at 154–158° and weighed 60 g. Recrystallization of the combined solids from acetone and ether gave 110 g. of pure product melting at 162°—a yield of 74.5%.

Analyses of many different samples gave values lying between 87.1 and 87.6% for carbon and 5.5 and 6.2% for hydrogen, the corresponding values for an equimolar compound of the ketone and the oxanol being 87.8 and 5.4%. The molecular weight was determined by both the freezing point and boiling point methods in a large variety of solvents and found not to vary more than 5% from a mean value of 363, instead of 369 calculated for an equimolar mixture. Assuming this molecular weight, one mole of substance liberated 0.9 mole of gas from methylmagnesium iodide.

The substance is sparingly soluble in all common solvents except boiling acetone and boiling chloroform. As would be expected, it is less soluble in all solvents than either of its components. Its solutions, like those of the unsaturated ketone, are yellow in color.

Preparation with the Peroxide.—A solution of the magnesium derivative was made by adding 11.2 g. of α-bromo-α,β,β-triphenylpropiophenone to an ethereal solution of phenylmagnesium bromide, prepared from 0.66 g. of magnesium, and boiling the mixture for half an hour. This solution was cooled in a freezing mixture and treated with 5 g. of pure peroxide which was added in small quantities while the solution was stirred vigorously. The mixture was boiled for two and one-half hours. A pale yellow precipitate that formed at the outset increased as the reaction proceeded. After

having stood overnight the mixture was poured into iced acid, which precipitated 3.5 g. of solid.

The washed and dried solid was boiled with 75 cc. of dry ether for four hours for the purpose of extracting the saturated ketone. The residue—1.1 g.— after two recrystallizations from acetone, melted at 161°, and showed no depression in the melting point when mixed with the product obtained with oxygen. An analysis confirmed the identity of the two products.

Anal. Calcd.: C, 87.8; H, 5.4. Found: C, 87.4; H, 5.4.

Oxidation, Oxotetraphenylpropanone (X).—To a solution of 5 g. of the substance in 15 cc. of hot glacial acetic acid, 4.1 g. of chromic anhydride was added slowly. The solution was heated for two hours on a steam-bath, then poured on cracked ice. The resulting solution was extracted with ether. The ether extract, deep yellow in color, was freed from acetic acid, which also removed nearly a gram of benzoic acid, dried, concentrated, and diluted with petroleum ether. It deposited 0.77 g. of a product which after one recrystallization from alcohol melted at 157°.

Anal. Calcd. for $C_{27}H_{20}O_2$: C, 86.2; H, 5.3. Found: C, 86.4; H, 5.6.

Composition and melting point correspond to that of a substance which Japp and Klingemann[2] obtained by the action of chromic acid on the unsaturated ketone in cold acetic acid. We repeated their experiment and proved that our product was the same as theirs.

Addition of more petroleum ether to the filtrate from the oxido compound led to the separation of another crystalline compound which was identified as benzil and the mother liquors, on distillation with steam, yielded benzophenone.

Reaction with Acetyl Chloride.—1,2,3-Triphenyl-3-chloro Indene (IX).—Since the crystalline product contains an active hydrogen atom, an attempt was made to acetylate it with acetyl chloride. To this end 5 g. of the substance was boiled with acetyl chloride but all of it was recovered after thirty hours' boiling. A solution of 10 g. of the substance in excess of acetyl chloride was then sealed in a tube and heated in a steam-jacketed autoclave for fifteen hours. The orange colored solution was shaken with ice water and alcohol-free ether until it was free from acetyl chloride. The ethereal layer was washed with bicarbonate solution, dried, concentrated and mixed with low-boiling petroleum ether. It deposited a chloro compound which after recrystallization from benzene and petroleum ether melted at 115–116°.

Anal. Calcd. for $C_{27}H_{19}Cl$: C, 85.6; H, 5.1. Found: C, 85.7; H, 5.1.

For the purpose of identification the chloro compound was transformed into the methoxyl and ethoxyl compounds by dissolving it in solutions of potassium hydroxide in the corresponding alcohols. The products crystallized in large transparent prisms melting at 144 and 172°. In the literature the melting points of these substances are given as 153 and 172° but an examination of the original specimens[3] showed that the melting point of the methoxyl compound is incorrect and should be changed to 144°.

The yield of pure chloro indene—5.75 g. from 10 g. of substance—indicated that acetyl chloride had converted both components of the mixture into the indene derivative. This was confirmed, later, by treating each component separately with acetyl chloride in the same manner. Two grams of the unsaturated ketone gave 1.55 g. and 2 g. of the oxanol gave 1.6 g. of the same chloro compound.

Action of Alcoholic Potassium Hydroxide.—A suspension of 2.27 g. of the finely powdered solid in 150 cc. of a 20% solution of potassium hydroxide in methyl alcohol was boiled for twenty minutes and then filtered, to remove a small quantity of un-

[2] Japp and Klingemann, *J. Chem. Soc.*, **57**, 669 (1890).

[3] Kohler, *Am. Chem. J.*, **40**, 222 (1908).

changed substance. The filtrate, cooled in a freezing mixture, deposited plates which after repeated recrystallization from ether melted at 153–154°, and were identified as the unsaturated ketone by analysis and mixed melting point.

The filtrate from the unsaturated ketone was diluted with water and then extracted with ether. The ethereal layer was concentrated to a small volume and cooled. It deposited the characteristic flat needles of the alpha hydroxy ketone (VII), completely identified by a comparison with a sample on hand. That the oxanol was the source of the hydroxy ketone was established by dissolving 0.5 g. of pure oxanol in 15 cc. of 20% methyl alcoholic potassium hydroxide, boiling the solution for twenty minutes, then diluting it with water and cooling. The yield of hydroxy ketone was 0.43 g.

Action of Halogen Acids.—A small quantity of the solid was recovered completely after it had been heated in a sealed tube with concentrated hydrochloric acid for two days at 100°. A similar experiment in which 2 g. of the solid was heated with 5 cc. of 48% aqueous hydrobromic acid at 100° for seven days resulted in a brown granular solid which decomposed briskly at 130°. This solid was, doubtless, a mixture of bromo triphenyl indene and oxanol. On recrystallization from benzene and petroleum ether it yielded 0.85 g. of pure oxanol melting at 159° and completely identified by analysis.

The oxanol was obtained more readily by dissolving 1 g. of the substance in 10 cc. of a 30% solution of hydrobromic acid in glacial acetic acid, and allowing the solution to stand overnight. The solvent was removed under reduced pressure, and the oily residue heated with alcohol. The bromo indene was thus converted into the ethoxy indene and the mixture of oxanol and ethoxy indene was separated by recrystallization from alcohol. It yielded 0.4 g. of oxanol.

The oxanol can be obtained from the crystalline product also by treatment with hydriodic acid. Thus 2 g. of the substance was heated with 6 cc. of 45% aqueous hydriodic acid for four hours. The mixture was then diluted with water and extracted with ether. The extract, washed with thiosulfate, dried, and concentrated, deposited 1.85 g. of crude product. By a somewhat troublesome crystallization first from acetone and petroleum ether, and finally from methyl alcohol, the crude product was separated into oxanol melting at 159° and a second pure substance which crystallized in prisms and melted at 135°.

Anal. Calcd. for $C_{27}H_{20}$: C, 94.1; H, 5.8. Found: C, 93.9; H, 6.0.

The substance has the composition and melting point of 1,2,3-triphenylindene. This hydrocarbon was not available for comparison but a sample was obtained by means of a reaction that was much easier to carry out than the one by which it was made originally,[4] namely, by the action of hydriodic acid on 1,2,3-triphenyl-3-ethoxyindene. A suspension of one gram of the ether was heated with 9 cc. of 45% aqueous hydriodic acid for an hour. The mixture was then diluted with water and extracted. The ethereal layer was washed with thiosulfate, dried, and evaporated. It left a colorless oil which after several extractions with petroleum ether readily solidified. The product was the same as that which had been obtained in the preceding experiment.

Action of Hydriodic Acid and Red Phosphorus, 1,2,3-Triphenylhydrindene (XII) and 1,1,2,3-Tetraphenylpropanone.—A suspension of 5 g. of the substance and 1.5 g. of red phosphorus in 12 cc. of constant boiling hydriodic acid was boiled for forty-six hours in an all-glass apparatus equipped with a Bunsen valve to exclude oxygen, then diluted with water and filtered. The filtrate manipulated as in the preceding experiment yielded two products, the one crystallizing in thick needles and melting at 154°, and the other crystallizing in large prisms and melting at 121°.

The higher melting compound has the composition, molecular weight, crystal form and melting point of 1,2,3-triphenylhydrindene, recently described by Schlenk

[4] Kohler, *Am. Chem. J.*, **40**, 229 (1908).

and Bergmann.[5] Moreover, any open chained hydrocarbon having the composition represented by $C_{27}H_{22}$ would necessarily have an ethylenic linkage and would therefore be attacked by ozone, but our hydrocarbon was recovered almost completely after it had been treated with ozonized oxygen for four hours. The dihydro compound is doubtless formed by further reduction of 1,2,3-triphenylindene which was obtained in the preceding experiment but which was not found among the products of the more effective combination of hydrogen iodide and phosphorus.

The lower melting compound is likewise a hydrocarbon.

Anal. Calcd. for $C_{27}H_{24}$: C, 93.1; H, 6.9. Found: C, 93.2; H, 6.7.

Since a hydrocarbon with this composition is necessarily open chained and saturated, it is presumably tetraphenylpropane, the final reduction product of the unsaturated hydrocarbon. We therefore undertook its preparation from the corresponding saturated ketone—tetraphenylpropanone (XIII) with sodium amalgam as follows. Eighty grams of 5% sodium amalgam was added to a solution of 6 g. of the ketone in 80 cc. of dry benzene and 100 cc. of absolute alcohol. After fifteen hours the colorless solution was decanted and evaporated in a current of air. The residue, freed from alkali and water in the usual manner, was crystallized from ether. It did not behave well in this solvent but it crystallized readily from acetone, from which it separated in clusters of needles containing a molecule of solvent, and melting at 160–161°.

Anal. Calcd. for $C_{30}H_{30}O_2$: C, 85.2; H, 7.2. Found: C, 85.1; H, 7.3.

The second step in the reduction was effected with hydriodic acid. One gram of tetraphenylpropanol was heated in a sealed tube with 0.5 g. of red phosphorus and 2 cc. of constant boiling hydriodic acid for six hours at 160°. After the usual manipulations, this procedure yielded 0.3 g. of a solid which crystallized in prisms, melted at 121°, and was in every way identical with the lower melting hydrocarbon obtained previously.

$$(C_6H_5)_2CH—CH(C_6H_5)COC_6H_5 \longrightarrow (C_6H_5)_2CHCH(C_6H_5)CHOHC_6H_5 \longrightarrow (C_6H_5)_2CHCH(C_6H_5)CH_2C_6H_5$$

XIII XIV

Reduction.—Tetraphenylpropenone, one of the components of the crystalline product, is very readily reduced to tetraphenylpropanone with zinc and acetic acid, and since solutions of the former are yellow, while those of the latter are colorless, it is easy to follow the course of the reduction by observing the color. When solutions of the crystalline product itself in glacial acetic acid are boiled with zinc dust, they likewise soon become colorless but the result is a mixture of products that is difficult to separate. Thus when 4 g. of zinc dust was added to a solution of 10 g. of the substance in 50 cc. of boiling glacial acetic acid, the solution became colorless in thirty minutes. By dilution with water, extraction with ether and the customary treatment of the ether extract, the solution yielded 9.6 g. of solid melting at 153–156°. From this solid it was comparatively easy to separate 3.4 g. of pure tetraphenylpropanone melting at 180° by fractional crystallization from acetone and ether, but further separation of the remaining material was exceedingly difficult. It was finally accomplished by resorting to carbon disulfide, in which the oxanol is readily soluble and from which it crystallizes well. The yield of pure oxanol was 4.4 g. and that of the saturated ketone 4.5 g.

Reaction with Phenylmagnesium Bromide.—To an ethereal solution of phenylmagnesium bromide prepared from 1.35 g. of magnesium was added 5 g. of the finely powdered solid. It dissolved immediately with evolution of heat and the solution became yellow in color. After boiling the mixture for half an hour a sample was withdrawn and decomposed with iced acid; it regenerated the solid melting at 162°. Ben-

[5] Schlenk and Bergmann, *Ann.*, **463**, 52 (1928).

zene was therefore added and ether distilled until the boiling point was raised to 52°. After the solution had been boiled at this temperature for twenty minutes, it was decomposed with iced acid and manipulated in the usual manner. The washed and dried ethereal layer, upon dilution with petroleum ether, deposited 2.4 g. of a solid substance which after recrystallization from alcohol melted at 184–186°. By analysis and by comparison with an authentic sample this substance was identified as the glycol represented by VIII.

The filtrate from the glycol contained mainly oily products but ultimately yielded a small quantity of a substance which melted at 123° and which was identified as the hydroxy ketone, VII. This experiment was subsequently repeated with pure oxanol and it was thus established that this substance is the source of both the hydroxy ketone and the glycol.

Reaction with Ethylmagnesium Bromide, Preparation of the Oxanol.—Fifteen grams of the substance was added, gradually and with vigorous stirring, to a solution which had been prepared from 4.1 g. of magnesium and which was kept in a freezing mixture throughout the reaction. The mixture was stirred at this temperature for forty-five minutes, then decomposed with iced acid. The dried ethereal extract on concentration gradually deposited a solid which after a few recrystallizations yielded 7.2 g. of pure oxanol. In another experiment in which the stirring was continued for three hours the yield dropped to 4.2 g.

The filtrate from the oxanol yielded a second product which was subsequently obtained also by the action of ethylmagnesium bromide on the unsaturated ketone but which has not yet been identified.

II. ACTION OF OXYGEN ON THE MAGNESIUM DERIVATIVE FROM BENZALDESOXYBENZOIN AND ETHYLMAGNESIUM BROMIDE

To an ethereal solution of ethylmagnesium bromide, prepared from 26 g. of magnesium, 100 g. of benzaldesoxybenzoin was added slowly and with vigorous stirring while the solution was cooled in a freezing mixture. After stirring for forty-five minutes, a rapid stream of dry oxygen was passed into the solution, the stirring and cooling being maintained throughout the operation. After twenty minutes the gray color of the reagent changed to yellow and twenty-five minutes later the color was again gray and a precipitate began to form. The stream of oxygen was maintained for four hours.

On decomposition with iced acid the mixture of solid and solution deposited 32 g. of a new solid melting at 148–152°. The ethereal filtrate on concentration and gradual dilution deposited first 25 g. of a granular solid melting at 100–130°, and finally 3.5 g. of still another solid melting at 169°. The residual oils, distilled under diminished pressure, yielded 6.5 g. of the product melting at 169° and about one gram each of two hydrocarbons which melted the one at 123° and the other at 143°. These hydrocarbons were not investigated.

The product melting at 169° was readily identified as the saturated ketone, $(C_6H_5)(C_2H_5)CHCH(C_6H_5)COC_6H_5$, which is the sole product when the reaction is carried out in the absence of oxygen.[6] The granular solid melting at 100–130° was a mixture which by a laborious fractional crystallization from benzene and ether was separated into a chloro compound which has not yet been identified and the hydroxy ketone which was the principal product of the reaction.

α-Hydroxy-α,β-diphenylbutyrophenone, $C_2H_5CH(C_6H_5)CH(C_6H_5)OHCOC_6H_5$.—The principal product of the reaction, after recrystallization, melted at 154°. It is moderately soluble in most common organic solvents and crystallizes readily from nearly all of them in tufts of needles.

[6] Kohler, *Am. Chem. J.*, **35**, 399 (1906).

Anal. Calcd. for $C_{28}H_{22}O_2$: M, 330; C, 83.6; H, 6.7. Found: M, 329; C, 83.5; H, 6.9.

The substance was made synthetically in the following manner. α-Chloropropylbenzene was prepared from ethylphenylcarbinol essentially as directed by Errera,[7] but by distillation under diminished pressure it was obtained as a colorless liquid boiling without decomposition at 104° (17–18 mm.). A solution of 12 g. of the chloro compound in absolute ether was added gradually to 1.5 g. of magnesium turnings suspended in a little ether which was increased to 100 cc. after the reaction had started. The mixture was boiled for twenty minutes, then cooled and filtered rapidly into a separating funnel from which it was added, drop by drop, to a solution of 10 g. of benzil in 20 cc. of absolute ether. A deep purple color was produced and it persisted throughout the reaction. After stirring for an hour, the mixture was poured into iced acid—whereupon the color changed to yellow. The washed and dried ethereal solution, on gradual dilution with petroleum ether, deposited first 4.2 g. of benzil and then 2.1 g. of the hydroxy ketone.

Reduction.—A suspension of two grams of the hydroxyl compound and 0.6 g. of red phosphorus in 5 cc. of constant boiling hydriodic acid was digested on a steam-bath for forty hours, then diluted with water and extracted with ether. The ethereal solution by suitable treatment yields along with a considerable quantity of oily products 0.6 g. of the corresponding saturated ketone—establishing both the character of the carbon chain and the location of the hydrocarbon residues.

Action of Acetyl Chloride, $C_2H_5CH(C_6H_5)\overset{\displaystyle OCOCH_3}{\overset{|}{C}}(C_6H_5)COC_6H_5$.—A solution of 5 g. of the hydroxy ketone in 40 g. of acetyl chloride was heated for fifteen hours. The excess of acetyl chloride was removed under diminished pressure, leaving 5.25 g. of a crystalline residue, which after repeated crystallization yielded 3.1 g. of the pure acetate. It crystallized in large transparent prisms and melted at 160–161°.

Anal. Calcd. for $C_{25}H_{24}O_3$: C, 80.6; H, 6.5. Found: C, 80.5; H, 6.5.

Action of Hydrogen Chloride, $C_2H_5CH(C_6H_5)CCl(C_6H_5)COC_6H_5$.—A solution of 3 g. of the substance in 300 cc. of absolute alcohol was saturated with dry hydrogen chloride and set aside for forty hours. The solvent was removed under diminished pressure; it left an oily residue which on treatment with ether and methyl alcohol yielded 2.1 g. of the chloro compound. By recrystallization from methyl alcohol, it was obtained in elongated prisms melting at 93–95°.

Anal. Calcd. for $C_{23}H_{21}OCl$: C, 79.1; H, 6.0. Found: C, 79.0; H, 6.1.

The Methyl Ether, $C_2H_5CH(C_6H_5)C(OCH_3)C_6H_5COC_6H_5$.—Attempts to regenerate the hydroxy ketone from the chloro compound were unsuccessful because the hydroxyl compound is both reduced and cleaved by bases. It was comparatively easy, however, to replace the chlorine with methoxyl. Thus a solution of one gram of the chloro compound in dry methyl alcohol was shaken for twelve hours with 0.5 g. of dry silver oxide, then diluted and extracted with ether. The ether on evaporation deposited a halogen-free solid which after recrystallization from petroleum ether melted at 81–82°.

Anal. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 6.9; OCH_3, 9.0. Found: C, 83.6; H, 6.8; OCH_3, 8.7.

Summary

The structure of the magnesium derivatives which are formed by adding Grignard reagents to unsaturated ketones cannot be determined by converting them into peroxides.

[7] Errera, *Gazz. chim. ital.*, **6**, 222 (1886).

In one of the two cases investigated the action of free oxygen on the magnesium derivative resulted in the formation of equimolar quantities of an unsaturated ketone and a new type of oxanol. In the other case the oxidation product was an alpha hydroxy ketone.

CONVERSE MEMORIAL LABORATORY
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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

HYDROGENOLYSIS OF OXYGENATED ORGANIC COMPOUNDS

BY RALPH CONNOR[1] AND HOMER ADKINS

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This paper deals with the cleavage of carbon to carbon or carbon to oxygen bonds accompanied by the addition of hydrogen. This type of reaction applied to hydrocarbons has been referred to by Ellis[2] as "hydrogenolysis," since it is clearly analogous to the reactions commonly termed hydrolysis, alcoholysis and ammonolysis which involve the *cleavage* of a bond *accompanied* by the *addition* of water, alcohol or ammonia.

$$CH_3COCR_2COOC_2H_5 \xrightarrow{H_2O} \underset{\text{Hydrolysis}}{CH_3COOH} + R_2CHCOOH + C_2H_5OH \qquad (I)$$

$$CH_3CHOHCR_2COOC_2H_5 \xrightarrow{H_2} \underset{\text{Hydrogenolysis}}{2C_2H_5OH + R_2CHCH_2OH} \qquad (II)$$

The cleavage of oxygenated organic compounds with addition of hydrogen has been observed several times to occur as the result of the action of hydrogen in the presence of a catalyst. Recently the use of higher pressures of hydrogen and especially of the copper–chromium oxide catalyst has greatly extended the field of operation and rendered more important the application of hydrogenolysis as a tool in the transformation of organic compounds.

Previous work in this Laboratory has shown that the linkages indicated by dotted lines in the formulas I to VII are susceptible to hydrogenolysis over a copper–chromium oxide catalyst.

$$\underset{\text{I}^3}{C_6H_5CHR....OH} \quad \underset{\text{II}^4}{C_6H_5CHRCH_2....OH} \quad \underset{\text{III}^5}{HO....CHRCH_2COOEt} \quad \underset{\text{IV}^4}{RC(=O)....OC_2H_5}$$

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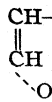
[1] The authors are indebted to E. I. du Pont de Nemours and Company for the support of a fellowship enjoyed by Dr. Connor during the academic year 1931–1932.

[2] C. Ellis, "Hydrogenation of Organic Substances," 3d ed., D. Van Nostrand Company, New York, 1930, p. 564.

[3] Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

[4] Adkins and Folkers, *ibid.*, **53**, 1095 (1931).

[5] Folkers and Adkins, *ibid.*, **54**, 1145 (1932).



V[3] $CH_3C(OH)....C(CH_3)_2COOEt$ VI[4] $C_6H_5CH_2....CH(C_6H_5)_2$ VII[6]

The cleavage of similar linkages through the action of hydrogen in the presence of a catalyst has been observed by earlier investigators, among which may be cited the following. Sabatier and Murat[7] noted that the hydrogenation of benzyl alcohol over nickel gave toluene. Sabatier and Mailhe[8] isolated ethyl butyrate, acetone, isopropyl alcohol, propionic acid and dehydroacetic acid from the hydrogenation of acetoacetic ester over nickel. The opening of the furan ring by a platinum catalyst was reported by Adams and Kaufmann.[9] The formation of ethers from acetals was accomplished by nickel catalysts.[10,11] Propanediol-1,2 has been obtained from mannitol over a member of the iron or platinum group.[12]

It was the purpose of the investigation herewith described to increase the information available with regard to the relationship of structure to ease of cleavage with hydrogen, of carbon to oxygen and of carbon to carbon linkages. To this end a number of glycols, β-hydroxy and malonic esters, and furan derivatives have been subjected to the action of hydrogen under pressure in the presence of a copper–chromium–barium oxide catalyst.[13]

In Table I are listed the results of the hydrogenolysis of several glycols, hydroxy esters, substituted malonic esters, and furan derivatives and of certain hydrogenations incidental to the work. The products were characterized in many cases by the preparation of solid derivatives in addition to the usual determination of boiling or melting points or analysis. The iodoform reaction was extensively used for the detection of methyl monalkyl carbinols and the method of Wright for methanol.[14] (For the sake of economy in publication, almost twenty pages describing the experi-

[6] Zartman and Adkins, THIS JOURNAL, **54**, 1668 (1932).

[7] Sabatier and Murat, *Ann. chim.*, [9] **4**, 258 (1915).

[8] Sabatier and Mailhe, *Bull. soc. chim.*, [4] **3**, 232 (1908).

[9] Adams and Kaufmann, THIS JOURNAL, **45**, 3029 (1923).

[10] Sigmund and Marchart, *Monatsh.*, **48**, 267 (1927); Sigmund and Uchaan, *ibid.*, **51**, 234 (1929); Cabanac, *Compt. rend.*, **188**, 1257 (1929).

[11] Covert, Connor and Adkins, THIS JOURNAL, **54**, 1651 (1932).

[12] I. G. Farbenind., German Patent 541,326, October 25, 1927 [*C. A.*, **26**, 1939 (1932)].

[13] The authors believe that the data herewith presented are for the present to be interpreted only as a measure of the influence of various structures upon the ratio of competitive reactions under specified conditions. An attempt to apply these results to the influence of the substituent group upon the strength of bonds (in an electrochemical sense) is not justified because the ratio of rates of competitive reactions may not be at all the same as the ratio of the forces binding the atoms together at the various linkages which are undergoing rupture. *Cf.* Adkins, *J. Chem. Education*, **9**, 1865 (1932).

[14] Wright, *Ind. Eng. Chem.*, **19**, 750 (1927).

TABLE I

HYDROGENATION AND HYDROGENOLYSIS OF VARIOUS ORGANIC COMPOUNDS[a]

No.	Compound	Moles	Catalyst, g.	Time, hrs.	Products
1	Cyclohexanediol-1,3	0.30	3[c]	3.0	Cyclohexanol 95%
2	Cyclohexanediol-1,3	.30	6[c]	0.0	Cyclohexanol 80%
3	Cyclohexanediol-1,2	.25	3[c]	6.3	Cyclohexanol 20%; cyclohexanediol-1,2
4	Cyclohexanediol-1,4	.25	3[c]	8.5	Cyclohexanediol-1,4 96%
5	Propanediol-1,3	.50	3[c]	1.2	Propanol-1 74% (94%)
6	Butanediol-1,3	.50	3[c]	4.5	Butanol-2 65%; butanol-1 17%; butanediol-1,3 9%
7	Butanediol-1,3	.50	3[c]	0	Butanol-2 56%; butanol-1 32%
8	2-Methyl-pentanediol-2,4	.50	3[c]	0.5	Propanol-2 86%; 2-methylpentanol-4 13%
9	2-Methyl-pentanediol-2,4	.29	5[c]	0	Propanol-2 62%; 2-methylpentanol-4 10%
10	Aldol	1.13	2[f]	1.0	Butanediol-1,3 39%; ethanol, butanol and condensation products
11	Aldol	0.82	2[f]	1.2	Butanediol-1,3 41%; ethanol, butanol and condensation products
12	Aldol[h]	1.13	3[b]	4.3	No hydrogenation
13	Diacetone alcohol	0.80	2.0[b]	0.5	2-Methyl-pentanediol-2,4 41%; 2-methyl-pentanol-4, propanol-2
14	Diacetone alcohol	.80	2.0[b]	0.07	2-Methyl-pentanediol-2,4 59%; 2-methyl-pentanol-4 6%; propanol-2 25%
15	Diacetone alcohol	.80	0.5[b]	6.0	2-Methyl-pentanediol-2,4 41%; acetone, propanol-2 42%; diacetone alcohol 0%
16	Diacetone alcohol	.88	3[f]	4.0	2-Methyl-pentanediol-2,4 89%; 2-methyl-pentanol-4 6%
17	Pentanediol-1,2	.50	5[c]	10.0	Pentanediol-1,2 73%; amyl alcohols, traces of butanol and methanol 26%
18	Pinacol	.50	5[c]	10.0	Propanol-2 17%; dimethylisopropylcarbinol 16%; pinacol 63%
19	Glycerol (98%)	.50	5[c]	4.0	Propanediol-1,2 85%; condensation products 12%
20	Pentaerythritol	.75	10[c]	5.0	Isobutanol and methanol 99%
21	Mannitol	.25	5[c]	9.0	Propanediol-1,2 24%; alcohols 22%; condensation products 20%
22	α-Methyl-*d*-glucoside	.25	5[c]	8.0	Propanediol-1,2 23%; alcohols 10%
23	4-Methyl-2,6-dimethylolphenol[i]	.30	6[b]	0.2	Mesitol (2,4,6-trimethylphenol) 50%; di-(2-hydroxy-3,5-dimethylphenyl)methane 25%
24	4-Methyl-2,6-dimethylolphenol[h]	.40	8[b]	5.0	Tar
25	Ethyl acetoacetate	.50	3[c]	8	Ethanol, butanol-1, butanol-2, ethyl butyrate 86%
26	Hexahydrobenzyl β-hydroxybutyrate	.32	5[c]	6	Butanol-1 and butanol-2 (cyclohexylcarbinol) 75%
27	Ethyl hexahydrosalicylate	.20	3[c]	3	2-Methyl-cyclohexanol-1 92%
28	Ethyl α-ethylacetoacetate	.20	3[c]	8	*n*-Butanol 41%; diethylcarbinylcarbinol (containing 7% residual ester) 41%
29	Ethyl α-ethylacetoacetate	.30	5[c]	5	*n*-Butanol 50%; diethylcarbinylcarbinol (containing 2% ester) 47%
30	Ethyl α-isopropylacetoacetate	.30	5[c]	13	Isoamyl alcohol 60%; 3-methyl-2-ethylbutanol-1 27%; ester 2%
31	Ethyl α-*n*-butylacetoacetate	.30	13[c]	26.5	*n*-Hexanol 43%; ethyl caproate 10%; 2-ethyl-butanol-1 21%; loss 18%
32	Ethyl α-hexahydrobenzyl-β-hydroxybutyrate	.20	5[c]	5	3-Cyclohexylpropanol-1 96%
33	Ethyl α-benzylacetoacetate	.20	5[c]	5	3-Phenylpropanol-1 89%
34	Ethyl α-(β-phenethyl)-acetoacetate	.20	5[c]	4.5	4-Phenylbutanol-1 97%
35	Ethyl α-methyl-β-ketovalerate	.18	3[c]	8	Propanol-1 46%
36	Diethyl β-methyl-α,γ-diacetylglutarate	.20	13[c]	16	A di-primary glycol 96%
37	Diethyl β-phenyl-α,γ-diacetylglutarate	.10	8[c]	17	A di-primary glycol 92%
38	Ethyl α,α-diethylacetoacetate	.20	3[c]	8	Diethylcarbinylcarbinol 99%
39	Ethyl α,α-di-*n*-butylacetoacetate	.20	3[c]	10	Di-*n*-butylcarbinylcarbinol 99%
40	Ethylmalonic ester	.50	15[c]	8	Butanol-1 18%; 2-methylbutanol-1 72%
41	Butylmalonic ester	.44	6[c]	9	Hexanol-1 26%; 2-methylhexanol-1 64%
42	Benzylmalonic ester	.31	10[c]	8	3-Phenylpropanol-1 19%; 2-benzylpropanol-1 68%
43	Phenylmalonic ester	.30	10[c]	8	Ethylbenzene 71%; β-phenylethanol 9%
44	Dimethylmalonic ester	2.39	30[c]	4	Isobutanol 88%; 2,2-dimethylpropanediol-1,3 5%
45	Methylethylmalonic ester	1.22	15[c]	5	2-Methylbutanol-1 80%; slightly impure 2-methylbutanol-1 16%
46	Methylisopropylmalonic ester	1.43	20[c]	23	2,3-Dimethylbutanol-1

TABLE I (*Concluded*)

No.	Compound	Moles	Catalyst, g.	Time, hrs.	Products
47	Diethylmalonic ester	0.50	10[e]	12	Diethylcarbinylcarbinol 94%
48	*n*-Propylmethylcarbinylethylmalonic ester	.82	15[e]	30	3-Methyl-2-ethylhexanol-1 80%; *n*-propylmethylcarbinylethylmalonic ester 18%
49	*n*-Propylmethylcarbinylethylmalonic ester	.30	5[e]	20	3-Methyl-2-ethylhexanol-1 78%; *n*-propylmethylcarbinylethylmalonic ester 8%
50	Isoamylethylmalonic ester	.30	10[e]	7	5-Methyl-2-ethylhexanol-1 91%
51	Isoamylethylmalonic ester	.30	10[e]	2.3	5-Methyl-2-ethylhexanol-1 87%; isoamylethylmalonic ester 9%
52	Isoamylethylmalonic ester	.68	10[e]	6.5	5-Methyl-2-ethylhexanol-1 90%; isoamylethylmalonic ester 6%
53	Ethyl α-phenylbutyrate	.50	8[e]	1.7	Hydrocarbons 8%; ethyl α-phenylbutyrate 25%; 2-phenylbutanol-1 60%
54	Ethyl α-phenylbutyrate 2-Phenylbutanol-1	.10 .25	3[e]	2.5	*Sec.*-butylbenzene 28% 2-Phenylbutanol-1 66%
55	Furfuryl alcohol	5.1	10[e]	57.5	Methylfuran 20%; pentanol-1 10%; furfuryl and tetrahydrofurfuryl alcohols 17%; pentanediol-1,2 14%; pentanediol-1,5 15%; intermediates and residue 10%
56	Furfuryl alcohol	5.1	10[e]	4	*n*-Pentane 0.3%; pentanol-1 36%; furfuryl and tetrahydrofurfuryl alcohols 13%; pentanediol-1,2 14%; pentanediol-1,5 15%; intermediates and residue 11%; methylfuran 36%
57	Methylfuran	1.0	4[e]	4	*n*-Pentane 4%; methyltetrahydrofuran 15%; pentanol-2 33%; pentanol-1 30%; intermediates, residue and loss by drying 15%
58	Ethyl salicylate	0.86	5[f]	8	Ethyl hexahydrosalicylate 58%; high boiling product 28%
59	Methyl salicylate	.33	10	9	Ethyl hexahydrobenzoate 8%; ethyl hexahydrosalicylate 79%
60	Methyl salicylate	.82	...	6.5	Methyl salicylate 96%
61	Heptaldehyde	4.63	3[e]	5.0	Heptanol-1, water and condensation products 78%
62	Ethyl acetoacetate + cyclohexylcarbinol	0.38	2[c]	0.4	Ethyl β-hydroxybutyrate and cyclohexylcarbinol 76%; hexahydrobenzyl β-hydroxybutyrate 21%
63	Ethyl acetoacetate + cyclohexylcarbinol	.38	2[c]	0.5	Hexahydrobenzyl β-hydroxybutyrate 29%
64	Ethyl acetoacetate + cyclohexylcarbinol	.38	2[c]	2.0	Hexahydrobenzyl β-hydroxybutyrate 36%
65	Cyclohexyl carbinol + ethyl β-hydroxybutyrate	(134.5 g.)	...	9.0	Hexahydrobenzyl β-hydroxybutyrate (3.9 g.); unchanged material (127.5 g.)
66	Ethyl α,α-diethylacetoacetate	0.11	1[b]	1.0	Ethyl α,α-diethyl-β-hydroxybutyrate 89%
67	Ethyl cinnamate	.85	2[b]	1.0	Ethyl β-phenylpropionate 97%
68	Benzoin	.64	6[d]	8.0	Diphenyl ethylene glycol
69	Ethyl benzalacetoacetate	.27	3[f]	5.0	Ethyl α-hexahydrobenzyl-β-hydroxybutyrate 98%
70	Diacetylmethane	.33	3[f]	1.3	Pentanediol-2,4 39%; low boiling material 52%
71	Diacetylmethane	.48	1[e]	3.5	Diacetylmethane 74%; low boiling material 26%
72	Tetrahydrofurfuryl alcohol	1.0	10[e]	11	Methyltetrahydrofuran and water 5%; tetrahydrofurfuryl alcohol 77%; pentanediol-1,5 13%
73	Methylfuran	0.61	5[f]	2	Methyltetrahydrofuran 83%; methylfuran 6%
74	Methyltetrahydrofuran	.5	5[e]	6	Methyltetrahydrofuran 74%

[a] The pressure was 175 ± 35 atmospheres and the temperature 250° except that it was 200° in Nos. 1, 6, 8, 12, 23, 24, 55, 59, 60 and 68; 190° in 58 and 69, 175° in 61, 66 and 70; 175 to 200° in 71; 135 to 165° in 14; 150° in 16, 62, 63, 64, 65 and 67; 125° in 10 and 11 and 120° in 15.

[b] A copper–chromium oxide catalyst made according to the directions first published.[3]

[c] A nickel catalyst prepared by the precipitation of nickel carbonates ("B method") using sodium carbonate as a precipitant.[15]

[15] Adkins and Covert, *J. Phys. Chem.*, 35, 1684 (1932).

[d] Catalyst No. 28 RAC was a copper–chromium–barium oxide catalyst, previously described.[16]

[e] Copper–chromium–barium oxide catalysts prepared like catalyst 37 KAF.[16]

[f] A nickel catalyst prepared by the use of ammonium carbonate as a precipitant.[17]

[h] The catalyst was red and inactive after runs 12, 24, 25 and 71.

[i] The authors are greatly indebted for certain compounds to Dr. H. A. Shonle of Eli Lilly and Company, to Dr. V. H. Wallingford of the Mallinckrodt Chemical Works and to Messrs. C. F. Koelsch, B. W. Howk, Rudolph Nagy and E. F. Struss of this Laboratory.

mental details of characterization, etc., were deleted from the original manuscript of this paper.)

Correlation of Results

Hydrogenolysis of Glycols and Corresponding Carbonyl Containing Compounds.—The formation from esters of good yields of propanediol-1,2 and pentanediol-1,5, of fair yields of butanediol-1,4, and the failure to obtain 1,3-glycols, indicated that 1,3-glycols are most susceptible to hydrogenolysis.[5] This hypothesis was borne out by the fact that cyclohexanediol-1,3 was completely converted to cyclohexanol by the time the temperature of the bomb reached 250°. However, the relative stability of the cyclohexanediols-1,2 and -1,4 was found to be the reverse of that observed for propanediol-1,2 and butanediol-1,4. Cyclohexanediol-1,4 was perfectly stable at 250° while a 20% yield of cyclohexanol was obtained from the 1,2-glycol after six hours.

The 1,3-glycols (or corresponding carbonyls) may undergo hydrogenolysis to give four sets of reaction products as illustrated below. The

$$\begin{array}{l} \\ R_2COH \\ | \\ CH_2 \\ | \\ R_2'COH \end{array} \begin{array}{l} \xrightarrow{H_2} \\ \xrightarrow{H_2} \\ \xrightarrow{H_2} \\ \xrightarrow{H_2} \end{array} \begin{array}{ll} R_2CHCH_2C(OH)R_2' + H_2O & \text{(III)} \\ R_2C(OH)CH_2CH_2R_2' + H_2O & \text{(IV)} \\ R_2CHOH + R_2'C(OH)CH_3 & \text{(V)} \\ R_2'CHOH + R_2C(OH)CH_3 & \text{(VI)} \end{array}$$

results of the hydrogenolysis of three glycols of this type, *i. e.*, $HOCH_2CH_2CH_2OH$, $CH_3CHOHCH_2CH_2OH$, and $(CH_3)_2CHOHCH_2CHOHCH_3$, indicated the effect of branching of the chain upon the ease of and the point of cleavage of the carbon chain as well as upon the relative stability of primary and secondary hydroxyl groups. That branching of the chain greatly facilitated hydrogenolysis is shown by the fact that the reaction of propanediol-1,3 required 1.2 hours at 250°, while the reaction of butanediol-1,3 was complete by the time the temperature of the bomb reached 250°, or in 4.5 hours at 210°. The reaction of the more labile 2-methylpentanediol-2,4 was complete within a half hour at 200°.

[16] Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1139 (1932).

[17] Covert, Connor and Adkins, *ibid.*, **54**, 1651 (1932).

Propanediol-1,3 and butanediol-1,3 showed no carbon to carbon cleavage, while the more branched chain 2-methylpentanediol-2,4 underwent cleavage giving from 62 to 86% of propanol-2, the point of cleavage being nearer the more branched end of the glycol molecule. It was surprising to find that the hydroxyl group on a primary carbon atom was in the case of these glycols more labile toward hydrogenolysis than was a hydroxyl on a secondary carbon atom, yet this was true in the hydrogenolysis of butanediol-1,3, from which almost twice as much butanol-2 as butanol-1 was produced. The greater lability of the primary as contrasted with the secondary hydroxyl is further evidenced by the formation of 2-methylcyclohexanol-1, rather than of cyclohexylcarbinol, from ethyl hexahydrosalicylate. Moreover, unpublished work by Wojcik in this Laboratory indicates that this is not simply a function of the character of the carbinol group, for substitution on the 2 carbon atom appears to be more effective in labilizing oxygen to carbon linkages than when the substitution is on the 1 (or carbinol) carbon atom. However, it should be noted that in the monosubstituted β-hydroxybutyric esters the secondary rather than the primary hydroxyl group was eliminated.

Sufficient branching of the chain made possible the hydrogenolysis of the carbon–carbon bond even in the case of the relatively stable 1,2-glycols. Although pentanediol-1,2 gave a 26% yield of alcohols, there was present only a trace of methanol. With pinacol, however, 17% of isopropyl alcohol and 16% of dimethylisopropylcarbinol were formed.

The cleavage of 2-methylpentanediol-2,4 and of 2-methyl-4-ketopentanol-2 (diacetone alcohol) appeared to occur so readily that diacetone alcohol could not be hydrogenated to the glycol without the formation of considerable isopropyl alcohol. The temperature of the hydrogenation appeared to make little difference, for yields of 41, 59 and 41% of 2-methylpentanediol-2,4 were obtained in the runs on diacetone alcohol at 120, 135–165 and 150°, respectively. Furthermore, the amount of catalyst did not seem to be the deciding factor for the above runs were made in the presence of 0.5, 2.0 and 2.0 g. of the same catalyst, respectively. On the basis of the data at hand it seems that a rapid hydrogenation is the most favorable condition for a good yield of the glycol, for the times for the hydrogenations were six hours, four minutes and thirty minutes in the order named.

It is possible that the oxide catalyst is alkaline enough to act as a catalyst for the reversal of the reaction by which diacetone alcohol is formed.

$$2CH_3COCH_3 \rightleftharpoons CH_3COCH_2COH(CH_3)_2 \qquad \text{(VII)}$$

This hypothesis is borne out by the fact that a nickel catalyst made by precipitation with ammonium carbonate and which should contain no alkali gave no isopropyl alcohol, but an 89% yield of the glycol accompanied by a 6% yield of 2-methylpentanol-4.

Aldol behaved similarly in that it did not give a high yield of the glycol

by hydrogenation. It is worth noting that with nickel as a catalyst 39 and 41% yields of the glycol were obtained irrespective of whether freshly distilled or the technical aldol was used. The copper–chromium oxide catalyst induced no hydrogenation, even at 200°, and was itself reduced to the inactive form.

Only a few compounds containing more than two hydroxyl groups were investigated. Glycerol gave a good yield of propanediol-1,2. Mannitol and α-methyl-*d*-glucoside were hydrogenated with surprising ease. The reaction products were not investigated thoroughly, but in both cases some of the lower alcohols (including ethanol and methanol) and propanediol-1,2 were obtained. The presence of much water caused high losses and may have prevented the detection of some products. The complexity of these cases can be seen from the fact that each of the hydroxy groups in mannitol is beta (*i. e.*, labile) to another and that two of them are beta to two others. Pentaerythritol underwent a very smooth cleavage to give methyl and isobutyl alcohols. Hydrogenation of 4-methyl-2,6-dimethylolphenol gave a 50% yield of mesitol (2,4,6-trimethylphenol) and a 25% yield of di-(2-hydroxy-3,5-dimethylphenyl)-methane. This hydrogenation, to be successful, must be rapid, for when the material is subjected to slow hydrogenation the product is a tar.

The Hydrogenolysis of β-Hydroxy Esters.—The compounds subjected to the action of hydrogen were in most cases β-keto esters. However, since hydrogenation of the carbonyl group takes place at much lower temperatures than does cleavage or hydrogenation of the carbethoxy group, the compounds actually undergoing hydrogenolysis were β-hydroxy esters or 1,3-glycols. The possible reactions involved are as follows

$$\begin{array}{lcll} CH_3 & (CH_3) & \xrightarrow{H_2} & C_2H_5OH + R_2CHCH_2OH \quad \text{(VIII)} \\ | & (|) & \xrightarrow{H_2} & \\ CHOH & (CHOH) & \xrightarrow{H_2} & CH_3CHOHCR_2CH_3 + H_2O \quad \text{(IX)} \\ | & (|) & \xrightarrow{H_2} & \\ CR_2 & (CR_2) & \xrightarrow{H_2} & CH_3CHOHCHR_2 + CH_3OH \quad \text{(X)} \\ | & (|) & \xrightarrow{H_2} & \\ COC_2H_5 & (CH_2OH) & \xrightarrow{H_2} & CH_3CH_2CR_2CH_2OH + H_2O \quad \text{(XI)} \end{array}$$

In the case of unsubstituted acetoacetic ester only reactions IX and XI occurred. With monosubstituted esters, reactions VIII and XI occurred chiefly with enough of IX to give a trace of a secondary alcohol. A test for methanol gave such a slight color that considering the delicacy of the test it is doubtful if reaction X occurred at all. With disubstituted acetoacetic esters only reaction VIII was found to take place.

Although the work on butanediol-1,3 previously mentioned indicated that the 2,3-carbon–carbon bond in acetoacetic ester did not cleave, additional proof was obtained by the hydrogenation of hexahydrobenzyl β-hydroxybutyrate. In this case ethanol could come only from cleavage and not from hydrogenation of a carbethoxy group. No ethanol was found.

The ratio of carbon–carbon cleavage to carbon–oxygen cleavage in monosubstituted derivatives of acetoacetic ester is a function of the substituent group. This is shown in Table II.

TABLE II

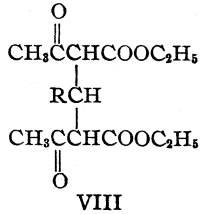
THE HYDROGENOLYSIS OF MONOSUBSTITUTED ACETOACETIC ESTER DERIVATIVES

Compound	% Carbon–carbon cleavage (± 5%)
Ethyl acetoacetate	0
Ethyl hexahydrosalicylate	0
Ethyl α-ethylacetoacetate	50
Ethyl α-isopropylacetoacetate	60
Ethyl α-butylacetoacetate	71
Ethyl α-hexahydrobenzylacetoacetate	100
Ethyl α-benzylacetoacetate	100
Ethyl α-(β-phenethyl)-acetoacetate	100
Ethyl α,γ-dimethylacetoacetate	100

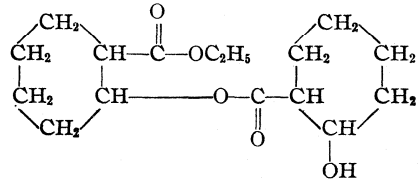
These data indicate that the weight and chemical character of the substituent group are important factors in determining the ease of cleavage of the carbon–carbon linkage.

It also appears that the hydrogenolysis of carbon–carbon linkages differed according not only to the substituent group α to the carbethoxy group, but also according to the substituent γ to it. For, with the α-monosubstituted acetoacetic esters, there was 50 to 100% cleavage to give the primary alcohol and ethanol, while ethyl α,γ-dimethylacetoacetate underwent complete carbon–carbon cleavage to give *n*-propanol. These facts indicate that the ease of hydrogenolysis of the carbon–carbon linkage was enhanced more by the group CH_3CH_2CHOH— than by the group CH_3CHOH—. The —CH_2OH group facilitated carbon to carbon cleavage less than did these groups for only traces of methanol were produced from monosubstituted acetoacetic esters, and there was less carbon to carbon cleavage with the monosubstituted malonic than with the corresponding acetoacetic esters.

A marked difference in the type of hydrogenolysis occurring was observed in the case of two more complex monosubstituted acetoacetic esters, *i. e.*, diethyl α,γ-diacetyl-β-methylglutarate, or the corresponding β-phenyl compound, as illustrated in formula VIII where R is methyl or phenyl



VIII



IX

In the case of these compounds there occurred little or no carbon to carbon cleavage but only hydrogenolysis of the carbon to oxygen linkage with the formation of primary glycols.

In the hydrogenation of β-hydroxy esters it has not been possible to isolate the glycol. In those cases in which hydrogenation was not complete there was present, besides the alcohols normally expected, only the esters of the acids corresponding to the alcohols—*never* a glycol or hydroxy ester. When 0.5 mole of acetoacetic ester had absorbed only 60% of the amount of hydrogen theoretically necessary for reduction of the carbonyl and carbethoxy groups, followed by hydrogenolysis, there was present neither glycol or hydroxy ester, but only butyl alcohols and butyric ester. Therefore it seems that hydrogenolysis of the β-hydroxy ester (or 1,3-glycol) is so much easier than hydrogenation of the carbethoxy group that the glycol cannot ordinarily be obtained. In only one case noted below was a 1,3-glycol isolated from the hydrogenation of a β-oxygenated ester.

The hydrogenolysis of monosubstituted acetoacetic esters, as a preparational method for alcohols is doubtless impractical because of the diversity of products and the similarity of the boiling points of some of them. The catalytic cleavage of disubstituted acetoacetic esters might, on the other hand, be of some synthetic value, for these undergo carbon–carbon scission smoothly. The disubstituted malonic esters give the same products, however, and would probably be the ones oftenest used because of their greater ease of preparation.

The Hydrogenolysis of Malonic Esters.—It had previously been observed that *n*-propanol and ethyl propionate were formed by the hydrogenation of malonic ester and that 2-methylbutanol-1 (XII) was obtained from ethylmalonic ester.[5] In this investigation it has been found, however, that the monosubstituted malonic esters also undergo some carbon–carbon cleavage, with the formation of methanol (XIII).

$$\begin{array}{l} \mathrm{C_2H_5CH(COOC_2H_5)_2} + 4\mathrm{H_2} \longrightarrow \mathrm{C_2H_5CH(CH_2OH)_2} \\ \qquad \xrightarrow{\mathrm{H_2}} \mathrm{C_2H_5CH(CH_3)CH_2OH} + \mathrm{H_2O} \quad \text{(XII)} \\ \qquad \xrightarrow{\mathrm{H_2}} \mathrm{C_2H_5CH_2CH_2OH} + \mathrm{CH_3OH} \quad \text{(XIII)} \end{array}$$

This has been verified by the isolation of *n*-butanol from the products from ethylmalonic ester, qualitative tests for methanol, and by quantitative determination of the amount of methanol present on the basis of the density and refractive indices of the alcohol fractions.

The results indicated that 29% of the butylmalonic, 22% of the benzylmalonic and 20% of the ethylmalonic ester had cleaved to give methanol. Considering the possible errors involved, one may say that these groups all cause approximately the same amount of carbon–carbon cleavage. However, phenylmalonic ester gave no cumene, so far as it was possible to tell

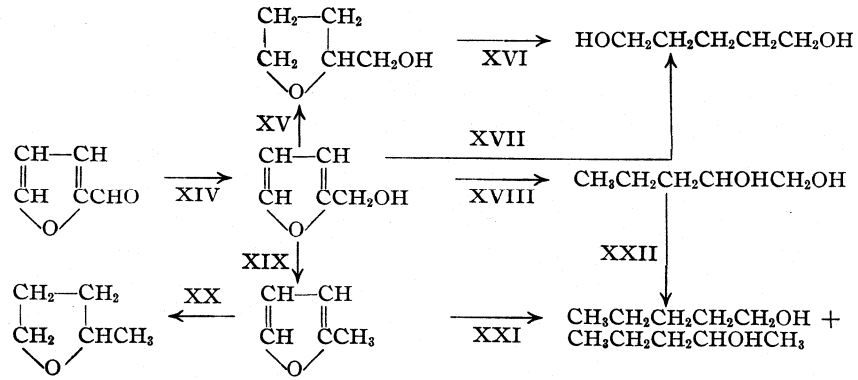
by fractionation, but only ethylbenzene, indicating complete carbon–carbon as well as carbon to oxygen cleavage.

The disubstituted malonic esters form the most practical intermediates for preparation of alcohols of all the groups of compounds subjected to hydrogenolysis. These reacted smoothly and so far as was possible to ascertain underwent 100% cleavage of the carbon–carbon bond to methanol and a dialkyl carbinyl carbinol. Six disubstituted malonic esters were hydrogenated and all behaved satisfactorily. Among these was the only case in which a 1,3-glycol was obtained from the hydrogenation of an ester. From 450 g. of dimethylmalonic ester there was obtained 12 g. of 2,2-dimethylpropanediol-1,3, corresponding to a 5% yield. This small yield indicates the futility of attempting to isolate the glycol in runs of an ordinary size.

Dehydration as a Possible Step in Carbon to Oxygen Cleavage.—In the cases reported in this paper where an hydroxyl group is replaced by a hydrogen, it is perhaps significant that dehydration is always possible. In the cases where dehydration is impossible (the disubstituted malonic esters) only carbon–carbon cleavage occurred. The converse, *i. e.*, that cleavage of carbon–oxygen takes place whenever dehydration is possible, is not true, for the disubstituted acetoacetic ester derivatives underwent carbon–carbon scission entirely while the monosubstituted malonic and acetoacetic esters and some glycols also had the carbon–carbon bond broken to varying extents. There is therefore the possibility (although in the opinion of the authors not a probability) that the cleavage of the carbon–oxygen linkage involves first dehydration and then hydrogenation. This mechanism could not be applied to the breaking of the furan ring to be discussed later. In the case of carbon–carbon cleavage, on the other hand, no plausible speculation as to the mechanism can be formulated at present.

The Reported Cleavage of Ethyl α-Phenylbutyrate.—It has been reported that ethylbenzene is formed in the hydrogenation of ethyl α-phenylbutyrate.[5] Inasmuch as this would seem to be an unusual type of cleavage it was further investigated. The result of these experiments indicated that the ethylbenzene previously obtained was probably formed from ethyl phenylacetate, present as an impurity in the sample of ethyl α-phenylbutyrate formerly available.

Hydrogenolysis of Furan Derivatives.—The hydrogenolysis of the carbon–oxygen bond had been noted earlier in the hydrogenation of furfuryl alcohol with a copper–chromium oxide catalyst.[3] Since this fell so clearly in line with the present work the reaction was further investigated upon a larger scale and for tetrahydrofurfuryl alcohol, methylfuran, methyltetrahydrofuran and pentanediol-1,2. The data on these compounds (Table I) indicate very clearly that the reactions follow the paths indicated in reactions XIV to XXII.



The chief reactions are the direct hydrogenolysis of furfuryl alcohol, cleavage occurring at each of the three oxygen to carbon linkages as indicated by reactions XVII, XVIII and XIX. Hydrogenation in the sense of reactions XV and XX does occur at 200 to 250° over the copper–chromium oxide catalyst but to a relatively small extent. Both reactions proceed almost quantitatively over a nickel catalyst. In contrast to the ease of hydrogenolysis of the unsaturated furfuryl alcohol was the relative stability of the saturated tetrahydrofurfuryl alcohol. Reaction XVI did occur but at only a small fraction of the rates of reactions XVII and XVIII. Furthermore, tetrahydrofurfuryl alcohol underwent hydrogenolysis to give pentanediol-1,5 almost exclusively, instead of the mixture of glycols produced from furfuryl alcohol. Pentanediol-1,2 as well as methylfuran underwent hydrogenolysis to give mixtures of pentanols, while pentanediol-1,5 and methyltetrahydrofuran did not react under similar conditions. It is thus clear that furan derivatives are much more readily hydrogenolyzed than are the corresponding tetrahydro compounds.[18]

Miscellaneous Hydrogenations.—In Table I the results of several hydrogenations not previously reported are recorded which do not require additional comment, except to note the aldolization that occurred in the hydrogenation of heptaldehyde, the formation of hexahydrobenzyl β-hydroxybutyrate from acetoacetic ester and cyclohexylcarbinol, and the behavior of ethyl salicylate. When the latter was subjected to hydrogenation, there was produced a high molecular weight compound which apparently had the structure indicated in formula IX. The compound was not produced if the hydrogenation was carried out in an ethanol solution. This behavior is understandable if it is noted that a molecule of ethyl salicylate has within it the same structure as the enol of a beta keto ester.

[18] Attention should be called to an error [Connor, Folkers and Adkins, THIS JOURNAL, **54**, p. 1140, line 5 (1932)] in which tetrahydrofurfuryl is printed where furfuryl was meant. The former alcohol is not produced from furfural under the conditions there described.

It has been previously reported that when acetoacetic ester is hydrogenated a condensation product results which is not formed if the hydrogenation is carried out in an ethanol solution. The analogy of ethyl salicylate to an enol of a β-keto ester is also evidenced by the fact that phenols are the only compounds in which a benzenoid ring has apparently been hydrogenated over a copper–chromium oxide catalyst.[5] It seems probable that the hydrogenation of ethyl salicylate over this catalyst actually proceeds through the β-keto ester of which salicylic ester is the enol.

TABLE III

ANALYTICAL DATA AND PHYSICAL CONSTANTS OF NEW COMPOUNDS

	Compound	B. p., °C.	Mm.
1	2-Ethyl-5-methylhexanol-1	84– 86	10
2	2-Ethyl-3-methylhexanol-1	83– 86	10
3	Ethyl hexahydrosalicylhexahydrosalicylate	192–196	6
4	Ethyl α-hexahydrobenzyl-β-hydroxybutyrate	147–148	10
5	Hexahydrobenzyl β-hydroxybutyrate	149–150	17
6	Ethyl α,α-diethyl-β-hydroxybutyrate	87– 89	9

	Formula	n_D^{25}	d_{25}^{25}	MR'D Found	MR'D Calcd.	C, % Found	C, % Calcd.	H_2, % Found	H_2, % Calcd.
1	$C_9H_{20}O$	1.4304	0.8232	45.33	45.05	74.93	75.00	13.92	13.89
2	$C_9H_{20}O$	1.4356	.8383	44.85	45.05	74.51	75.00	13.92	13.89
3	$C_{16}H_{26}O_5$	1.4781	1.1024	76.53	76.80	64.48	64.43	8.73	8.73
4	$C_{13}H_{24}O_3$	1.4600	0.9882	63.18	63.23	68.27	68.42	10.51	10.52
5	$C_{11}H_{20}O_3$	1.4565	1.0150	53.58	53.96	65.87	66.00	10.20	10.00
6	$C_{10}H_{20}O_3$	....	....	...	...	63.69	63.83	10.78	10.64

Summary

A number of glycols, hydroxy and malonic esters and derivatives of furan have been subjected to the action of hydrogen, over a copper–chromium oxide catalyst, in studying the effect of structure upon the hydrogenolysis of carbon to carbon and carbon to oxygen linkages. The particular points of interest have been the effect of branching of the carbon chain and of the position of substituents upon the ease of cleavage, especially of the ratio of cleavage, of C to C to that of C to O. It has been observed that 1,3-glycols undergo hydrogenolysis at a lower temperature, or more rapidly, than do 1,2- or 1,4-glycols. There is competition in the cleavage of C to C and C to O, the cleavage of the former being facilitated by branching or prolongation of the carbon chain, not only for 1,3- but also for 1,2-glycols.

The unsubstituted β-hydroxybutyric esters and 2-carbethoxycyclohexanol-1 showed C to O but no C to C cleavage. Other α-monosubstituted β-hydroxybutyric esters showed an amount of C to C cleavage which increased, apparently with increase in weight of the substituent. γ-Methyl-β-hydroxyvaleric ester also showed complete cleavage of C to C. The α,α-dialkyl-β-hydroxybutyric esters showed 100% C to C cleavage.

The monoalkyl malonic esters underwent a varying ratio of C to C as compared to C to O cleavage, depending upon the nature of the substituent. Six dialkylmalonic esters cleaved smoothly and completely to give methanol and dialkylcarbinylcarbinols. In contrast with this is the fact that α,γ-diacetyl-β-methyl(or phenyl)glutaric esters showed little if any C to C cleavage.

It appears that the C to O linkage in a primary carbinol group is in many cases more readily cleaved than in a secondary alcohol. The presence of a carbon to carbon double bond facilitates the cleavage of C to O linkages.

A considerable amount of information in regard to the hydrogenation and hydrogenolysis of a variety of organic compounds has been presented in tabular form and cannot be more briefly summarized here.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THE REDUCING ACTION OF THE GRIGNARD REAGENT. III. HYDROCARBONS FORMED DURING REDUCTION

BY C. R. NOLLER, W. E. GREBE AND L. H. KNOX

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Of the various types of reduction that may take place during the reaction of an aldehyde or ketone with a Grignard reagent,[1] the type most frequently encountered occurs only when a hydrogen bearing carbon atom is adjacent to the carbon atom that is combined with magnesium. This may be represented by the equation

$$R_2C{=}O + R_2CH{-}C(MgX)R_2 \longrightarrow R_2C(OMgX)H + R_2C{=}CR_2$$

where R may be either hydrogen or a radical.

Thus far no careful investigation has been made of the hydrocarbon formed during the reduction. Hess and Wustrow[2] reported that primary addition products of ethylmagnesium bromide, isobutylmagnesium bromide, and isobutylmagnesium chloride with cinnamic aldehyde had been isolated in a pure state and that on heating they lost in weight an amount equivalent to one mole of unsaturated hydrocarbon. Meisenheimer[3] was unable to confirm these results and also pointed out that while Hess and Wustrow claim the quantitative loss of isobutylene from the addition product of isobutylmagnesium bromide and cinnamic aldehyde, they actually isolated from the addition product of isobutylmagnesium chloride and cinnamic aldehyde only 8.5% of the theoretical amount of isobutylene as the dibromide. It should be mentioned that in Hess and Wustrow's

[1] For a summary of the different types of reduction and references to previous work on this subject, see the first article of this series, THIS JOURNAL, **53**, 635 (1931).

[2] Hess and Wustrow, *Ann.*, **437**, 256 (1924).

[3] Meisenheimer, *ibid.*, **442**, 180 (1925).

experiments with crotonic aldehyde in which the addition product was not isolated, the amount of unsaturated hydrocarbon isolated as dibromide was equivalent to about 25% of that expected from the amount of crotyl alcohol isolated. Meisenheimer states that while only a few investigations were made, in the reaction of benzaldehyde with ethylmagnesium and isobutylmagnesium bromides they were never able to isolate an amount of unsaturated hydrocarbon equivalent to the amount of benzyl alcohol formed and frequently they obtained no unsaturated hydrocarbon at all. He assumed that the discrepancy might be due to the removal of the hydrocarbon by some unknown condensation reaction. Blicke and Powers[4] isolated approximately 25% of the total amount of alkyl radical as propylene dibromide in a reaction that gave about 50% reduction of benzophenone to benzohydrol.

A knowledge of the relative amounts of unsaturated hydrocarbon and reduction product is part of the information necessary for a thorough understanding of the reducing action of aliphatic Grignard reagents. Whether or not the unsaturated hydrocarbon is accompanied by saturated hydrocarbons having the same number of carbon atoms should also be determined since one proposed mechanism[4] for the reduction indicates that such should be the case. Moreover, in certain reactions such as that of diisobutylmagnesium with benzophenone,[1] it is difficult to isolate the reduction product quantitatively and the isolation of the unsaturated hydrocarbon should be a satisfactory method for determining the amount of reduction providing that unsaturated hydrocarbon and reduction product are formed in equivalent amounts.

With these points in mind we have attempted to determine whether one mole of isobutylene can be isolated per mole of benzohydrol in the reaction of isobutylmagnesium bromide with benzophenone. The reaction was run in *n*-butyl ether solution in order to facilitate the isolation of the hydrocarbon. Since the most satisfactory method for determining the amount of benzohydrol was by filtering and decomposing its bromomagnesium salt,[4] it was necessary to work with fairly large quantities to obtain the required accuracy. This necessitated the condensation of the hydrocarbon and weighing it as a liquid.[5]

It was found as shown in Table I that when one takes into account the solubility of the bromomagnesium salt and of isobutylene in butyl ether, and also the mechanical losses, the amount of hydrocarbon isolated is equivalent to the amount of benzohydrol within less than 0.2%. Without such corrections the amount of reduction as calculated by the hydrocarbon

[4] Blicke and Powers, THIS JOURNAL, 51, 3378 (1929).

[5] Gasometric determination of the amount of hydrocarbon formed would allow the use of smaller quantities of reagents but all attempts to use such a procedure gave low results.

method is about 3% higher than that calculated by the benzohydrol method.

One mechanism proposed to account for both the normal addition and reduction postulates the intermediate formation of free radicals which may then undergo various reactions of addition and disproportionation.[4] Such a mechanism would predict also the formation of pinacol and of saturated hydrocarbon in addition to the reduction product, unsaturated hydrocarbon and normal addition product.

In previous work[6] we have never been able to detect the formation of benzopinacol during the reaction of an alkylmagnesium bromide with benzophenone, nor has any been obtained in the present work.[7] It was therefore of interest to determine whether any saturated hydrocarbon, in this case isobutane, was present in the isobutylene. The liquefied hydrocarbon was volatilized in portions and the isobutylene removed by washing with concentrated sulfuric acid. The combined residual gases were analyzed for us by Dr. F. Blacet and found by a micro-combustion method[8] to contain what was apparently isobutane, to the extent, however, of only 0.1% of the original hydrocarbon mixture. Since no attempt was made rigidly to dry our system, it seems entirely possible that sufficient moisture may have been present on the walls of the glass apparatus and in the rubber stoppers and connections to account for this minute amount.[9]

It has recently been shown that in the decomposition of hydrocarbons in the gaseous phase, the postulation of the primary formation of free radicals accounts not only for the products formed but also for the relative amounts of these products.[10] In the present instance, however, it appears to us that the reactions are best explained by using the older idea[11] that a primary addition product[12] is formed which then rearranges and that reduction takes place during the rearrangement.

The procedure used in this work is now being employed to determine the

[6] Noller and Hilmer, THIS JOURNAL, **54**, 2503 (1932); *cf.* also Ref. 1.

[7] The possibility that the reactions of the free radicals leading to the formation of normal addition product and of reduction product are much more rapid than that leading to pinacol formation does not seem likely since Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927), have found that when a mixture of magnesium and magnesium iodide is allowed to compete with phenylmagnesium iodide for benzophenone, about 50% of benzopinacol and 40% of triphenylcarbinol are formed.

[8] Blacet and Leighton, *Ind. Eng. Chem., Anal Ed.*, **3**, 266 (1931).

[9] Assuming two moles of Grignard reagent to react with one of water, the amount of water necessary to account for the amount of isobutane formed in a 0.05 mole run in which 75% reduction took place would be 0.3 mg.

[10] Rice, THIS JOURNAL, **53**, 1959 (1931).

[11] V. Braun and Kirschbaum, *Ber.*, **52**, 1725 (1919); Meisenheimer and Casper, *ibid.*, **54**, 1655 (1921), and Ref. 3.

[12] Direct evidence for the formation of such an addition product is given in the experimental part.

amount of unsaturated hydrocarbon and hence the amount of reduction in those cases where the halogenomagnesium salt of the reduction product is soluble in the reaction mixture.

Experimental

Apparatus.—The preparation of the Grignard reagent and all subsequent reactions were carried out in an atmosphere of nitrogen which was purified by the absorption train recommended by Fieser.[13] The apparatus for carrying out the reaction consisted of a reservoir for the Grignard reagent connected to a 50-cc. buret which was in turn connected through a three-way stopcock and rubber stopper to one of the small necks of a 500-cc. reaction flask. To the second opening of the three-way stopcock was sealed a tube for introducing the solution of benzophenone. This tube also served to admit nitrogen when sweeping out the apparatus. A mercury-sealed stirrer passed through the central neck of the flask and the remaining small neck carried a thermometer and a bent tube which connected the flask to the condensing system. This consisted of a train of three U-tubes made from 10-mm. glass tubing and measuring 4.5 by 16 cm. An enlargement was blown in the lower end of the tubes so that they might hold at least 5 cc. of liquid without interfering with the passage of gas. The first tube was indented to increase the condensing surface and was kept at room temperature by means of a water-bath in order to condense any high boiling substances that might distil. The second and third tubes were filled with copper turnings for condensing surface and small stopcocks were sealed to both ends of the tube. During the reaction they were immersed in solid carbon dioxide–acetone mixture contained in 570-cc. wide-mouthed Dewar flasks. The last tube was protected from the air by connecting it to a tube immersed a few millimeters in mineral oil.

Grignard Reagent.—The Grignard reagent was prepared in the usual manner from 24.4 g. of clean magnesium turnings, 137 g. of isobutyl bromide and 250 cc. of dry *n*-butyl ether. The reaction started almost immediately without the use of iodine and the temperature was kept below 30° during the reaction by means of a water-bath. The total time required for the addition of the bromide was about three hours. At the end of the reaction, the stirrer was removed and replaced by a line to a vacuum pump and the mixture heated at 20 mm. until butyl ether distilled. The product, freed from low boiling substances, was forced by nitrogen pressure through a 44 G3 Jena glass filter, on which a 3-mm. layer of ignited kieselguhr had been placed, into a graduated flask. The solution was analyzed by acid titration[14] and then diluted so that the concentration of active Grignard reagent was approximately 0.002 equivalent per cubic centimeter.

[13] Fieser, THIS JOURNAL, **46**, 2639 (1924).

[14] Gilman and co-workers, *ibid.*, **45**, 150 (1923); **51**, 1576 (1929).

It was then transferred to the storage reservoir and the concentration checked again by analysis.

Reduction of Benzophenone.—The U-tubes of the apparatus previously described were weighed to the nearest centigram, immersed in the Dewar flasks containing a mixture of solid carbon dioxide and acetone and connected to the system. This was completely swept with purified nitrogen and then 27.5 cc. (0.055 equivalent) of the isobutylmagnesium bromide solution run into the reaction flask. This was cooled to −5° and a solution of 9.1 g. (0.05 mole) of benzophenone in 10 cc. of warm butyl ether was added drop by drop with constant stirring. On the addition of each drop of benzophenone solution, an orange precipitate formed which immediately dissolved imparting a pink color to the solution. Normally after about half of the benzophenone had been added the precipitate no longer went into solution. If, however, the addition of the benzophenone was very slow and the stirring rapid, it was possible to force all of the precipitate into solution and to obtain a clear pink solution after addition of the benzophenone was complete.[15] The reaction mixture was allowed to warm to room temperature and then gradually heated to 100° with constant stirring. In cases where no attempt was made to get all of the initial precipitate into solution at −5°, the undissolved precipitate readily went into solution at 90–100°. After stirring for thirty minutes at this temperature a slow stream of nitrogen was passed through the system to sweep all of the hydrocarbon into the condensers. The solution was then allowed to cool with continued stirring and a fine white precipitate formed.

The stopcocks of the condensers were closed and the condensers rapidly washed in alcohol and ether, wiped dry and weighed. From the increase in weight of the tubes, the percentage reduction was calculated.

The mixture in the reaction flask was filtered onto a Büchner funnel and washed three times with 10-cc. portions of dry benzene, care being taken not to suck air through the filter cake before the final washing. The precipitate was decomposed with a saturated solution of ammonium chloride and the liberated benzohydrol extracted three times with 50-cc. portions of ethyl ether. The combined extracts were placed in a tared beaker

[15] The occurrence of this precipitate is visible evidence of the formation of a primary addition product although attempts to isolate it have not been successful. By the use of a gasometric apparatus indication was obtained that the hydrocarbon is liberated as the precipitate dissolves. The fact that hydrocarbon is evolved and yet a clear solution obtained indicates that the bromomagnesium salt of benzohydrol has not yet formed since this material is quite insoluble (0.006 g. per cc. at 25°). That a supersaturated solution was not present was shown by the fact that the addition of a small amount of the bromomagnesium salt of benzohydrol did not cause precipitation. The above results would be those expected if the second intermediate compound $R_2C{=}O\cdots HMgX$ postulated by Hess and Rheinbold, *Ber.*, **54**, 2043 (1921), existed and were soluble in butyl ether.

and the ether evaporated on a warm hot-plate. While still warm the beaker was placed in a vacuum desiccator over phosphorus pentoxide for two hours, weighed again, and the percentage reduction calculated.

Corrections for Errors.—The two methods used above for determining the amount of reduction are obviously in error due to the solubility of the solid and gas and to mechanical losses. In order to determine approximately the extent of these losses a weighed amount of isobutylene was passed through the reaction flask containing 37 cc. of butyl ether and into the condensing system. The flask was then heated with stirring and the gas finally swept out as in a regular run. On weighing the absorption tubes an average loss of 0.02 g. was observed. By adding this to the observed recovery of isobutylene, a corrected value for the percentage reduction was calculated. In a similar manner by adding 9.2 g. (0.05 mole) of benzohydrol in 10 cc. of butyl ether to 27.5 cc. (0.055 equiv.) of Grignard reagent, filtering the precipitate and isolating the benzohydrol as in a regular reduction, an average loss of 0.26 g. was observed. From this data corrected values for the percentage reduction by this procedure were obtained. The data for several typical runs are given in Table I. It will be observed that the average values for the two methods check each other within 0.2%. Moreover, the various values for the benzohydrol method show a maximum deviation within themselves of 3.5% while those for the hydrocarbon method of only 1%, indicating that the latter is the more accurate method of the two.

Analysis of the Hydrocarbon Gases.—The liquid hydrocarbon was transferred for analysis to a 100-cc. gas buret filled with mercury. This was readily accomplished by fitting the stopcock of the gas buret with a short piece of rubber tubing and filling the entire buret and tube with mercury. The glass tubing extending beyond the stopcock on the U-tube condenser was likewise filled with mercury and the U-tube inverted so that the liquid hydrocarbon was in the arm adjacent to this stopcock. The U-tube was connected to the buret by means of the rubber tubing, the stopcock on the buret opened and the leveling tube lowered. When the liquid in the U-tube came into equilibrium with its vapor and bubbling had ceased, the stopcock on the U-tube was quickly opened and closed. In this way a small amount of liquid hydrocarbon entered the buret and vaporized. The volume of the gas was noted and it was then transferred to a gas absorption pipet, where it was thoroughly washed with concentrated sulfuric acid. The residual gas was then transferred to a storage buret and its volume measured. A total of 102.1 cc. of gas gave 1.2 cc. (Sample A) or 1.2% unabsorbed by concentrated sulfuric acid. A second sample of gas collected more carefully showed a total of 1.25 cc. (Sample B) out of 349.8 cc. or 0.357% unabsorbed by concentrated sulfuric acid. We are indebted to Dr. F. Blacet for the microanalysis of both samples of this residual gas.

The results are listed in Table II and indicate that the combustible portion of the residual gas is isobutane and that it is present to the extent of about 0.1% of the original hydrocarbon mixture.

TABLE I

AMOUNT OF REDUCTION AS CALCULATED FROM THE AMOUNTS OF BENZOHYDROL AND ISOBUTYLENE RECOVERED

Benzohydrol isolated		Isobutylene isolated			
Wt.	%	Wt.	%	% Benzohydrol (corrected)	% Isobutylene (corrected)
6.45	70.1	2.05	73.2	72.9	73.9
6.47	70.3	2.07	73.9	73.2	74.6
6.69	72.7	2.07	73.9	75.5	74.6
6.62	72.0	2.06	73.6	74.8	74.3
6.58	71.5	2.07	73.9	74.4	74.6
6.64	72.2	2.07	73.9	75.0	74.6
	Av. 71.5		73.7	74.3	74.4

TABLE II

ANALYSIS OF GAS NOT ABSORBED BY CONCENTRATED SULFURIC ACID

Sample	Vol. used cu. mm.	Contraction, cu. mm.	Vol. of CO_2, cu. mm.
A	94.61	27.84	32.11
B	42.31	50.52	52.31

	Vol. calcd. as C_4H_8		Vol. calcd. as C_4H_{10}		% C_4H_{10} in residue		% C_4H_{10} in original hydrocarbon
	By contr.	By CO_2	By contr.	By CO_2	By contr.	By CO_2	
A	9.28	8.03	7.95	8.03	8.4	8.5	0.10
B	16.84	13.10	14.43	13.08	34.1	31.0	.11

Summary

1. In the reduction of benzophenone by isobutylmagnesium bromide, one mole of isobutylene has been isolated per mole of benzohydrol. Use is made of this fact in developing a new method for determining the amount of reduction caused by aliphatic Grignard reagents.

2. The isobutylene contains less than 0.1% of isobutane. This together with the fact that no benzopinacol is isolated indicates that it is unlikely that the reaction is preceded by the formation of free radicals.

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[CONTRIBUTION FROM THE LABORATORIES OF THE MT. SINAI HOSPITAL, NEW YORK]

OPTICALLY ACTIVE 5,5′-DISUBSTITUTED HYDANTOINS[1]

BY HARRY SOBOTKA, MARJORIE F. HOLZMAN AND JOS KAHN[2]

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In 1916, 5,5′-phenylethylhydantoin was introduced under the trade name "nirvanol" as a hypnotic and sedative. This drug shows certain advantages in comparison with the related disubstituted barbituric acids, but its wider application has been curtailed by its toxic properties manifested by what is commonly referred to as "nirvanol disease." Several attempts have been made to modify and improve phenylethylhydantoin by replacement of the substituting groups. Thompson, Bedell and Buffett[3] prepared methyl-, propyl-, isopropyl-, butyl-, and isobutyl-phenylhydantoin. Hill[4] prepared various furoyl-alkylhydantoins. Herbst and Johnson[5] quite recently published data on benzyl- and phenethyl-alkylhydantoins. Shonle[6] includes some of Herbst and Johnson's hydantoins in a general discussion of hypnotics.

It seems to have escaped the attention of those working with hypnotics of the hydantoin group, that 5,5′-disubstituted hydantoins contain an asymmetric carbon atom and that these synthetic products are racemic mixtures.

Optically active 5-monosubstituted hydantoins have been prepared by Lippich[7] from amino acids plus urea or cyanate. Dakin[8] studied the spontaneous racemization of such hydantoins during synthesis and found that no racemization took place in the case of levo-isovaline. This amino acid is the only naturally occurring one which gives rise to a disubstituted hydantoin. The dextrorotatory ethylmethylhydantoin of Dakin is the first asymmetric disubstituted hydantoin to be recorded.[9]

We succeeded in separating racemic phenylethylhydantoin into its pure optically active components by means of brucine, which forms a less soluble salt with the dextro hydantoin than with the levo isomer. The optical rotation of the enantiomers is $\pm 123°$, their melting point 237°. Dextro- and levo-phenylethylhydantoin can be hydrolyzed to dextro- and levo-

[1] The expenses of this investigation were defrayed by a grant obtained through the kindness of Dr. B. Schick.

[2] Hernsheim Research Fellow, 1931.

[3] Thompson, Bedell and Buffett, THIS JOURNAL, **47**, 874 (1925).

[4] Hill, Abstract, Meeting of American Chemical Society, Buffalo, September, 1931, Biochemical Section.

[5] Herbst and Johnson, THIS JOURNAL, **54**, 2463 (1932).

[6] Shonle, *Ind. Eng. Chem.*, **23**, 1104 (1931).

[7] Lippich, *Ber.*, **41**, 2974 (1908).

[8] Dakin, *Am. Chem. J.*, **44**, 59 (1911).

[9] A substance which may be classified as an optically active disubstituted hydantoin is the spiro-hydantoin of Pope and Whitworth, *Chem. & Ind.*, **49**, 748 (1930).

phenylethylglycine. This pair of amino acids may also be obtained from racemic phenylethylglycine[10] through optical resolution of its formyl compound with quinine. The optically active amino acids in turn may be converted into the corresponding hydantoic acids and hydantoins. Since all these reactions are accomplished without any intercurrent racemization, the optical forms of phenylethylhydantoin are individually accessible from racemic phenylethylglycine as starting point.

The derivatives of phenylethylglycine display a noteworthy resistance against racemization. Dakin explained this stability in the ethylmethyl series by the absence of a hydrogen atom on the asymmetric carbon atom, while derivatives of monosubstituted aminoacetic acids may lose their optical activity through enolization. We believe that Dakin's explanation also holds in the present instance.

The sense of rotation remained unchanged throughout the reactions in the phenylethyl series. This is in contrast to the transition of levo-isovaline into dextrorotatory ethylmethylhydantoin. We assume, therefore, that the configuration on the asymmetric carbon atom in levo-ethylmethylglycine (isovaline) is analogous to that in dextro-phenylethylglycine, as both become more dextrorotatory by closure of the hydantoin ring. Following Levene's conceptions and experiences in homologous series, one may frequently draw conclusions as to the relative order of the substituents around the central carbon atom; but too little is known regarding the influence of the phenyl group to refer definitely the constellation of a phenylethyl and a methylethyl derivative to each other.

Other new hydantoins were prepared containing as substituents allyl-isopropyl (as in "allonal") and bromoallyl-isopropyl (as "noctal"). Sufficient quantities of allyl-isopropylhydantoin were available to attempt its optical resolution. The dextrorotatory product isolated had a specific rotation of +7.5°. Owing to the poor yield, the question could not be settled whether or not this product represents the pure dextro form; however, on theoretical grounds, no high rotation would be expected in this compound.

Experimental

Resolution of Racemic Phenylethylhydantoin into its Optically Active Components.—Equivalent amounts of 5,5'-phenylethylhydantoin (1 part) m. p. 198°, and of brucine (2.3 parts) are dissolved in absolute alcohol (10–15 parts). On standing, rosets of crystals separate (about 1.6 parts), consisting of the brucine salt of dextro-phenylethylhydantoin. An excess of dilute sulfuric acid is added to a solution of these crystals in absolute alcohol and sufficient water is added to reduce the alcohol content to 10%. The free dextro-phenylethylhydantoin crystallizes in white flaky platelets. They are recrystallized several times from dilute alcohol until free from brucine. The pure substance melts sharply at 237°, and the purest specimens showed a rotation $[\alpha]_D$ +123° in alcoholic solution (0.5514 g. in 25 cc., 2-dm. tube, α_D +5.36°). The specific

[10] Jawelow, *Ber.*, **39**, 1195 (1906).

rotation in alkaline aqueous solution was +169° (0.2521 g. in 25 cc., 2-dm. tube, α_D +3.40°).

Anal. Calcd. for $C_{11}H_{12}O_2N_2$ (204.10): C, 64.67; H, 5.93; N, 13.72. Found: C, 64.09; H, 6.18; N, 13.96.

The mother liquor from the brucine-dextro-hydantoin is carefully acidified until it becomes cloudy. On standing, the levo-phenylethylhydantoin separates in solid crystals. It is purified in the same manner as its enantiomer until its melting point reaches 235–237°; $[\alpha]_D$ −121° (0.2562 g. in 25 cc. alcohol, 2-dm., α_D −2.49°); −167° in aqueous alkali (0.2981 g. in 25 cc., 2-dm., α_D −4.00°).

Anal. Calcd. for $C_{11}H_{12}O_2N_2$ (204.10): C, 64.67; H, 5.93; N, 13.72. Found: C, 64.04; H, 6.11; N, 13.74.

Racemic phenylethylglycine (*dl*-α-amino-α-phenylbutyric acid)[5,10] was prepared by hydrolysis of racemic phenylethylhydantoin with 75% sulfuric acid for forty-eight hours. The sulfate of the amino acid is obtained in crystalline form and is purified by reprecipitation from alcoholic solution with ether. It may be used directly for formylation (see below). The free amino acid is characterized by its beautiful copper salt, which crystallizes in dark blue polygonal platelets with 2 moles of crystal water per atom of copper. On standing over phosphorus pentoxide, it is converted into the lavender colored anhydrous salt.

Anal. Calcd. for $(C_{10}H_{12}O_2N)_2Cu\cdot 2H_2O$ (455.81): N, 6.16; Cu, 15.14. Found: N, 5.95; Cu, 15.30.

Racemic Formylphenylethylglycine.—Five grams of amino acid sulfate is refluxed for three hours on the water-bath with 2 g. of sodium formate and 10 g. of 95% formic acid. The formic acid is removed at reduced pressure, the temperature being kept below 55°. Fresh formic acid is added two or three times and the reaction product recrystallized from water; m. p. 193°.

Anal. Calcd. for $C_{11}H_{14}O_4N$ (224.13): N, 6.28. Found: N, 5.64. No amino nitrogen.

After many trials it was found that the resolution of this racemate can best be accomplished with quinine in 20% alcohol. The salt of the dextro-formyl compound is the less soluble. The alkaloid is removed in aqueous solution by alkali, and precipitation of the supernatant with acid yields the free **dextro-formylphenylethylglycine,** m. p. 212°, $[\alpha]_D$ +126° (0.2510 g. in 25 cc. aqueous alkali, α_D in 2-dm. tube +2.53°). An identical product with $[\alpha]_D$ +126° (0.2524 g., 25 cc., 2-dm. tube, α_D +2.55°) is obtained by formylation of dextro-phenylethylglycine. This confirms the optical purity of the compound.

On the other hand, deformylation by means of dilute sulfuric acid results in the formation of **dextro-phenylethylglycine,** which is found identical with the dextrorotatory amino acid as obtained by hydrolysis of the dextro-hydantoin; $[\alpha]_D$ +41° (0.1006 g. in 10 cc. aqueous alkali, 2-dm. tube, α_D +0.82°).

Anal. Calcd. for $C_{10}H_{13}O_2N$ (179.12): N, 7.82. Found: N, 8.25. Calcd. for anhydrous copper salt, $(C_{10}H_{12}O_2N)_2Cu$ (419.78): N, 6.69. Found: N, 6.66.

Levo-phenylethylglycine is likewise obtained from the respective hydantoin; $[\alpha]_D$ −41° (0.1014 g. in 10 cc. aqueous alkali, 2-dm. tube, α_D −0.83°).

Anal. Calcd.: N, 7.82. Found: N, 7.90.

Dextro-phenylethylglycine ethyl ester is prepared from the dextro amino acid by treatment with dry hydrogen chloride in ethyl alcohol for three hours. After removal of the alcohol *in vacuo,* the crystalline residue was washed with ether. The yield of the amino acid ester hydrochloride is increased by an additional precipitate from the ether

washings with petrolic ether. The free ester decomposed around 270°; $[\alpha]_D$ +36° (0.076 g. in 10 cc. water, 2-dm. tube, α_D +0.55°).

Anal. Calcd. for $C_{12}H_{17}O_2N$ (207.15): N, 6.76. Found: N, 6.89.

The syntheses of racemic, dextro- and levo-phenylethylhydantoin from the corresponding amino acids (or their ethyl esters) were usually carried out by means of urea. The rate of formation and of disappearance of the intermediary phenylethylhydantoic acid $(C_6H_5)(C_2H_5)C(COOH)NHCONH_2$ was studied in one case for the racemic series. Five grams of amino acid plus 17.5 g. of urea were dissolved in 25 cc. of water and heated on the water-bath. Five-cc. samples were withdrawn at intervals and cooled. In the first samples, no hydantoin had yet formed and the hydantoic acid was isolated from the clear solution by precipitation with sulfuric acid. The hydantoin started to crystallize in the fifth hour and the synthesis was complete in forty-eight hours.

Hours	1	2	3	5	16	48
Hydantoic acid in 5 cc. of supernatant, mg	211	283	277	256	145	none

The phenylethylhydantoic acids have no definite melting points but liquefy with loss of water between 170 and 180°. They solidify again at higher temperature and then approach the melting point of the hydantoin; $[\alpha]_D$ +60° (and −62°) (0.2411 g. and 0.2532 g. in 25 cc. aqueous alkali, 2-dm. tube, α_D +1.15° and −1.25°, resp.).

5,5'-Phenylethyl-3-phenyl-2-thiohydantoin was synthesized from phenylethylglycine and phenylthiourea; m. p. 143°.

Anal. Calcd. for $C_{17}H_{16}ON_2S$ (296.18): N, 9.45. Found: N, 9.12.

Amide of Isopropylcyanoacetic Acid (Isopropylmalonic Acid Amide Nitrile).—Equivalent amounts of the sodium cyanoacetic ethyl ester and 2-iodopropane are refluxed in alcohol for several hours. After dilution with water, the isopropyl cyanoacetic ester is separated and distilled *in vacuo* at 25°.[11] The colorless liquid is shaken with concentrated aqueous ammonia for several days. Isopropylcyanoacetamide is obtained and recrystallized from benzene; m. p. 124°.[12]

Anal. Calcd. for $C_6H_{10}ON_2$ (126.10): N, 21.21. Found: N, 21.65.

Its solution is treated with allyl iodide, $CH_2{=}CHCH_2I$ in the presence of sodium ethylate for several hours. The reaction mixture is taken up in ether and the washed and dried ethereal solution evaporated to dryness.

The **isopropylallylcyanoacetamide** is recrystallized from small amounts of amyl alcohol; m. p. 87°

Anal. Calcd. for $C_9H_{14}ON_2$ (166.13): N, 16.86. Found: N, 17.20.

This amide is added to a solution of potassium hypobromite in excess alkali and after two hours of standing it is heated on the water-bath for three hours to finish the reaction. Upon acidification, **isopropylallylhydantoin** of m. p. 187° crystallizes.

Anal. Calcd. for $C_9H_{14}O_2N_2$ (182.13): C, 59.28; H, 7.69; N, 15.38. Found: C, 58.90; H, 7.63; N, 15.04.

This product was also synthesized, by reversing the order of introduction of the alkyl groups, via the ester and the amide[13] of allylcyanoacetic acid. This preparation showed identical properties.

While brucine, cinchonine or Betti's base proved ineffective[14] in the resolution of

[11] Hessler, THIS JOURNAL, **35**, 1992 (1913).

[12] Henry, see Beilstein, fourth ed., Vol. II, p. 669.

[13] Henry, see Beilstein, fourth ed., Vol. II, p. 776.

[14] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI, p. 60.

this racemic hydantoin, **dextrorotatory allylisopropylhydantoin** could be obtained through the quinine salt; $[\alpha]_D$ +7.0° (0.1870 g. in 10 cc. alcohol, 2-dm. tube, α_D +0.26°). Owing to the poor yield, the question could not be settled whether this product represented the pure dextro form.

β-Bromoallylisopropylhydantoin, m. p. 214–215°, was obtained in unsatisfactory yield from isopropylcyanoacetamide plus propylene dibromide, $CH_2{=}CBrCH_2Br$, and oxidative rearrangement with potassium hypobromite.

Pharmacological and clinical experiments with these substances will be reported in detail elsewhere.[15] It was found in various animal species and by various methods of administration, that the Min. Eff. Dose and the Min. Lethal Dose of the dextro substance are 25 to 50% higher than for the levo substance, leaving the racemate in the middle (see table below).

While this difference is relatively insignificant in view of the therapeutic application, a striking difference was discovered between the two isomers as concerns the causation of the "nirvanol disease" upon oral administration. The incidence of "nirvanol disease" in 25 cases treated with an average aggregate dose of 4.2 g. of the racemate was 21 cases or 84%; in 14 cases, treated with an average amount of 2.1 g. only of the levorotatory drug, 9 cases or 64.5%. In a series of 18 cases which received an average of 2.8 g. each of dextro-phenylethylhydantoin, 5 cases (28%) developed the disease, while in another series of 15 adults who received much higher amounts of the dextro form, only 2 (13.5%) were affected.

These observations shed new light on the mechanism, allergic or otherwise, by which drugs and synthetic chemicals in general produce reactions in the human body.

Animal	Dose	Route of administration	Dextro	Racemic	Levo
			milligrams		
Rabbit	M. L. D.	Subcut.	350	250	250
Guinea pig	M. L. D.	Subcut.	250	200	200
Rat	M. E. D.	Subcut.	100	80[a]	80
Dog	M. E. D.	Perorally	100	<100	70
Pigeon	M. E. D.	Intraven.	75	[b]	50

[a] Allylisopropylhydantoin, 200 mg. [b] β-Bromoallylisopropylhydantoin, 40 mg.

We wish to thank Priv.-Doz. Dr. E. Rothlin, Basel, for giving us the results of his animal experiments with these substances.

Summary

5,5′-Phenylethylhydantoin was separated into its pure optically active forms. These optical antipodes were also independently synthesized from the optically active phenylethylglycine obtained by optical resolution of its racemate. The stability against racemization and the sense of rotation of these derivatives are discussed.

A brief report on the pharmacological and clinical value of dextro- and levo-phenylethylhydantoin shows that the substances differ slightly in

[15] Sobotka, Peck and Kahn, *J. Pharm. Exp. Ther.*, in press; Schick, Sobotka and Peck, *Am. J. Dis. Child.*, in press.

hypnotic effect. The dextro form, however, is three times less toxic as judged by the greatly reduced incidence of "nirvanol disease."

Allylisopropylhydantoin and β-bromoisopropylhydantoin were prepared and tested.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE C. F. KETTERING FOUNDATION FOR THE STUDY OF CHLOROPHYLL AND PHOTOSYNTHESIS]

OCCURRENCE OF DECOMPOSITION PRODUCTS OF CHLOROPHYLL. I. DECOMPOSITION OF CHLOROPHYLL IN THE DIGESTIVE SYSTEM OF THE COW

BY PAUL ROTHEMUND AND O. L. INMAN

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The study of natural porphyrins, especially copro-, uro- and ooporphyrin, was of greatest importance in ascertaining the constitution of hemin. Phylloerythrin, a biological decomposition product of chlorophyll, is for similar reasons of particular interest for studies in the chlorophyll series. L. Marchlewski[1] discovered it in the fresh feces of cows fed on green food. In the same year Loebisch and Fischler[2] isolated it from ox bile under the name bilipurpurin. Marchlewski[3] proved the identity of these two substances and their identity with MacMunn's cholehematin. Marchlewski also showed that phylloerythrin is derived from chlorophyll and not from hemoglobin. The porphyrin nature of phylloerythrin was demonstrated by H. Fischer and H. Hilmer,[4] who also proved D. Kémeri's porphyrin from human feces to be identical with phylloerythrin. By chemical methods H. Fischer and co-workers succeeded in preparing the substance from chlorophyll derivatives such as chlorophyllide $a + b$, pheophytin $a + b$, pheophorbide a, methylpheophorbide a, pheoporphyrin a_5.[5]

In a preliminary note[6] we announced that phylloerythrin occurs in the stomachs of herbivorous animals (cow and sheep). It has the formula I according to H. Fischer and he considers this structure of fundamental importance for the understanding of the nature of chlorophyll a. The study of decomposition products of chlorophyll in the animal body presents many possibilities. (1) Waste products can be examined. This method led to the discovery of phylloerythrin.[1] (2) Examination of the contents

[1] Marchlewski, *Bull. intern., acad. polonaise des sciences et des lettres*, A, 638–642 (1903).

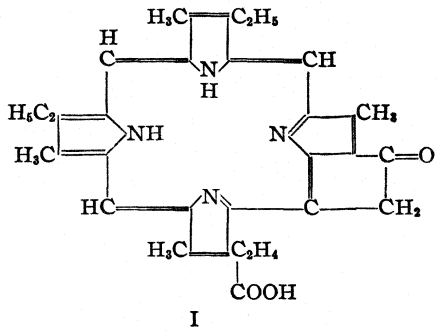
[2] Loebisch and Fischler, *Monatsh.*, 335–350 (1903).

[3] Marchlewski, *Bull. soc. chim. biol.*, **6**, 464–472 (1924).

[4] Fischer and Hilmer, *Z. physiol. Chem.*, **143**, 1–8 (1925).

[5] H. Fischer and O. Süs, *Ann.*, **482**, 225–232 (1930); H. Fischer, O. Moldenhauer and O. Süs, *ibid.*, **486**, 107–177 (1931).

[6] Inman and Rothemund, *Science*, 221 (1931).



I

of the digestive tract of lower animals has been tried: H. Fischer and A. Hendschel[7] examined the changes chlorophyll undergoes in the digestive system of caterpillars and isolated phyllobombycin, a crystallized substance free from magnesium, phytol and methoxyl. Following the suggestion of H. Fischer that the actual location in the animal body where phylloerythrin is formed should be investigated, we used the contents of the digestive tract of the cow and sheep in the present studies.

The contents of the stomachs were collected separately and immediately after the animals were killed. The material thus obtained was extracted within a few hours with a pyridine–chloroform mixture or with glacial acetic acid and ether. Such extraction yielded from the third stomach a dark red ether solution. The character of the absorption spectrum of this solution indicated a mixture of porphyrins. Willstätter's method of hydrochloric acid fractionation led to the isolation of crystallized phylloerythrin and other porphyrins, of which rhodo-, phyllo- and pyrroporphyrin could be identified. Two other substances, probably porphyrins, were found spectroscopically, but have not yet been crystallized. They occur only in minute quantities and we cannot say at the present time whether they are chlorophyll decomposition products already known or new substances.

The place for the formation of these porphyrins seems to be mainly the third stomach. Spectroscopic examination of the contents of the first and second stomachs, extracted according to our method, showed the presence of traces of phylloerythrin. The quantity of material used in these cases was 20 kg. In order to find whether the other porphyrins are present in the first and second stomachs, it would be necessary to extract larger quantities of material than we used. The contents of the fourth stomach of the cow contain the same porphyrins as the third stomach. No evidence was obtained for the presence of pigments like phyllobombycin. While examining the contents of the third and fourth stomachs of sheep we paid special attention to the possible presence of chlorophyll decomposition products of the pheophorbide type in order to determine the place of

[7] H. Fischer and A. Hendschel, *Z. physiol. Chem.*, **198**, 33–42 (1931).

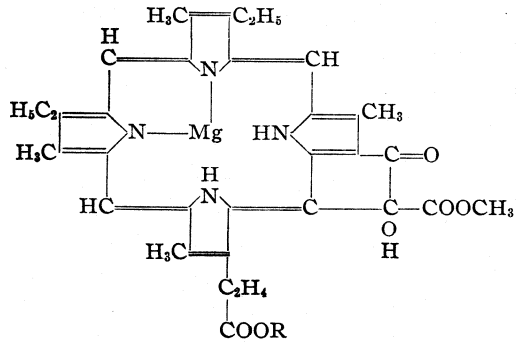
formation of the probophorbides, which H. Fischer[8] has recently isolated from the feces of sheep. Four kilograms of material from the third or fourth stomach is usually sufficient to demonstrate the presence of probophorbides, although it is not possible to isolate the different components *a–d* from the small quantity obtained.

The results of these studies are given in the following table.

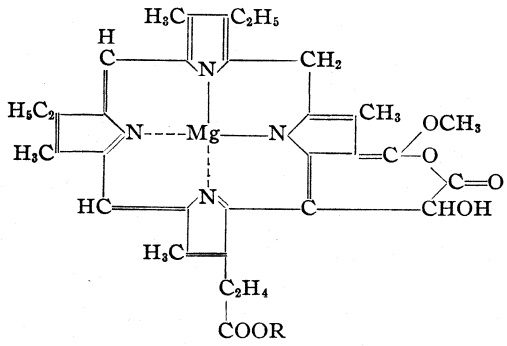
Animal	Stomach	
Cow	1 and 2	Traces of phylloerythrin
	3 and 4	Phylloerythrin, rhodo-, phyllo-, pyrroporphyrin and two other pigments
Sheep	3 and 4	Phylloerythrin and probophorbides
Calf on a milk diet		No porphyrins found

The formula of chlorophyll *a* as suggested by H. Fischer is given in formula II, while J. B. Conant prefers formula III.[9]

II
R = Phytyl



III



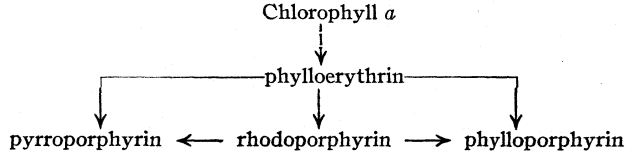
The formation of phylloerythrin from chlorophyll *a* in the digestive tract includes the following reactions: splitting off of the magnesium and the phytol groups, change of the molecule to porphyrin, and decarboxylation,

[8] H. Fischer and A. Hendschel, *Z. physiol. Chem.*, **206**, 255–278 (1932).

[9] Recently the formula of chlorophyll *a* has been changed [Fischer and Siebel, *Ann.*, **499**, 84–108 (1932); Stoll and Wiedmann, *Helv. Chim. Acta*, **15**, 1128–1136, 1280–1285 (1932)]. These changes, however, have retained the five-membered ring attached to the fundamental structure of the molecule.

accompanied by the reduction of an hydroxyl group. This series of changes must be followed by reactions producing the other simpler porphyrins (rhodo-, phyllo- and pyrroporphyrin): opening of the ring attached to the porphin structure, further decarboxylation and an oxidation–reduction reaction.

The decomposition of chlorophyll *a* in the digestive system of the cow may be represented tentatively by the following scheme



The fact that these chemical changes of the chlorophyll *a* molecule take place under normal physiological conditions as they exist in the stomachs of ruminants, seems to the authors to favor the view that the added five-membered ring of phylloerythrin (formula I) is present in the structure of the molecule of chlorophyll *a*, as shown in formula II.

Experimental

The contents of the different stomachs of cows and sheep were collected separately at the slaughter house about fifteen minutes after the animals had been killed; the material was taken to the laboratory and worked up immediately. Two kilograms of stomach contents was drained on a Buchner funnel with a pump and extracted with 2100 cc. of a mixture of chloroform and pyridine containing 1800 cc. of chloroform and 300 cc. of pyridine. The extraction is performed by alternately macerating without the use of the vacuum and draining with but slight suction. Finally the material is sucked dry by the strong suction of the pump.

The extracts of about 40 kg. were distilled *in vacuo* almost to dryness and the residue was dissolved in a small quantity of pyridine, filtered and transferred to a separatory funnel containing 3 liters of ether. Five per cent. hydrochloric acid was added to render the reaction slightly acid to Congo paper and the mineral acid solution was changed into an acetic acid solution ("discolored" reaction on Congo paper) by adding a few cc. of concentrated aqueous sodium acetate solution. The resulting pink ether solution was washed several times with distilled water and fractionated with hydrochloric acid according to Willstätter and Mieg.

The 0.5% HCl fraction was transferred into fresh ether and extracted with 0.35% HCl and the porphyrin from this extract was shaken into ether. After drying and evaporating the ether solution yielded long needle-shaped crystals; yield, 4 mg. recrystallized from ether. The spectrum in ether plus a little pyridine was identical with that of phylloporphyrin (measurement with the Zeiss–Loewe–Schumm spectroscope for chemists, also direct comparison, by means of the comparison prism, with phylloporphyrin prepared from pheophytin).[10] The esterification of the porphyrin was performed with methanolic hydrochloric acid. The ester, recrystallized from pyridine–methanol, melts at 231–232°; a mixture with phylloporphyrin methyl ester (from pheophytin) showed no depression.

The higher hydrochloric acid fractions were worked up similarly to the procedure

[10] H. Fischer, L. Filser, W. Hagert and O. Moldenhauer, *Ann.*, **490**, 35 (1931).

given for the 0.5% fraction. The porphyrin resulting from extraction with 1.3% HCl was identified with pyrroporphyrin from pheophytin by direct spectroscopic comparison. Methyl ester: HCl number, 2.5; m. p. 239–240° (no depression on mixture with methyl ester from pheophytin). Also, rhodoporphyrin from the 4% HCl fraction was identified spectroscopically, by the hydrochloric acid number of the ester and the melting point of the methyl ester (265°, no depression). The amounts of pure porphyrins were: pyrroporphyrin ester, about 5 mg.; rhodoporphyrin ester, 3 mg. Phylloerythrin was found in the 8% HCl fraction. Eleven milligrams of this porphyrin was obtained and identified; m. p. of the methyl ester, 263°; no depression with phylloerythrin ester from bile; m. p. of the mixture with rhodoporphyrin ester from cow stomach, 245° (depression 18°).

No porphyrin was found in the extracts with higher concentrations of hydrochloric acid.

The 6% HCl fraction yielded a substance which shows the following spectrum in pyridine–ether:

I, 646.4–641.0	II, 611.1–574.5	III, 562.8–540.5
643.7	592.8	551.7
IV, 526.6–505.6	E.A. 448	Int. II, III, IV, I
516.1		

Direct comparison with verdoporphyrin shows difference in spectrum.

Spectrum of the 7% HCl fraction in pyridine–ether

I, 634.8–629.2 faint 611	II, 603.4–574.1	III, 563.6–539.3
632.0	588.8	551.5
IV, 525.7–506.5	E.A. 445	Int. II, III, IV, I
516.1		

The spectrum is distinctly different from the spectrum of chloroporphyrin e_6 with respect to the absorption bands II, III and IV, although band I is identical and the hydrochloric acid numbers are the same.

In the cases of the 6 and 7% HCl fraction the yields were too small to prepare the pure methyl esters for characterization.

Instead of the pyridine–chloroform mixture glacial acetic acid may be used for the extraction of the stomach contents. One kilogram of the material was ground up in a large mortar with 600 cc. of glacial acetic acid, the solution was extracted three times with 500 cc. of ether and the ether was decanted; 400 cc. of acetic acid was added and three more ether extractions were made with 500 cc. of ether each time. The ether–acetic acid mixture was poured into the separatory funnel, the acetic acid removed by several washings with water and the ether solution subjected to hydrochloric acid fractionation. The yields obtained by this method are lower than those obtained by pyridine–chloroform extraction.

Summary

1. A series of porphyrins has been found in the stomach of the cow under normal physiological conditions.

2. Phylloerythrin and probophorbide are present in the stomach of sheep.

3. These porphyrins are decomposition products of chlorophyll. The stomach contents of animals on a milk diet do not contain these porphyrins.

4. The occurrence of these porphyrins supports a formula for chlorophyll containing a five-membered ring added to the porphin structure.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

ASYMMETRIC SYNTHESES. I. THE ACTION OF OPTICALLY ACTIVE NITRITES ON CYCLIC KETONES

BY MARGARET PEZOLD AND R. L. SHRINER

RECEIVED JULY 5, 1932 PUBLISHED DECEMBER 13, 1932

Most authentic and well recognized chemical asymmetric syntheses involve the creation of a new asymmetric carbon atom in a molecule which has been rendered optically active by combination with an active group. Subsequent removal of the original active group then leaves an active molecule without the use of the usual resolution of a racemic modification.[1] The success of such asymmetric syntheses depends on a difference in the rate of formation of two diastereoisomers. In the present study a new type of asymmetric synthesis was observed in the reaction of an active nitrite with a ketone.

The formation of an α-isonitroso ketone or α-oximino ketone by the action of a nitrite on a ketone is a well-known reaction. It is utilized as the first step in the synthesis of dimethylglyoxime[2] and in the preparation of 1,2-diketones.[3] The mechanism ascribed to the reaction is usually represented as follows

$$\underset{\text{I}}{\text{RCOCH}_2\text{R}} + \underset{\text{II}}{\text{R'ONO}} \longrightarrow \underset{\text{III}}{\text{RCOCHR}} \rightleftharpoons \underset{\text{IV}}{\text{RCOCR}} + \text{R'OH}$$

(III: RCOCHR with N=O; IV: RCOCR with N—OH)

The product actually isolated is undoubtedly an oxime (IV) as shown by its reactions and by the fact that it is light yellow in color whereas nitroso compounds are usually green. The nitroso compound (III) is usually indicated as the intermediate because of other reactions of nitrites and nitrous acid. Chief among these may be mentioned the formation of, (1) nitrosoamines[4] from secondary amines and nitrous acid; (2) *p*-nitrosodimethylaniline[5] from dimethylaniline and nitrous acid; (3) *p*-nitrosophenol or quinone monoxime[6] from phenol and nitrous acid. Wallach[7] has prepared nitroso pinene and reduced it to pinane-oxime. Ponzio[8] and

[1] Marckwald, *Ber.*, **37**, 349 (1904); *ibid.*, **37**, 1368 (1904); McKenzie, *J. Chem. Soc.* **85**, 1249 (1904); *ibid.*, **87**, 1373 (1905).

[2] Behrend and Tryller, *Ann.*, **283**, 244 (1894); Gandarin, *J. prakt. Chem.*, [2] **77**, 414 (1908); Biltz, *Z. anal. Chem.*, **48**, 164 (1909); Adams and Kamm, THIS JOURNAL, **40**, 1285 (1918).

[3] V. Pechmann, *Ber.*, **20**, 3162 (1887); Russanow, *ibid.*, **24**, 3504 (1891); Fittig, Daimler and Keller, *Ann.*, **249**, 182 (1889); Otte and v. Pechmann, *Ber.*, **22**, 2115 (1889).

[4] Fischer and Hepp, *ibid.*, **19**, 2991 (1886); **20**, 1247 (1887); **45**, 1098 (1912).

[5] Baeyer and Caro, *ibid.*, **7**, 810, 963 (1874); Meldola, *J. Chem. Soc.*, **39**, 37 (1881).

[6] Goldschmidt, *Ber.*, **17**, 213 (1884); Baeyer and Caro, *ibid.*, **7**, 811, 967 (1874).

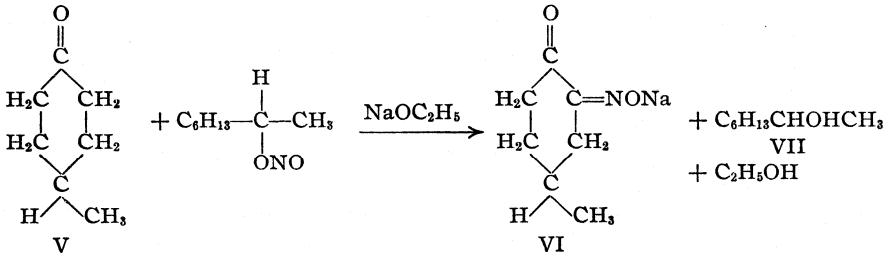
[7] Wallach, *Ann.*, **245**, 251 (1888); *ibid.*, **389**, 186 (1912).

[8] Ponzio and co-workers, *Gazz. chim. ital.*, **53**, 305 (1923); **53**, 297 (1923); **56**, 247 (1926).

co-workers still regard the geometric and structural isomers of the oximes as the forms (III) and (IV) above.

It is evident that the nitroso compound (III) contains an asymmetric carbon atom and hence if any indication could be obtained showing its presence proof of the intermediate step would be shown. However, no resolution of form (III) is possible since it is undoubtedly tautomeric with (IV).

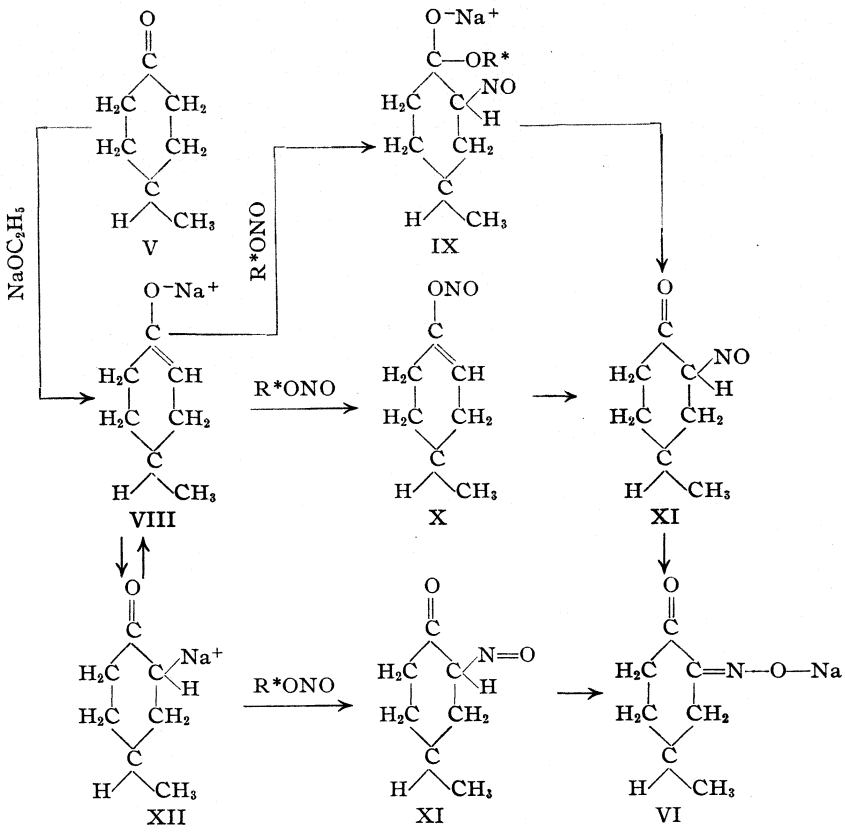
In order to obtain evidence indicating intermediate steps the above reaction was carried out between a cyclic ketone, 4-methylcyclohexanone, and the optically active nitrites, (*d*)- and (*l*)-2-octyl nitrite in an alcohol ether solution. The main reaction was



It will be noted that 4-methylcyclohexanone (V) has no asymmetric carbon atoms and does not exist in isomeric forms whereas in the oxime (VI) the carbon atom (4) carrying the methyl group is now asymmetric. When (*d*)-2-octyl nitrite was used it was actually found that the sodium salt of the oxime (VI) which precipitated from the solution was optically active and *levo*-rotatory. On the other hand, (*l*)-2-octyl nitrite gave a *dextro*-rotatory sodium salt of the oxime. The only other optically active product in the above reaction is octanol-2 (VII) or possibly some sodium 2-octylate. In a separate experiment it was shown that sodium octylate did not precipitate under the conditions used and also that sodium ethylate on (*l*)-2-octyl nitrite produced (*l*)-sodium octylate whereas the oxime obtained with this same nitrite was *dextro* rotatory. Similar condensations with cyclohexanone gave optically inactive products.

The formation of these oximes in an optically active state involves an asymmetric synthesis of a new and unusual type since the active group is split off during the reaction. The optically active oxime must have been produced by a preferential reaction occurring at some intermediate stage. Many mechanisms suggest themselves as possibilities, among which may be mentioned those shown: (R* = (*d*) or (*l*)-2-octyl radical).

According to the first mechanism the active nitrite adds to the double bond of the enol form (VIII) giving (IX), which splits off NaOR*producing (XI) which in turn rearranges to the oxime (VI). This mechanism shows an actual combination between the active group and the cyclic ketone.



The second mechanism depends for its success on a difference in the rate of reaction of the (*d*) and (*l*) forms of (VIII) with the active nitrite to produce (X), which then rearranges to (XI) and finally to the oxime (VI).

The third possibility likewise involves a preferential rate of reaction between the active nitrite and one of the four optical isomers of (XII). It represents a direct introduction of the nitroso group on the carbon atom. The present experimental evidence does not enable a mechanism to be assigned but does definitely show that asymmetric intermediates are involved.

Experimental

Preparation of 4-Methylcyclohexanone.—A mixture of 94 g. of 4-methylcyclohexanol in 30 cc. of concentrated sulfuric acid (sp. gr. 1.84) and 125 cc. of water was placed in a 2-liter, three-necked flask, fitted with a mercury-sealed stirrer, condenser, thermometer and a dropping funnel. To this mixture a solution of 90 g. of sodium dichromate in 125 cc. of water and 30 cc. of concentrated sulfuric acid was added slowly over a period of forty minutes with stirring. The temperature was allowed to rise to 65° and then external cooling was applied with an ice–salt bath. After one-third of the dichromate solution was added the temperature rise was rapid and had to be watched

carefully. The mixture was allowed to remain on the ice–salt bath for six hours with stirring. The mixture was steam distilled and the ketone separated. The aqueous layer was distilled again, obtaining more ketone. The product was dried over anhydrous calcium chloride and distilled[9] at 168 to 170°. The yield of 65 g. was 70.4% of the theoretical.

(*d*) and (*l*) Octanol-2.—Octanol-2 was resolved by crystallization of the brucine salts of the acid phthalic ester according to the procedure given in "Organic Syntheses."[10] The (*d*)-octanol-2 distilled at 85–86° at 20 mm.; α_D^{25} +10.15°: the (*l*)-octanol-2 at 83–84° at 20 mm.; α_D^{25} −10.30°.

(*dl*)-2-Octyl Nitrite.—In a 3-liter, three-necked flask, 165 g. of sodium nitrite and 130 g. of (*dl*)-octanol-2 were placed. The mixture was cooled to 10° by surrounding the flask with ice and salt. The flask was fitted with a mechanical stirrer and a dropping funnel, one neck remaining open. By means of the dropping funnel 40 cc. of concentrated sulfuric acid was very slowly added. The mixture was stirred vigorously and the temperature kept below 25°. After all the acid had been added, the stirring was continued and water added. The light yellow oil which rose to the surface was poured into a large separatory funnel. More water was added with stirring, the salt mixture allowed to settle, and the oil again poured into the separatory funnel. The extraction was continued until no more oil separated. The nitrite was washed several times with distilled water to remove sulfuric acid and dried over calcium chloride for a few moments. The crude (*dl*)-2-octyl nitrite was obtained which yielded on distillation 110 g. of pure nitrite, b. p. 72–74° at 18 mm., n_D 1.4272, d_{20}^{20} 0.852.

(*d*)-2-Octyl Nitrite.[11]—The (*d*)-2-octyl nitrite was prepared by the procedure given above for the inactive nitrite: b. p. 70–75° at 18 mm., α_D^{25} +6.90, n_D 1.4270, d_{20}^{20} 0.852.

(*l*)-2-Octyl Nitrite.—The (*l*)-2-octyl nitrite was prepared by the same procedure as that given for (*dl*)-2-octyl nitrite: b. p. 70–75° at 18 mm., α_D^{25} −7.53, n_D 1.4270, d_{20}^{20} 0.852.

Condensation of Cyclohexanone with (*dl*)-2-Octyl Nitrite.—In a 500-cc. three-necked flask fitted with a reflux condenser, stirrer and dropping funnel was placed a mixture containing 2.3 g. of sodium dissolved in 50 cc. of absolute alcohol plus 70 cc. of absolute ether. The contents of the flask were kept at a temperature between −10° and −15° by surrounding the flask with ice and salt mixture. A solution of 10 g. of cyclohexanone and 19.7 g. of (*dl*)-2-octyl nitrite in 250 cc. of absolute ether was added slowly to the sodium ethylate solution. Stirring was continued for three hours. The light tan condensation product was filtered with suction. Since the product was very hygroscopic the air which passed through the precipitate was dried by a U-tube containing anhydrone. The product was washed with absolute ether until the odor of octyl alcohol could no longer be detected. It was then dried in a vacuum desiccator over phosphorus pentoxide; yield 10.5 g. (68.8%).

Anal. Calcd. for $C_6H_8O_2NNa$: N, 9.40. Found: N, 9.44, 9.38.

Condensation of Cyclohexanone with (*d*)-2-Octyl Nitrite.—Cyclohexanone condensed with (*d*)-2-octyl nitrite, α_D = +6.9, according to the above procedure. The condensation product, identical with that obtained above, was dissolved in absolute alcohol and found to be optically inactive.

Condensation of 4-Methylcyclohexanone with (*l*)-2-Octyl Nitrite.—This condensation was carried out under the same experimental conditions as the condensation of

[9] Sabatier and Mailhe, *Compt. rend.*, **140**, 352 (1905); Perkin, *J. Chem. Soc.*, **89**, 836 (1906); Wallach, *Ann.*, **346**, 249 (1906).

[10] "Organic Syntheses," J. Wiley and Sons, Inc., New York, 1926, Vol. VI, p. 68.

[11] Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

cyclohexanone and octyl-2-nitrite. To 2.3 g. of sodium dissolved in 50 cc. of absolute alcohol was added 70 cc. of absolute ether. This mixture was cooled to $-10°$ and 11.45 g. of methyl-4-cyclohexanone and 10.85 g. of *l*-2-octyl nitrite (α_D $-7.53°$) in 250 cc. of absolute ether added slowly with stirring. The condensation product was washed with absolute ether and dried; yield, 2.16 and 2.50 g. In this condensation less than a molar quantity of nitrite was used in order to prevent any possible formation of dioxime. The rotations obtained on two runs of product were α_D^{25} $+16.51$ and α_D^{25} $+17.55°$. The product racemized in twelve hours.

Anal. Calcd. for $C_7H_{10}O_2NNa$: N, 8.58. Found: N, 8.25, 8.40.

Condensation of 4-Methylcyclohexanone with (*d*)-2-Octyl Nitrite.—The condensation was carried out in exactly the same manner as the condensation of 4-methylcyclohexanone with *l*-2-octyl nitrite. The rotation of the *d*-2-octyl nitrite condensation product gave α_D^{25} $-12.2°$. The rotation dropped to zero in ten hours.

Anal. Calcd. for $C_7H_{10}O_2NNa$: N, 8.58. Found: N, 8.45, 8.33.

Each of the above sodium salts of the oximes was dissolved in alcohol and acidified with dilute hydrochloric acid. Addition of ferric chloride to this solution gave a red color in each case. Another alcohol solution which had been acidified with acetic acid gave a grass-green color with dilute copper acetate solution, which is characteristic of the α-oximes[12] whereas the β-oximes give no color. Since all of the above oximes gave the same grass-green color they probably have the same configuration.

Action of Sodium Ethylate on (*l*)-2-Octyl Nitrite.—A solution of 0.23 g. of sodium in 5 cc. of absolute alcohol and 7 cc. of absolute ether was prepared. This solution was cooled to $-10°$ and 1.1 g. of (*l*)-2-octyl nitrite in 25 cc. of ether was added with stirring. The mixture was kept at $-10°$ and stirred for three hours. There was no precipitate and the ether solution containing sodium octylate showed a negative rotation. The (*l*)-2-octyl nitrite was hence converted to the (*l*)-sodium-2-octylate without any Walden inversion. After standing at room temperature for six hours no precipitate had appeared, which showed that the sodium derivatives of the active oximes were not contaminated with sodium-2-octylate.

Summary

The condensation of 4-methylcyclohexanone with (*d*)-2-octyl nitrite in the presence of sodium ethylate produces a levo sodium derivative of the oxime. The (*l*)-2-octyl nitrite produced the (*d*)-oxime. Cyclohexanone and (*d*) or (*l*)-2-octyl nitrite gave optically inactive products.

Several mechanisms for this new type of asymmetric synthesis are discussed.

URBANA, ILLINOIS

[12] Taylor and Marks, *J. Chem. Soc.*, 2303 (1930); *ibid.*, 2018 (1931).

[CONTRIBUTION FROM THE FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

SOLUBILITY RELATIONSHIPS AMONG OPTICALLY ISOMERIC SALTS. II. THE CAMPHORATES OF ALPHA-PARA-TOLYLETHYLAMINE

BY A. W. INGERSOLL AND FRANK B. BURNS

RECEIVED JULY 5, 1932 PUBLISHED DECEMBER 13, 1932

An analysis of the equilibria and solubility relationships among the isomeric salts of optically active and racemic bases and acids has been presented in Part I.[1] A maximum of five types of salts (including stable double salts) may be formed when the isomeric base and acid ions are combined in all possible ways. These are (*d*B*d*A or *l*B*l*A); (*d*B*l*A or *l*B*d*A); *dl*B*dl*A; (*d*B*dl*A or *l*B*dl*A); (*dl*B*d*A or *dl*B*l*A). One or both of the partially racemic types may be unstable; also it can be shown that not more than three of the nine varieties of salts can coexist in a solution, no matter what proportions of active base and acid ions are originally introduced. Thus in Part I it was shown that when a partially active base (or acid) is combined in solution with a racemic acid (or base), the resulting mixture must constitute one of eight possible *cases* (Nos. 1–8)[2] characterized by differences in the stability and order of solubility of the salts. When both the base and the acid are partially active, twelve additional cases (9–20)[2] are possible. These cases have been discussed as to their bearing on the problem of separating the active and inactive components of partially active substances, with particular reference to the problem of complete optical resolution.[3]

As yet only a few of these cases have been illustrated by actual instances. Many more groups of salts must be examined before it can be learned whether, and how frequently, each case will be encountered. Also little is known of the relative solubilities of isomeric salts when four, or even five, of the types are stable and can be compared. Hence, in continuation of the work, various groups of isomeric salts are being prepared from such asymmetric bases and acids as can be obtained in at least one active form and the inactive form. For the purposes in mind the group studied must consist of at least one variety of all of the stable types, that is, the first three types shown above and one or both of the other types when these are stable. Whenever possible the salts are completely purified, so that their common physical properties as well as their solubilities can be compared. It is expected that when the properties of a considerable number of such groups of salts are known, many interesting regularities will appear.

[1] Ingersoll and White, THIS JOURNAL, **54**, 274 (1932).

[2] The cases were described in Part I. To avoid repetition in future papers they were assigned permanent reference numbers.

[3] Ingersoll, THIS JOURNAL, (a) **47**, 1168 (1925); (b) **50**, 2264 (1928).

In the previous papers there were described two instances of Case 4,[3a] one of Case 8 (or 12),[1] and one of Case 7 (or 9).[3b] The double salts present in Cases 7 and 8, namely, *dl*B*dl*A and either (*d*B*dl*A or *l*B*dl*A) or (*dl*B*d*A or *dl*B*l*A), may be accompanied in solutions by one of the varieties of simple salts (*d*B*d*A or *l*B*l*A) or (*d*B*l*A or *l*B*d*A). Thus these cases always overlap one of the cases 9–20. Also four of the five types of salts can then be prepared. In the instance of Case 7 just referred to the order of solubility was

(*d*B*d*A or *l*B*l*A) < (*d*B*dl*A or *l*B*dl*A) < (*d*B*l*A or *l*B*d*A) < *dl*B*dl*A (a)

In the present paper there is described another instance of Case 7 but this overlaps Case 10 and the order of solubility of the four stable salts is

(*d*B*l*A or *l*B*d*A) < (*d*B*dl*A or *l*B*dl*A) < *dl*B*dl*A < (*d*B*d*A or *l*B*l*A) (b)

The instance in question is the group of salts formed from the active and inactive forms of camphoric acid and α-*p*-tolylethylamine. The resolution of this base was briefly described by Stenberg,[4] who obtained the *d*-base as *l*-malate and the *l*-base from the residue as *d*-camphorate. The salts were not described. Although Stenberg's work was confirmed, it was found that both active forms of the base could be obtained much more easily by the use of *d*-camphoric acid alone. Thus an aqueous alcoholic solution of equivalent amounts of *d*-acid and *dl*-base could be made to deposit both the *l*B*d*A and *d*B*d*A hydrogen camphorates in greatly unequal proportions; both salts were purified with high yields. This is one of the uncommon instances in which complete resolution can be effected by the use of a single agent. In order, however, to classify the instance and test the method of complete resolution, partially active base (*l*B + *dl*B) was combined with *dl*-camphoric acid and the salts crystallized. With some difficulty there was finally obtained a less soluble fraction of pure *l*B*dl*A salt and a residue of impure *dl*B*dl*A salt. The latter was also prepared pure from its pure components. The four salts were found to have the solubility order shown in (b) above. This order differs from any previously observed.

Experimental

Resolution of *dl*-α-*p*-Tolylethylamine.—The base, b. p. 204–205°, was prepared by the reduction of *p*-methylacetophenone oxime with sodium amalgam or, better, with sodium and absolute alcohol.[5] Its resolution with *l*-malic acid by Stenberg's method was confirmed, but seven recrystallizations of the head fraction were necessary to obtain the pure *d*-base and the yield was small. *d*-Camphoric acid was then used. In a typical experiment 40 g. of the acid was dissolved in 200 cc. of 95% ethanol and 27.5 g. of the base added. Water (400 cc.) was added and the mixture boiled until clear. On cooling, the first crop was 21.8 g. of coarse octahedra (*l*B*d*A, acid salt). After evaporation to 400 cc., the cooled solution deposited a mass of slender prisms (chiefly *d*B*d*A

[4] Stenberg, *Z. physik. Chem.*, **70**, 534 (1910).

[5] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1931, Vol. XI, p. 58.

salt) mixed with more of the tetrahedra. Further crops containing more of the prisms and some oily material were obtained by concentrating the mother liquor in stages. The main fractions were then separately recrystallized from about 15 parts of water with decolorizing carbon and the mother liquors used to recrystallize the smaller fractions. By combining similar fractions and inoculating the solutions with whichever salt was present in excess, a nearly quantitative separation of the pure salts was made. The combined yield from four similar runs was 136 g. of the *l*B*d*A salt (monohydrate), 118 g. of the *d*D*d*A salt, and 17 g. of partially oily intermediate fractions.

***l*-α-*p*-Tolylethylamine *d*-camphorate** crystallizes as the monohydrate from water or dilute ethanol in well-developed or truncated octahedra. A water solution (19.637 g.) saturated at 25° contained 0.1948 g. of anhydrous salt; hence the solubility is 1.00 g. of anhydrous salt or 1.05 g. of hydrated salt per 100 g. of water. The anhydrous salt melts at 173° (corr.).

Anal. Hydrated salt: 1.1835 g. lost 0.0635 g. at 95°. Calcd. for $C_{19}H_{29}O_4N \cdot H_2O$: H_2O, 5.10. Found: H_2O, 5.27.

Rotation. Anhydrous salt: 1.6435 g. made up to 25 cc. in 95% ethanol gave α_D^{25} +1.15° in 2 dm.; $[\alpha]_D^{25}$ +8.75°; M_D +29.3°(10^2).

***d*-α-*p*-Tolylethylamine *d*-camphorate** forms anhydrous, slender prisms, m. p. 187° (corr.). The solubility in water at 25° is 2.49 g. per 100 g. water.

Rotation. Subs., 1.7240 g. made up to 25 cc. in 95% ethanol gave α_D^{25} +3.19 in 2 dm.; $[\alpha]_D^{25}$ +23.1°; M_D +77.5(10^2).

***l*-α-*p*-Tolylethylamine.**—Pure *l*B*d*A salt was treated with excess dilute sodium hydroxide and the base distilled with steam, extracted with benzene, and distilled; b. p. 205°; d_4^{25} 0.9190.

Rotation. Without solvent α_D^{25} −31.5°, $[\alpha]_D^{25}$ +34.3°.

***d*-α-*p*-Tolylethylamine.**—This base was obtained from the pure *d*B*d*A salt as described for the *l*-base; b. p. 205°; d_4^{25} 0.9185; α_D^{25} +31.8°; $[\alpha]_D^{25}$ +34.6°. The rotation values for both forms are slightly smaller than Stenberg's values, −36.4° and +36.9° at 20°. Samples of the salts described above were therefore recrystallized, but their properties and the rotations of the active bases were not appreciably changed.

***l*-α-*p*-Tolylethylamine *dl*-camphorate** was first prepared by combining 20 g. of *dl*-camphoric acid with 13.5 g. of mixed bases having $[\alpha]_D^{25}$ −28.5° (about 82% excess *l*-base) and crystallizing the salts from water. These separated first as a mass of small needles and irregular particles. By prolonged fractionation there were obtained 18.2 g. of large, square tablets (*l*B*dl*A salt, monohydrate) and smaller fractions resembling the first deposit. The salt was identical with that prepared from pure *l*-base and *dl*-acid. After drying at 95° it melted at 169° (corr.). The solubility, calculated for the hydrated salt, was 1.53 g. per 100 g. of water at 25°.

Anal. Calcd. for monohydrate: H_2O, 5.10. Found: H_2O, 5.36.

Rotation. Anhydrous salt, 1.8190 g. made up to 25 cc. in 95% ethanol gave α_D^{25} −0.45 in 1 dm.; $[\alpha]_D^{25}$ −6.18°; M_D −20.7°(10^2).

After many crystallizations of the smaller fractions mentioned above the extreme fraction still showed a faint levo rotation. Since it was similar to the salt prepared from pure *dl*-base, and *dl*-acid, it was probably the slightly impure *dl*B*dl*A salt.

***dl*-α-*p*-Tolylethylamine *dl*-camphorate** forms spherules of microscopic needles from water and is anhydrous, m. p. 180° (corr.). The solubility is 1.66 g. per 100 g. of water at 25°.

Summary

1. The complete resolution of *dl*-α-*p*-tolylethylamine with *d*-camphoric acid is described.

2. Four stable, isomeric α-*p*-tolylethylamine camphorates have been prepared and found to illustrate Case 7 (or 10) and the solubility order *l*B*d*A < *l*B*dl*A < *dl*B*dl*A < *d*B*d*A.

NASHVILLE, TENNESSEE

[CONTRIBUTION NO. 99 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

REDUCTIONS IN THE MORPHINE SERIES. I. DIHYDROPSEUDOCODEINE[1,2]

BY ROBERT E. LUTZ AND LYNDON F. SMALL

RECEIVED JULY 6, 1932 PUBLISHED DECEMBER 13, 1932

In respect to their behavior on catalytic hydrogenation, the alkaloids of the morphine series may be divided sharply into two classes. The one class includes all of those derivatives having an ethylenic double linkage in the 7,8-position of the hydroaromatic ring. Hydrogenation of such compounds in the presence of platinum or palladium under the ordinary conditions of temperature and pressure results in addition of one molecule of hydrogen at the hydroaromatic unsaturation, without disturbance of the 4,5-ether bridge.[3] This type of reduction, which we designate as normal (*i. e.*, in the sense, expected), is met in the cases of morphine,[4] codeine (I),[4a] isocodeine,[5] codeinone,[6] hydroxycodeinone[7] and α-[8] and γ-methylmorphimethines.[9,10]

The other class of morphine derivatives, in which the hydroaromatic unsaturation lies between carbon atoms 6 and 7, has heretofore been re-

[1] This investigation was supported by a grant from the Committee on Drug Addiction of the National Research Council from funds provided by the Bureau of Social Hygiene, Inc.

[2] Presented in part at the New Orleans meeting of the American Chemical Society, March 30, 1932.

[3] The halogeno derivatives of morphine and codeine are exceptional in this respect, and the mechanism of their reduction is uncertain. Under some conditions, however, they also yield hydrogenation products in which the ether bridge is intact. See Mosettig, Cohen and Small, THIS JOURNAL, **54**, 793 (1932).

[4] (a) Oldenberg, *Ber.*, **44**, 1829 (1911); (b) German Patent 260,233 (1913); (c) Skita and Franck, *Ber.*, **44**, 2862 (1911).

[5] Speyer and Wieters, *ibid.*, **54**, 2647 (1921).

[6] Mannich and Löwenheim, *Arch. Pharm.*, **258**, 295 (1920).

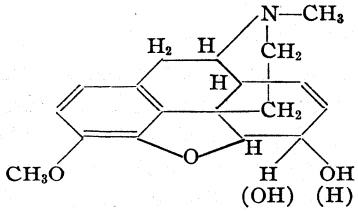
[7] Freund and Speyer, *J. prakt. Chem.*, **94**, 135 (1916); Freund and Speyer, German Patent 296,916 (1916); *Friedländer*, **13**, 880; U. S. Patent 1,468,805 (Sept. 25, 1923); Freund, U. S. Patent 1,485,673 (March 4, 1924).

[8] Von Braun and Cahn, *Ann.*, **451**, 55 (1927).

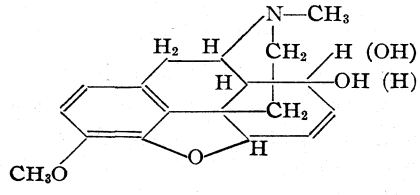
[9] Speyer and Koulen, *ibid.*, **438**, 34 (1924).

[10] The dimolecular oxidation product of morphine, pseudomorphine, also reduces normally (unpublished results, L. F. Small and F. L. Cohen) and this fact may be taken as evidence that the unsaturation in the two morphine nuclei still occupies the original 7,8-position.

ducible by the catalytic method always with addition of two molecules of hydrogen. One molecule of hydrogen is used in saturating the double linkage, and the second goes to open the 4,5-ether bridge, with formation of a phenolic hydroxyl at position 4. This behavior, which we shall refer to as abnormal reduction, is exhibited by the structural isomers of codeine and isocodeine, namely, pseudocodeine and allopseudocodeine (II),[11] as well as by other compounds which are known to be of the pseudocodeine type, as ϵ- and ζ-methylmorphimethines[9] and pseudocodeinone,[12] and has been accepted as evidence of the presence of a pseudocodeine type of structure.[13]



I. Codeine and Isocodeine



II. Pseudocodeine and Allopseudocodeine

In the course of the pharmacological experiments which are being carried out in connection with our morphine studies, pseudocodeine has been found to be of exceptional interest[14] and the preparation of a normal non-phenolic dihydropseudocodeine for comparative studies assumed considerable importance. From the theoretical standpoint there appears to be no reason why the catalytic addition of hydrogen to the allyl ether system present in pseudocodeine should proceed exclusively with scission of the ether grouping, whatever the mechanism of the reaction. Systematic experiments have, in fact, shown us that the mode of hydrogenation of pseudocodeine is not invariable, but rather is dependent upon several factors (Table IV). Under suitable conditions the reduction may be caused to proceed in the normal way to the extent of 85%, resulting in a new, non-phenolic dihydropseudocodeine. This substance, which still contains the 4,5-ether bridge, is the analog of the non-phenolic dihydrocodeine and dihydroisocodeine obtained by catalytic reduction of codeine

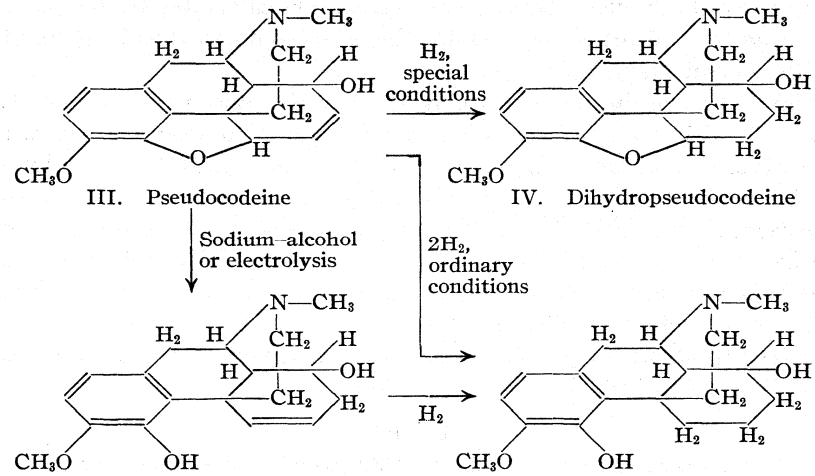
[11] (a) Speyer and Wieters, *Ber.*, **54**, 2647 (1921); (b) Speyer and Krauss, *Ann.*, **432**, 233 (1923).

[12] Karl A. T. Hill, Dissertation, Frankfurt a/M, 1925, p. 41. The position of the double linkage in the hydroaromatic ring III of pseudocodeinone is in doubt, for pseudocodeinone condenses with benzaldehyde [Knorr and Hörlein, *Ber.*, **40**, 3353 (1907)] and gives other reactions indicating the presence of the —CO—CH_2— grouping; *cf.* Schöpf, *Ann.*, **452**, 212, Note 2 (1927).

[13] (a) Schöpf and Winterhalder, *ibid.*, **452**, 237 (1927); (b) Schöpf and Hirsch, *ibid.*, **489**, 235, footnote (1931); (c) Small and Cohen, THIS JOURNAL, **53**, 2221 (1931).

[14] "Studies on Morphine, Codeine and their Derivatives. II. Isomers of Codeine," by Nathan B. Eddy, *J. Pharmacol.*, **45**, 361 (1932).

and isocodeine under ordinary conditions, and is also isomeric with the phenolic dihydropseudocodeine (V) which Speyer prepared by electrolytic or sodium and alcohol reduction of pseudocodeine.[15] In contrast to the new dihydropseudocodeine, Speyer's phenolic dihydropseudocodeine still contains an alicyclic double bond and may be hydrogenated (one mole of hydrogen) to the same tetrahydropseudocodeine (VI) as is obtained through the abnormal catalytic hydrogenation (two moles of hydrogen) of pseudocodeine itself.



III. Pseudocodeine

IV. Dihydropseudocodeine

V. Phenolic dihydropseudocodeine

VI. Tetrahydropseudocodeine

Since the new non-phenolic dihydropseudocodeine (IV) represents the normal dihydro product and is comparable to other dihydro compounds in the morphine series, we shall refer to it simply as dihydropseudocodeine, and distinguish the previously known dihydropseudocodeine (V) with the qualification "phenolic." A similar convention will be observed in the case of the isomeric phenolic and non-phenolic degradation products.

The hydrogenation of pseudocodeine, as is evident from the data listed in Table IV, always produces both dihydropseudocodeine and tetrahydropseudocodeine in amounts which vary considerably with the experimental conditions. Dihydropseudocodeine undoubtedly escaped previous detection only because of its relatively high solubility, for we have found it present even in those hydrogenations which were formerly thought to yield tetrahydropseudocodeine exclusively. In addition to these two products, a phenolic dihydropseudocodeine, which is different from the above-mentioned phenolic dihydropseudocodeine of Speyer, can sometimes be detected, and is apparently formed as an intermediate step in that phase of the reduction which ultimately gives tetrahydropseudocodeine. This

[15] Speyer and Krauss, *Ann.*, **432**, 249 (1923).

phenolic dihydro product, which resembles tetrahydropseudocodeine closely in physical properties and can be separated from it only with difficulty, will be described in more detail in our next communication. It is present in the crystalline precipitate which often separates during the hydrogenation of pseudocodeine in concentrated solutions. This precipitate is completely soluble in alkali and can therefore contain no pseudocodeine; nevertheless, when it is brought into solution and subjected to further hydrogenation, a notable absorption takes place. The observed variation of hydrogen absorbed from absorption calculated on the basis of the dihydro- and tetrahydropseudocodeine isolated can thus be accounted for in several instances.

The variation in relative yields of phenolic and non-phenolic end-products with changing conditions shows that a number of factors are operative. Chief among these are solvent, nature of catalyst, and hydrogen-ion concentration. Amount of catalyst, rate of reduction and temperature seem to have little, if any, effect on the course of the reaction. When the free base pseudocodeine is used in alcohols (alkaline reducing conditions) the minimum yields of dihydropseudocodeine, 5 to 9%, are obtained. With ethyl acetate the yield rises to 15 or 20%, and in glacial acetic acid increases to about 40%. The effect of solvent, which is roughly parallel for different catalysts, is shown in Table I.

TABLE I

EFFECT OF SOLVENT AND CATALYST ON YIELD OF DIHYDROPSEUDOCODEINE

Solvent	PtO_2	Pd-$BaSO_4$	Pd-$CaCO_3$
Methyl alcohol	5%	....	.....
Ethyl alcohol	7– 9%	9.5%	6%
Ethyl acetate	24–27%	15%	16–20%
Gl. acetic acid	35–40%	28%	.....

The most marked influence upon the course of pseudocodeine hydrogenation seems to be exerted through changes in hydrogen-ion concentration, a fact which we have further verified by extension of the reduction process in acid media to other pseudocodeine types. Our results are not consistent enough to permit of a reasonable theoretical explanation, but they have proved very useful as a practical solution of the difficulties met in obtaining normal reduction products from all pseudocodeine types. As will be seen from Table II, the yield of dihydropseudocodeine in aqueous medium is highest when a strong acid, as hydrochloric or sulfuric, is present in some excess, but is relatively low in very weakly acid solutions, as in the case of pseudocodeine hydrochloride in water, or pseudocodeine base in excess of dilute acetic acid. With a palladium catalyst, excess of strong acid beyond a certain limit lowers the yield of dihydro product sharply. Inexplicably, the best yields of dihydropseudocodeine were obtained when pseudocodeine hydrochloride was hydrogenated in glacial acetic acid. In this medium an

excess of strong base (the alkaloid itself, or sodium acetate)[16] or of strong acid lowers the yield, in some cases very considerably. For the normal reduction, platinum is more favorable than palladium; yields in strongly acid aqueous solution approach those obtained with the salt in glacial acetic acid.

TABLE II

EFFECT OF HYDROGEN-ION CONCENTRATION. PERCENTAGE YIELD OF DIHYDROPSEUDOCODEINE

Substance	Solvent	PtO_2	$Pd-BaSO_4$
Base	5–8% Acetic acid	9.5	10
Hydrochloride	Water	11–23	28–31
Base	Excess 1–3% HCl	68–70	44
Base	Excess 7% H_2SO_4	76	66
Base	Excess 10% HCl	65	7
Base	Gl. AcOH + 10% NaOAc	39	45
Base	Gl. AcOH	35–40	28
Hydrochloride	Gl. AcOH	71–85	51–59
Base	Gl. AcOH + 2% HCl	49	18–20

Very few observations upon the effect of hydrogen ion on the course of hydrogenation of alkaloids belonging to the morphine series have been reported previously. An investigation carried out by Schöpf and Winterhalder[17] on the effect of P_H on the hydrogenation of thebaine is to a certain extent in agreement with our results. Thebaine, which contains a system somewhat similar to pseudocodeine, although complicated by the presence of an enol-ether group and another double bond, was found to give the non-phenolic dihydrothebaine in yields which increased from 11 to 22% when the medium was changed progressively from P_H 7 to 2, although the yield of the phenolic substance, dihydrothebainone, was not notably decreased. Studies on the reduction of thebaine and certain of its degradation products in absolutely acid-free medium were made by Wieland and Kotake,[18] who found that under these conditions the result was a reductive scission of the ether ring without hydrolysis of the enol ether grouping.

The new dihydropseudocodeine (IV) crystallizes in thin rectangular scales melting (when anhydrous) at 155°.[19] It forms well-crystallized salts and methiodide. The latter was degraded by boiling with dilute alkali, and yielded the oily dihydro-ε-methylmorphimethine (XI),[20] an isomer of the phenolic dihydro-ε-methylmorphimethine (VII) which Speyer obtained by degradation of phenolic dihydropseudocodeine meth-

[16] Hall and Conant, THIS JOURNAL, **49**, 3047, 3062 (1927), have shown that sodium acetate or amines function in acetic acid as relatively strong bases. Thus the hydrochloride of the alkaloid, as a salt, is probably nearly neutral in character in glacial acetic acid solution.

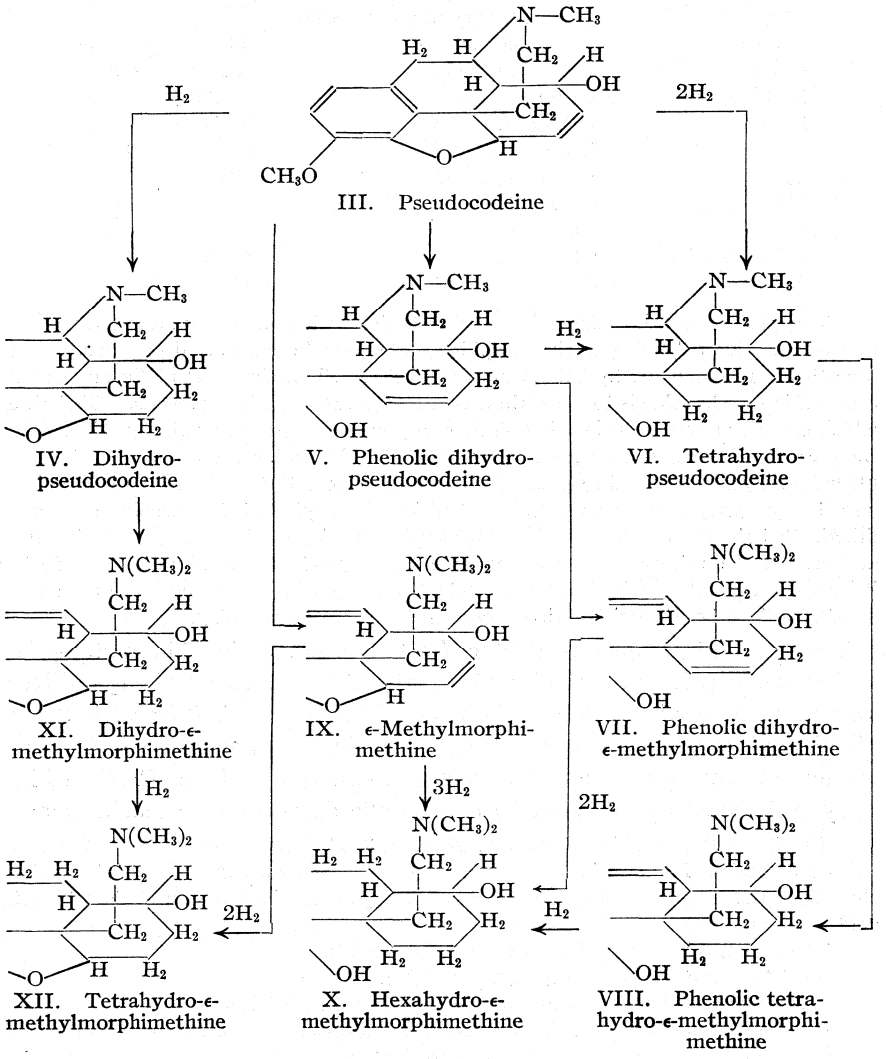
[17] Schöpf and Winterhalder, *Ann.*, **452**, 244 (1927).

[18] Wieland and Kotake, *Ber.*, **58**, 2009 (1925).

[19] The phenolic dihydropseudocodeine of Speyer melts at 128°.

[20] In view of the fact that the term ε-methylmorphimethine is firmly established in the literature it seems advisable to adhere to the "methine" nomenclature in this series instead of using the more flexible and exact "des-N-methyl-" [Willstätter, *Ann.*, **317**, 268 (1901)] system. Thus, dihydro-ε-methylmorphimethine instead of des-N-methyldihydropseudocodeine, hexahydro-ε-methylmorphimethine instead of dihydro-des-N-methyltetrahydropseudocodeine, etc.

iodide. Dihydro-ϵ-methylmorphimethine could not be induced to crystallize, but formed crystalline salts, and reduced with absorption of one molecule of hydrogen to give (non-phenolic) tetrahydro-ϵ-methylmorphimethine (XII), a substance which we were likewise able to prepare directly by application of our special hydrogenation conditions to ϵ-methylmorphimethine (IX).



The catalytic reduction of ϵ-methylmorphimethine under the ordinary conditions of hydrogenation was first carried out by Speyer and Koulen,[9] who observed absorption of three molecules of hydrogen with formation of

hexahydro-ϵ-methylmorphimethine. Our hydrogenation studies have necessitated a repetition of the Speyer and Koulen experiment, in which under comparable conditions we obtain results agreeing essentially with those of Speyer. When, however, the hydrogenation is conducted in the manner which we have found to favor normal reduction of pseudocodeine, an absorption of less than three molecules of hydrogen is observed. The products obtained are hexahydro-ϵ-methylmorphimethine (X) and a non-phenolic tetrahydro-ϵ-methylmorphimethine (XII). The latter results from normal hydrogenation and is identical with the new tetrahydro-ϵ-methylmorphimethine mentioned above. Its appearance proves that the hydrogenation of ϵ-methylmorphimethine under special conditions actually takes a course parallel to that observed for pseudocodeine itself. Table III summarizes the effect of varying conditions upon the relative yields of tetrahydro- and hexahydro-ϵ-methylmorphimethine. These results are roughly parallel to those given in Table II for pseudocodeine. In no case could the hydrogenation of ϵ-methylmorphimethine be so conducted that normal reduction was the principal reaction.

TABLE III

HYDROGENATION OF ϵ-METHYLMORPHIMETHINE. EFFECT OF CONDITIONS ON YIELD OF PRODUCTS

Substance	Solvent	Catalyst	% Tetrahydro	% Hexahydro
Hydrochloride	Gl. AcOH	PtO_2	29	45
Hydrochloride	0.7% HCl	PtO_2	39	39
Hydrochloride	H_2O	Pd-$BaSO_4$	25	Main product
Hydrochloride	H_2O	PtO_2	Trace	Main product
Base	Alcohol	Pd-$CaCO_3$	..	Main product

Hexahydro-ϵ-methylmorphimethine crystallizes from ethyl acetate in hair-like needles or thick prisms, depending upon the speed of crystallization, and melts at 168° (Speyer, 155°). Although phenolic in nature[21] the base is soluble in alkali only with difficulty. The solid crystalline base dissolves slowly and in but slight degree in aqueous sodium hydroxide. If a solution of hexahydro-ϵ-methylmorphimethine in acid is made alkaline, a momentary precipitate is observed at the isoelectric point; this precipitate dissolves in the excess alkali, but separation of crystalline hexahydro-ϵ-methylmorphimethine begins almost immediately. A small amount of base remains in the alkaline solution and separates when ammonium chloride is added. The base is almost completely removed from its very dilute solution in alkali by a few extractions with ether. The peculiar alkali-insolubility often shown by similar substances which carry a phenolic hydroxyl group at C-4 and which are completely hydrogenated in ring III has been discussed in a previous paper.[22]

[21] Speyer and Koulen, Ref. 9, were able to prepare a diacetyl derivative.

[22] Small and Cohen, THIS JOURNAL, 54, 802 (1932). A reasonable explanation of

In the pseudocodeine series the weakening in acidity of the phenolic hydroxyl appears with scission of the nitrogen-containing ring. Tetrahydropseudocodeine (VI), which was prepared by abnormal hydrogenation of pseudocodeine and which is typically phenolic in alkali solubility, was converted to the methiodide and degraded by heating with potassium hydroxide. The oily material which precipitates in this degradation was found to be the phenolic tetrahydro-ϵ-methylmorphimethine base (VIII) and not its potassium salt as claimed by Speyer.[23] The crystalline methine base thus obtained proved to be practically alkali-insoluble, although derived directly from the alkali-soluble tetrahydropseudocodeine,[24] and reduced readily with absorption of one molecule of hydrogen to the same hexahydro-ϵ-methylmorphimethine described above.

The assumption seems justified that the mechanism of the hydrogenation of pseudocodeine, ϵ-methylmorphimethine, and other pseudocodeine types under the special conditions described is in each case the same. The simultaneous formation of dihydropseudocodeine and tetrahydropseudocodeine must involve at least two competing processes. Dihydropseudocodeine results from normal addition of one molecule of hydrogen to an ethylenic bond, and, having ring III completely saturated, is as stable as dihydrocodeine or dihydroisocodeine toward further reduction. Tetrahydropseudocodeine, on the other hand, must result either from a primary 1,4-addition of hydrogen, beginning on oxygen and carbon atom 7, *i. e.*, the ends of the allyl ether system, as postulated by Schöpf,[13a,25] or from a direct reductive scission of the ether bridge, a reaction which must be attributed to the activating influence of the adjacent allylic double bond. If the latter hypothesis is correct, the 6,7-double linkage of pseudocodeine does not take a direct part in the addition of the first molecule of hydrogen, but is saturated in the second stage of the reduction.

Dihydropseudocodeine can be demethylated with boiling hydriodic acid to give directly the hydriodide of the new dihydro-γ-isomorphine. Attempts at the normal hydrogenation of the isomers of morphine as well as

this phenomenon cannot be advanced. Tetrahydropseudocodeine (VI) is an exception to this general rule.

[23] The melting point 162–163° was given by Speyer and Krauss for phenolic tetrahydro-ϵ-methylmorphimethine. We find the melting point to lie at 197°. From our analysis of this base and through its smooth hydrogenation to hexahydro-ϵ-methylmorphimethine we are certain that we actually have phenolic tetrahydro-ϵ-methylmorphimethine under examination.

[24] A closure of the 4,5-ether bridge by a rearrangement during the degradation is so improbable that it hardly merits discussion. Such a rearrangement, involving a shift of 2H to the newly-formed double bond at C—9, C—10, must in any case lead to the nonphenolic tetrahydro-ϵ-methylmorphimethine (XII), which cannot be hydrogenated to hexahydro-ϵ-methylmorphimethine.

[25] This point will be elaborated in a paper dealing with the isomeric phenolic dihydropseudocodeines.

of allopseudocodeine and other pseudocodeine types will be described in later papers.

In its physiological action, dihydropseudocodeine resembles pseudocodeine. Like the latter it is entirely non-convulsant; it is more analgesic and more emetic, and appears to be slightly more active in its effect on respiration. In these respects pseudocodeine and dihydropseudocodeine show the same differences as do the pairs codeine–dihydrocodeine and isocodeine–dihydroisocodeine. Further particulars on the physiological action will appear in publications by Dr. N. B. Eddy from the Pharmacological Laboratory of the University of Michigan.

TABLE IV

EFFECT OF CONDITIONS ON HYDROGENATION OF PSEUDOCODEINE

The yields given represent the maximum and minimum obtained in a number of experiments. The platinum catalyst used was in every case platinum oxide; the palladium catalyst was palladium on barium sulfate, excepting in the first two experiments listed, which include reductions using both palladium on calcium carbonate and palladium on barium sulfate.

Catalyst	Conditions	Yield in % Dihydro	Tetrahydro
Pd or Pt	Base in EtOH or MeOH	5–10	72–90
Pd	Base in EtOAc	15–20	75–79
Pt	Base in EtOAc	24–27	65–72
Pd	Hydrochloride in H_2O	28–31	62
Pt	Hydrochloride in H_2O	11–23	69–88
Pd or Pt	Base in dilute AcOH	10	87–90
Pd	Base in 1% HCl	44	45
Pd	Base in 10% HCl	7	62
Pd	Base in 15% H_2SO_4	66	32
Pt	Base in HCl or H_2SO_4 (1–15%)	65–77	19–28
Pd or Pt	Base in glacial AcOH	30–40	58–64
Pd or Pt	Base in glacial AcOH with NaOAc	39–45	54–63
Pd	Hydrochloride in glacial AcOH	51–59	41–44
Pt	Hydrochloride in glacial AcOH with wide variation in temp. up to 60°	76–85	5–15
Pd	Hydrochloride in glacial AcOH + 0.3 cc. concd. HCl	19–20	66–70
Pt	Hydrochloride in glacial AcOH + 0.5 cc. concd. HCl or 1 g. concd. H_2SO_4	49–52	41–50

Experimental

Pseudocodeine.—The pseudocodeine used in these experiments was prepared according to the method of Knorr[26] and Speyer[27] by the hydrolysis of α-chlorocodide. In large-scale runs (500 to 1000 g. of α-chlorocodide) it was found advantageous, after the hydrolysis with dilute acetic acid, to precipitate the mixture of isomeric bases under ether with sodium hydroxide. The bases which first precipitated separated in the form of an oil, which dissolved in the ether layer; as more alkali was added, the concentration in the ether reached the point where crystallization started (the codeine isomers are only sparingly soluble in ether) and practically the entire yield of the mixed isomers

[26] Knorr, *Ber.*, **41**, 972 (1908).

[27] Speyer, *Ann.*, **432**, 246 (1923).

crystallized in the aqueous layer and could be filtered off and washed with water. The oil obtained from the ether layer contained practically no pseudocodeine, but some isocodeine and allopseudocodeine, and was added to the mixture of these bases which remained after pseudocodeine had been removed as the hydrochloride. The oily residue from the purification of pseudocodeine hydrochloride likewise contained some isocodeine and allopseudocodeine, which were separated by the Speyer procedure. The hydrolysis of α-chlorocodide in 580-g. portions gave yields of crude crystalline salts as follows: pseudocodeine hydrochloride, 215 to 277 g.; allopseudocodeine hydriodide, 86 to 96 g.; isocodeine binoxalate, 160 to 190 g. A small amount of oily material was always obtained at the end of the separation of the isomers.

Attempted reductions of pseudocodeine with sodium hydrosulfite, aluminum amalgam in moist ether, or by electrolysis with prepared (Tafel) or unprepared lead electrodes yielded only unchanged starting material. Sodium amalgam in acetic acid reduced part of the material to phenolic dihydropseudocodeine. Zinc in acetic or hydrochloric acid effected no reduction.

Isocodeine Acid Tartrate.—This salt was prepared for pharmacological study. The calculated amounts of isocodeine and tartaric acid were dissolved in methyl alcohol and the solution concentrated. The salt crystallized very slowly as diamond-shaped plates, exceedingly soluble in water. It was purified from methyl alcohol, and melted at 185–186° (corr.) with foaming. In aqueous solution it showed $[\alpha]_D^{24}$ −99.4°, c = 1.60.

Anal. Calcd. for $C_{22}H_{27}O_9N$: C, 58.77; H, 6.05. Found: C, 59.04; H, 6.18.

Dihydroisocodeine Acid Tartrate.—The hydrogenation of isocodeine was carried out according to the directions of Speyer and Wieters[11a] using palladium–barium sulfate as catalyst. The reduction proceeds equally well in dilute acetic acid, hydrochloric acid or oxalic acid solution. The most convenient procedure consisted in direct hydrogenation of the purified isocodeine binoxalate (from the separation of the codeine isomers) in water solution. The hydrogenated base was thrown out by strong alkali and crystallized from alcohol. A solution of 8.7 g. of dihydroisocodeine with 4.4 g. of *d*-tartaric acid in 60 cc. of water, when cooled slowly, yielded 11.6 g. of crystals, m. p. about 180°. The salt is soluble to the extent of 4.5 g. in 100 cc. of water at 24°. It contains three molecules of hydrate water, part of which is lost in the vacuum desiccator; in aqueous solution, $[\alpha]_D^{26}$ −62.4°, c = 1.94.

Anal. Calcd. for $C_{22}H_{29}O_9N + 3H_2O$: H_2O, 10.69. Found: H_2O, 10.28. Calcd. for $C_{22}H_{29}O_9N$: C, 58.50; H, 6.47. Found: C, 58.68; H, 6.79.

Hydrogenation of Pseudocodeine: Dihydropseudocodeine.—The catalysts used in the hydrogenation experiments listed in Table IV were prepared by the usual methods[28] and whenever possible the same batch of catalyst was used throughout a series of comparative reductions.

The solution of pseudocodeine base or salt was shaken with catalyst and hydrogen until absorption stopped. In many cases a fresh portion of catalyst was added to make sure that reduction was complete. The pseudocodeine reduced rapidly and completely excepting in those hydrogenations which were carried out in concentrated solution, from which the products of hydrogenation often crystallized during the experiment. This crystalline precipitate usually carried down some phenolic dihydropseudocodeine, and could be slowly reduced further, or more rapidly if sufficient solvent was added. The method of isolation of the reduction products in all experiments was practically the same.

[28] Platinum oxide, Adams and Shriner, THIS JOURNAL, **45**, 2171 (1923); palladium on barium sulfate, Schmidt, *Ber.*, **52**, 409 (1919); palladium on calcium carbonate, Busch and Stöve, *ibid.*, **49**, 1064 (1916).

After complete reduction, the catalyst was filtered off, the solution being warmed if necessary to dissolve any crystalline precipitate. Organic solvents, where used, were removed by adding water and distilling under diminished pressure. Glacial acetic acid solutions were first concentrated under vacuum and diluted with water. The aqueous suspension or solution was acidified, if necessary, to bring all material into solution, and an excess of sodium hydroxide solution added, with stirring. The flocculent amorphous precipitate which first formed redissolved, and the dihydropseudocodeine (non-phenolic) immediately separated in crystalline form. After the solution was cooled this base could be filtered off in nearly pure form; a small second fraction (contaminated by a little tetrahydropseudocodeine) could be obtained by extracting the alkaline filtrate with ether. This ethereal solution was evaporated to dryness, digested with sodium hydroxide, and the insoluble portion, crude dihydropseudocodeine, filtered off. The alkaline filtrate, containing some tetrahydropseudocodeine, was added to the original alkaline solution, the further treatment of which is described under tetrahydropseudocodeine. The crude dihydropseudocodeine from ether was purified by crystallization from 60% alcohol or from ethyl acetate; thin rectangular scales or plates of m. p. 121–122° (corr.). After drying at 100° it melted at 155° (corr.); $[\alpha]_D^{28}$ −41.4°, c = 1.59 (alcohol).

Anal. Calcd. for $C_{18}H_{23}O_3N + H_2O$: C, 67.67; H, 7.89; H_2O, 5.64. Found: C, 67.62; H, 7.97; H_2O, 5.74. Sample dried at 100°. Calcd. for $C_{18}H_{23}O_3N$: C, 71.71; H, 7.70. Found: C, 71.67; H, 7.80.

A solution of 0.5 g. of the base in 30 cc. of absolute alcohol was treated with 4 g. of sodium, with occasional addition of more alcohol, over a period of two hours. The base, 0.44 g., was recovered unchanged.

Dihydropseudocodeine Hydrochloride.—Prepared in absolute alcohol with alcoholic hydrogen chloride; it crystallizes from alcohol in thin rectangular scales melting at 239–241° (corr.) with decomp. and red color. In aqueous solution $[\alpha]_D^{28}$ −24°, c = 1.46.

Anal. Calcd. for $C_{18}H_{24}O_3NCl + 0.5H_2O$: H_2O, 2.66. Found: H_2O, 2.60, 2.63.

Anal. (Subs. dried at 155°) Calcd. for $C_{18}H_{24}O_3NCl$: C, 63.86; H, 7.16; Cl, 10.50. Found: C, 63.86; H, 7.05; Cl, 10.45, 10.40.

Dihydropseudocodeine Hydriodide.—Prepared in methyl alcohol and recrystallized from water. It showed the m. p. 287° (corr.) when heated rapidly, 268–269° (corr.), decomposing, when heated slowly. In aqueous solution, $[\alpha]_D^{28}$ −22.5°, c = 1.11.

Anal. (Sample dried at 155°) Calcd. for $C_{18}H_{24}O_3NI$: I, 29.55. Found: I, 29.54.

Dihydropseudocodeine Methiodide.—Prepared from methyl alcohol, crystallizes from water as octahedra melting at 190–195° (corr.) when heated rapidly, at 241–243° (corr.) with decomposition when heated slowly. In water it showed $[\alpha]_D^{28}$ −22.1°, c = 1.23.

Anal. Calcd. for $C_{19}H_{26}O_3NI + H_2O$: H_2O, 4.06. Found: H_2O, 3.68, 3.31.

Anal. (Subs. dried at 155°) Calcd. for $C_{19}H_{26}O_3NI$: I, 28.63. Found: I, 28.33.

Dihydro-ε-methylmorphimethine (Des-N-methyldihydropseudocodeine).—A solution of 12 g. of dihydropseudocodeine methiodide in 200 cc. of 12% sodium hydroxide was boiled for five minutes. The oily methine base was extracted from the cooled mixture with ether, from which it was obtained as an oil, not crystallizable even after purification through its salts. The oil was dissolved in 15 cc. of 25% acetic acid and treated with 6 g. of sodium iodide, yielding 10.3 g. of nearly pure hydriodide (decomp. 202–204°). This salt crystallized from water or alcohol as short hexagonal prisms of m. p. 232–235° (corr.) with decomp., turning red. In water it showed $[\alpha]_D^{28}$ +99.0, +100°, c = 1.66.

Anal. (Subs. dried at 155°) Calcd. for $C_{19}H_{26}O_3NI$: I, 28.63. Found: I, 28.57.

The hydrochloride was prepared from the oily base in acetone by addition of alcoholic hydrogen chloride, and was purified from absolute alcohol or acetone. It crystallized in long rectangular prisms of m. p. 222–224° (corr.) and showed the rotation $[\alpha]_D^{28}$ +123.0°, c = 1.21 (water).

Anal. Calcd. for $C_{19}H_{26}O_3NCl$: C, 64.80; H, 7.44. Found: C, 64.87; H, 7.57.

Tetrahydro-ϵ-methylmorphimethine (Dihydro-des-N-methyldihydropseudocodeine).—A solution of 2.14 g. of dihydro-ϵ-methylmorphimethine in 15 cc. of alcohol was hydrogenated in the presence of palladium–calcium carbonate. In one hour 147 cc. (standard conditions) or 1.0 mole of hydrogen was absorbed. The product obtained after evaporation of the solvent was an oil which yielded 2.25 g. of crystalline hydriodide when dissolved in dilute acetic acid and treated with sodium iodide; the base was not obtained in crystalline form even after purification through its hydriodide. The salt crystallizes from water as bundles of flat prisms, and has the m. p. 225–226° (corr.) with decomp.; in aqueous solution, $[\alpha]_D^{28}$ +17.4, 16.5, 18.6°, c = 1.3 to 1.7.

Anal. (Subs. dried at 155°) Calcd. for $C_{19}H_{28}O_3NI$: I, 28.50. Found: I, 28.28.

The hydrochloride, prepared in acetone with alcoholic hydrogen chloride, crystallized as needles from ethyl acetate or as long rectangular scales from methyl ethyl ketone, alcohol–acetone mixtures or from small volumes of water. It is very soluble in alcohol. It showed the m. p. 187° (corr.) and $[\alpha]_D^{28}$ +18.6, +20°, c = 1.11 (water). Under some conditions the salt apparently forms a trihydrate as well as a hemihydrate. Direct determinations of water were difficult as the salt sublimes slightly.

Anal. Calcd. for $C_{19}H_{28}O_3NCl + 0.5H_2O$: C, 62.69; H, 8.02. Found: C, 62.60, 62.63; H, 7.88, 8.06. Calcd. for $C_{19}H_{28}O_3NCl + 3H_2O$: H_2O, 13.2. Found (at 140°): H_2O, 13.02. Calcd. for $C_{19}H_{28}O_3NCl$: C, 64.43; H, 7.97. Found: C, 64.02; H, 8.16.

The salicylate, which was prepared in ether with ethereal salicylic acid, could be recrystallized from water as thin prismatic needles, melting at 198° (corr.); $[\alpha]_D^{27}$ −18.1°, c = 1.08 (water).

Anal. (Subs. dried at 100°) Calcd. for $C_{19}H_{27}O_3N \cdot C_7H_6O_3$: C, 68.54; H, 7.29. Found: C, 68.40; H, 7.27.

Tetrahydro-ϵ-methylmorphimethine acid tartrate crystallizes from water in thin square twinned scales of m. p. 195.5° (corr.) with frothing. In aqueous solution it shows $[\alpha]_D^{27}$ +27°, c = 1.29.

Anal. (Subs. dried at 100°) Calcd. for $C_{19}H_{27}O_3N \cdot C_4H_6O_6$: C, 59.08; H, 7.10. Found: C, 59.05; H, 7.19.

Tetrahydropseudocodeine.—The sodium hydroxide solution remaining after the separation of dihydropseudocodeine (usually a pink or red color developed) was cooled by adding ice, acidified with concd. hydrochloric acid, and made ammoniacal under ether. After two more ether extractions, the combined ethereal layers, containing all of the tetrahydropseudocodeine, were evaporated to dryness and the oily residue crystallized from 60% alcohol. Tetrahydropseudocodeine is soluble with difficulty in cold alcohol, and separates fairly pure and quite completely. The principal impurity present was a new phenolic dihydropseudocodeine, which could often be isolated in an amount roughly proportional to the difference in hydrogen absorption observed, from that which was calculated on the basis of the dihydropseudocodeine (non-phenolic) and tetrahydropseudocodeine isolated. Those reductions which were carried out in concentrated alcoholic solution yielded tetrahydropseudocodeine samples which, even after numerous crystallizations from alcohol, melted over the range 112–115°, and contained as much as 15% of the new phenolic dihydropseudocodeine. Mixtures of the phenolic dihydro-

pseudocodeine and tetrahydropseudocodeine all melt over approximately the same temperature range. The specific rotation of tetrahydropseudocodeine or its derivatives, containing traces of the above-mentioned impurities was generally 5–7° more positive than the rotation of the corresponding products in a state of purity.

Tetrahydropseudocodeine, freed from unsaturated material through prolonged hydrogenation, was purified by several crystallizations from alcohol, two crystallizations as the hydrochloride, and two more crystallizations as the base. The physical properties agree approximately with those reported by Speyer. It forms rhombic prisms or plates melting over a wide range; it begins to sinter at about 100°, and melts from 115–120° (corr.), even after long drying in vacuum. Frothing occurs above the melting point, apparently with loss of hydrate water. Heated slowly in a vacuum the base sinters to a glass below 100°, and distils easily at 160° (0.2 mm.). The hydrated base crystallizes unchanged from ethyl acetate, but if boiled in this solvent for a short time apparently loses its hydrate water and can be obtained only as an oil; the oil is converted to the crystalline hydrated base by dilute alcohol. For the specific rotation of the hydrated base we find $[\alpha]_D^{25}$ −9.9°, c = 1.08 (alcohol). The crystal form, melting points, rotations, and solubilities of the two phenolic dihydropseudocodeines and most of their salts are very similar to those of tetrahydropseudocodeine and its salts and cannot be used for identification. Tetrahydropseudocodeine gives two characteristic derivatives, a low-melting salicylate (the phenolic dihydropseudocodeine salicylates melt about 70° higher, and a high-melting methine which is soluble with difficulty in alkali and is extracted completely from alkaline solution with ether. Tetrahydropseudocodeine does not give a crystalline acid tartrate.

Tetrahydropseudocodeine hydrochloride melts at 263° (corr.) with darkening and subsequent decomposition. It is weakly dextrorotatory, in aqueous solution $[\alpha]_D^{25}$ +0.25, +1.9°, c = 1.01, 1.33.

Tetrahydropseudocodeine salicylate, prepared in ether with ethereal salicylic acid, crystallizes hydrated from alcohol as hexagonal plates or elongated prisms containing two molecules of water and melting at 135–136°. When the dihydrate is boiled in ethyl acetate solution or dried in a vacuum oven it is changed to a crystalline monohydrate of m. p. 165–166°. The monohydrate goes back to the dihydrate on crystallization from alcohol. The monohydrate shows the specific rotation in alcohol $[\alpha]_D^{24}$ −1.7°, c = 0.58.

Anal. Calcd. for $C_{25}H_{31}O_6N + 2H_2O$: H_2O, 7.54. Found: H_2O, 7.80. Calcd. for $C_{25}H_{31}O_6N + H_2O$: C, 65.32; H, 7.24; H_2O, 3.92. Found: C, 65.49; H, 7.51; H_2O, 3.90.

Tetrahydropseudocodeine methiodide has the specific rotation $[\alpha]_D^{26}$ −0.9°, c = 1.15 (water).

Phenolic Tetrahydro-ϵ-methylmorphimethine (Des-N-methyltetrahydropseudocodeine).—Twelve and eight-tenths grams of tetrahydropseudocodeine methiodide in 120 cc. of water was treated with 100 g. of solid potassium hydroxide and the solution boiled for fifteen minutes. The brown oil which separated solidified to a glass on cooling and was extracted into ether (difficultly soluble) or chloroform. Upon evaporation of the solvent an oily residue remained, which crystallized when dissolved in ethyl acetate and seeded; yield, 7.4 g. of nearly pure base. Purification from ethyl acetate gave prisms of m. p. 196–197° (corr.) with decomposition.[29] In alcohol, $[\alpha]_D^{28}$ +192°, c = 1.09; in chloroform, $[\alpha]_D^{26}$ +156.5°, c = 1.10.

Anal. (Subs. dried at 100°) Calcd. for $C_{19}H_{27}O_3N$: C, 71.88; H, 8.57. Found: C, 71.66; H, 8.48.

[29] Speyer and Krauss, *Ann.*, **432**, 254 (1923), found the m. p. 162–163° and reported the base alkali-soluble.

Solutions of the base in alcohol turn dark orange rapidly. In ethyl acetate or chloroform it is stable for a considerable time. A solution in hydrochloric acid turns deep red on standing for several days; the color is discharged by ammonia but reappears on acidification.

Phenolic tetrahydro-ϵ-methylmorphimethine is precipitated amorphous from its solutions in acids by addition of sodium hydroxide. It redissolves in excess of alkali, but crystallizes immediately from the alkaline solution, even in considerable dilutions. The crystalline precipitate was identified as phenolic tetrahydro-ϵ-methylmorphimethine; the separation is quite complete, for the alkaline filtrate gave no further precipitate with ammonium chloride. If the solution of phenolic tetrahydro-ϵ-methylmorphimethine in acid is diluted to a very large volume before addition of alkali, no precipitation takes place; three extractions of the alkaline solution with ether resulted in recovery of 90–95% of the base. The base in such an extremely dilute alkaline solution is apparently in loose combination with the alkali. It is probably not water-soluble, for addition of ammonium chloride precipitates the crystalline base.

Phenolic tetrahydro-ϵ-methylmorphimethine did not yield a crystalline hydrochloride, acid tartrate nor salicylate. The hydriodide, prepared in water, crystallized from acetone as thin truncated rectangular scales, m. p. 123–124° (corr.). The solid salt is not very stable, and the aqueous solution turns dark rapidly.

Anal. Calcd. for $C_{19}H_{23}O_3NI + 0.5H_2O$: H_2O, 2.02. Found: H_2O, 1.98. Calcd. for $C_{19}H_{23}O_3NI$: I, 28.50. Found: (sample dried at 110°) I, 28.50.

Hydrogenation of Phenolic Tetrahydro-ϵ-methylmorphimethine.—A solution of 1.0 g. of the base in 25 cc. of alcohol with 0.1 g. of palladium–calcium carbonate catalyst absorbed 70 cc. (stand. cond.) of hydrogen, or one mole, in one hour. The residue obtained after filtering and evaporating off the solvent was crystallized from ethyl acetate, and yielded 0.75 g. of hexahydro-ϵ-methylmorphimethine which was identified by mixed melting point and by comparison of the hydrochloride and hydriodide with known samples.

Normal Hydrogenation of ϵ-Methylmorphimethine: Tetrahydro-ϵ-methylmorphimethine (Non-phenolic).—The ϵ-methylmorphimethine for these experiments was prepared by the method of Knorr[30] and was used in the form of an oil, since it did not crystallize even after purification through the crystalline hydrochloride. In our first preparations of ϵ-methylmorphimethine hydrochloride we obtained the low-melting hydrated salt described by Knorr as melting at 150° and having the specific rotation $[\alpha]_D^{15}$ −154°. We observed as constants m. p. 149–150° and $[\alpha]_D$ −151°. When the hydrochloride was prepared in absolute alcohol with alcoholic hydrogen chloride, an anhydrous form was obtained, which melted at 211–212° (corr.) and showed in water $[\alpha]_D^{22}$ −154.5°, c = 1.19. An examination of the hydrated samples previously prepared showed that they had also become anhydrous. After the anhydrous form appeared we were no longer able to prepare the hydrated hydrochloride.

Anal. Calcd. for $C_{19}H_{23}O_3N \cdot HCl$: C, 65.20; H, 6.92. Found: C, 65.10; H, 6.98.

Two grams of ϵ-methylmorphimethine hydrochloride in 10 cc. of glacial acetic acid was shaken under hydrogen in the presence of 0.15 g. of platinum oxide. In one-half hour the reduction was complete, with an absorption of 363 cc. (standard) of hydrogen, or 2.72 moles (corrected for the catalyst). The solution was filtered, made alkaline with ammonia and extracted with ether, which yielded a mass of needle crystals on evaporation. Crystallization from ethyl acetate gave 0.8 g. of the sparingly soluble hexahydro-ϵ-methylmorphimethine of m. p. 161–163° (identification by mixed melting point and specific rotation). The ethyl acetate mother liquors, on evaporation, gave an oily base

[30] Knorr, Butler and Hörlein, *Ann.*, **368**, 305 (1909).

which was dissolved in acetone and converted to the crystalline hydrochloride by addition of alcoholic hydrogen chloride. A yield of 0.65 g. of tetrahydro-ϵ-methylmorphimethine hydrochloride was obtained. This was identified by its melting point, specific rotation $[\alpha]_D^{25}$ +19°, c = 1.14 (water), and by conversion through the oily base to the two characteristic salts—salicylate and acid tartrate. These salts were checked by melting point, rotation and mixed melting points with the corresponding salts of tetrahydro-ϵ-methylmorphimethine prepared via dihydropseudocodeine.

Two grams of ϵ-methylmorphimethine hydrochloride in 10 cc. of water containing 0.2 cc. of concd. hydrochloric acid and 0.1 g. of platinum oxide absorbed 344 cc. or 2.52 moles (corr. for catalyst) and yielded 0.7 g. of hexahydro-ϵ-methylmorphimethine and 0.87 g. of tetrahydro-ϵ-methylmorphimethine hydrochloride.

Two grams of ϵ-methylmorphimethine hydrochloride in water with palladium on barium sulfate gave 0.55 g. of tetrahydro-ϵ-methylmorphimethine hydrochloride. With platinum, under these conditions, the hexahydro derivative was practically the sole product.

A reduction of ϵ-methylmorphimethine base in alcohol with palladium–calcium carbonate gave chiefly hexahydro-ϵ-methylmorphimethine, and a small amount of oil which yielded an unidentified hydrochloride of specific rotation $[\alpha]_D^{29}$ +94°, c = 1.33 (water).

Hexahydro-ϵ-methylmorphimethine.—This base, prepared and purified as described in the above reductions, crystallized from ethyl acetate as fine hairs or granular prisms, depending upon the rate of cooling. It melts at 166.5–167.5° and has the specific rotation $[\alpha]_D^{28}$ +28°, c = 1.08 (alcohol).[31]

Anal. Calcd. for $C_{19}H_{29}O_3N$: C, 71.43; H, 9.14. Found: C, 71.22; H, 9.12.

In the solid state, or when freshly precipitated, the base dissolves very reluctantly in alkali. When a moderately dilute acid solution of the base is made alkaline (NaOH) an amorphous precipitate appears and redissolves; in a short time the base crystallizes from the alkaline solution. The filtrate still contains a small amount of the sodium salt, from which ammonium chloride precipitates the base. Extremely dilute solutions of the base in sodium hydroxide remain clear, but two extractions with ether remove practically all of the alkaloid.

The hydrochloride of hexahydro-ϵ-methylmorphimethine was prepared in acetone with alcoholic hydrogen chloride, and crystallizes as plates from absolute alcohol. It melts at 250–254° (corr.) with decomposition[32] and shows $[\alpha]_D^{28}$ +8.1°, c = 1.53 (water).

Anal. Calcd. for $C_{19}H_{30}O_3NCl$: Cl, 10.08. Found: (dried at 155°) Cl, 10.06.

The acid tartrate was prepared by dissolving the calculated amounts of hexahydro-ϵ-methylmorphimethine and *d*-tartaric acid in methanol, adding methyl ethyl ketone, boiling off a portion of the solvent and seeding. After long standing the salt crystallized very slowly; it is exceedingly soluble in cold alcohol or water. It melts at 114–115° (corr.) with frothing, and shows $[\alpha]_D^{27}$ +15.6°, c = 1.16 (water).

Anal. Calcd. for $C_{23}H_{35}O_9N + H_2O$: H_2O, 3.69. Found: H_2O, 3.69. Calcd. for $C_{23}H_{35}O_9N$: C, 58.81; H, 7.52. Found: (dried at 100°) C, 58.74; H, 7.54.

Summary

1. The catalytic hydrogenation of morphine derivatives of the pseudocodeine type, which usually proceeds with addition of two molecules of hydrogen and results in phenolic products, can be greatly influenced by

[31] Speyer and Koulen, *Ann.*, **438**, 55 (1924), found m. p. 155° and could detect no rotation.

[32] Speyer and Koulen give the m. p. 213°.

solvent, nature of catalyst, and especially by hydrogen-ion concentration. Pseudocodeine can thus be reduced in excellent yield to a new non-phenolic dihydropseudocodeine.

2. The degradation of dihydropseudocodeine to dihydro-ϵ-methylmorphimethine, and conversion of the latter to tetrahydro-ϵ-methylmorphimethine is described. The preparation of tetrahydro-ϵ-methyl-morphimethine through extension of the special hydrogenation method to ϵ-methylmorphimethine has been accomplished.

3. The degradation product from tetrahydropseudocodeine is correctly described and its relationship to hexahydro-ϵ-methylmorphimethine established.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF THE HEMOCYANIN OF OCTOPUS VULGARIS

BY THE SVEDBERG AND INGA-BRITTA ERIKSSON

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In three previous papers[1,2,3] reports have been given of the determination of the molecular weights and the sedimentation constants of hemocyanin from *Helix pomatia* and *Limulus polyphemus* by means of the ultracentrifugal methods developed in this Laboratory. Both of these hemocyanins (called *h*-hemocyanin and *l*-hemocyanin) differ markedly from all other proteins by having molecular weights of the order of millions. It seemed desirable to extend this study to other members of the hemocyanin group. The chemical and physico-chemical properties of the hemocyanin of *Octopus vulgaris* (*o*-hemocyanin) are well known, the protein having been the object of a great number of investigations.[4] The blood of octopus is comparatively easy to obtain in sufficient quantities and the protein is very stable. It was therefore chosen as a proper object for a detailed ultracentrifugal investigation.

Material.—The *o*-hemocyanin was prepared by one of us (T. S.) during a stay at the Stazione Zoologica of Naples, Italy.[5] To 50 cc. of octopus blood drawn in the manner described by Henze[6] was added 50 cc. of

[1] Svedberg and Chirnoaga, THIS JOURNAL, **50**, 1399 (1928).

[2] Svedberg and Heyroth, *ibid.*, **51**, 539 (1929).

[3] Svedberg and Heyroth, *ibid.*, **51**, 550 (1929).

[4] *E. g.*, Dhéré, Thèse, Fribourg, 1909; Dhéré, *J. physiol. path. gén.*, 1915–1922; Quagliariello, in Wintersteins "Handb. d. vergl. Physiolog.," Jena, 1922; Schmitz, *Z. physiol. Chem.*, **194**, 232 (1931); **196**, 71 (1931).

[5] For the interest and help shown him on this occasion by the director of the Station, Prof. R. Dohrn, and by Prof. L. Califano, sincere thanks are expressed.

[6] Henze, *Z. physiol. Chem.*, **33**, 370 (1901).

saturated ammonium sulfate solution and some toluene as a preservative. After standing for a week in the refrigerator at 0°, the precipitate was centrifuged off and bottled up with some toluene. Examined in the microscope it proved to be crystalline. It was brought to Upsala in this state. Here it was washed two times on the centrifuge with one-half saturated ammonium sulfate solution. A part of the precipitate was dissolved in water and then dialyzed against distilled water for a week. The hemocyanin which had completely precipitated in the collodion bag was divided into two parts; one was dissolved in phosphate buffer 0.005 *M* in Na_2HPO_4 and 0.005 *M* in KH_2PO_4 (P_H 6.8), the other in 0.07 *M* sodium acetate. Another part of the ammonium sulfate precipitate (crystals) was dissolved in 0.01 *M* Na_2HPO_4 and dialyzed against the same solvent for a week (P_H approx. 8.0). A further portion of 50 cc. of octopus blood was precipitated with ammonium sulfate and a trace of acetic acid according to the method given by Henze.[6] This material, however, deteriorated with time and therefore was not used in the present work. For the sake of comparison with the crystallized *o*-hemocyanin, a quantity of octopus blood (75 cc.) to which some toluene had been added was also taken to Upsala for investigation.

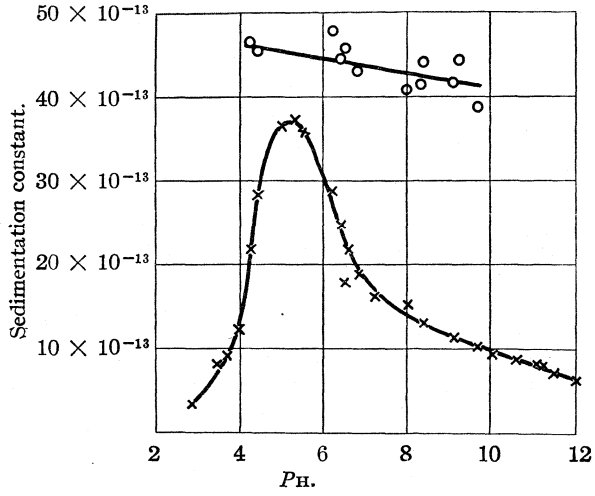


Fig. 1.

The partial specific volume was measured pycnometrically at 20° in the concentration range 1.3–3.2% and the P_H range 6.8–8.4. No systematic drift with concentration or P_H was observed. From five determinations the mean value 0.740 resulted. This is almost identical with the values 0.738 and 0.735 previously found for *h*-hemocyanin and *l*-hemocyanin,[1,2] respectively.

Sedimentation Constant and P_H Stability Region.—The velocity of sedimentation of the crystallized *o*-hemocyanin was measured in the P_H range 2.9 to 12.0. In order to secure as accurate P_H values as possible most of the determinations were carried out in the following way. Samples

TABLE I

CRYSTALLIZED HEMOCYANIN FROM OCTOPUS BLOOD, SEDIMENTATION VELOCITY MEASUREMENTS

Concn. of protein 0.4–0.8%; centr. force about 100,000 times gravity; thickness of col. of soln., 1.2 cm.; source of light, mercury lamp; light filter, nickel oxide glass; aperture of lens, F:50; plates, Imperial process; time of exp., 15 sec.; methol hydroquinone developer, 1 min.

Solvent	Total molar	P_H history of soln.	$s_{20} \times 10^{13}$ A	B
HAc	0.2	6.8→8.4→ 2.9	..	3.5
HAc, NaAc	.2	6.8→8.4→ 3.5	..	8.3
HAc, NaAc	.176	6.8→ 3.7	..	9.3
HAc, NaAc	.2	6.8→8.4→ 4.0	..	12.5
HAc, NaAc (1% in NaCl)	.02	6.8→ 4.3	46.7	21.6
HAc, NaAc (1% in NaCl)	.02	6.8→ 4.4	45.4	28.5
HAc, NaAc	.2	6.8→ 4.7	Soly. too low for detn.	
HAc, NaAc	.2	6.8→ 5.0	..	40.4
HAc, NaAc	.2	6.8→8.4→ 5.0	..	32.8
Na_2HPO_4, KH_2PO_4	.2	6.8→8.4→ 5.3	..	37.4
Na_2HPO_4, KH_2PO_4	.2	8.1→ 5.7	..	35.9
Na_2HPO_4, KH_2PO_4	.2	6.8→ 6.2	..	33.4
Na_2HPO_4, KH_2PO_4	.2	8.1→ 6.2	..	24.8
Na_2HPO_4, KH_2PO_4	.2	6.8→ 6.2	47.8	28.6
Na_2HPO_4, KH_2PO_4	.2	6.8→8.4→ 6.4	44.7	24.7
Na_2HPO_4, KH_2PO_4	.2	6.8→ 6.5	45.1	17.8
Na_2HPO_4, KH_2PO_4	.2	8.1→ 6.6	..	21.6
Na_2HPO_4, KH_2PO_4	.2	6.8	43.1	17.2
Na_2HPO_4, KH_2PO_4	.2	6.8	..	17.9
Na_2HPO_4, KH_2PO_4	.2	6.8	..	20.5
Na_2HPO_4, KH_2PO_4	.2	8.1→ 7.3	..	17.8
Na_2HPO_4, KH_2PO_4	.2	6.8→8.4→ 7.3	..	15.8
Na_2HPO_4, KH_2PO_4	.2	6.8→ 7.3	..	15.6
Na_2HPO_4, KH_2PO_4	.2	6.8→ 8.0	42.3	14.8
Na_2HPO_4, KH_2PO_4	.2	6.8→ 8.0	39.4	15.8
Na_2HPO_4	.2	6.8→ 8.3	41.2	..
Na_2HPO_4	.2	6.8→ 8.4	43.1	13.2
Na_2HPO_4	.2	8.4	45.2	..
Na_2HPO_4, NaOH	.2	6.8→8.4→ 9.1	41.9	11.5
Na_2HPO_4, NaOH	.2	6.8→ 9.2	44.4	..
Na_2HPO_4, NaOH	.2	6.8→8.4→ 9.7	37.8	10.2
Na_2HPO_4, NaOH	.2	6.8→ 9.7	40.3	..
Na_2HPO_4, NaOH	.2	6.8→8.4→10.0	..	9.5
Na_2HPO_4, NaOH	.2	6.8→10.6	..	8.9
Na_2HPO_4, NaOH	.2	6.8→8.4→11.1	..	8.4
Na_2HPO_4, NaOH	.2	6.8→8.4→11.2	..	8.1
Na_2HPO_4, NaOH	.2	6.8→8.4→11.5	..	7.2
Na_2HPO_4, NaOH	.2	6.8→8.4→12.0	..	6.3

of the hemocyanin solution about 0.5% in protein were dialyzed (in the cold) against the proper buffer solutions and the P_H measured in the buffer after equilibrium with the protein had been reached. In Table I and Fig. 1 the measurements are summarized.[7]

Another series of determinations of sedimentation velocity was carried out on octopus blood in the P_H range 2.8 to 11.1. The sedimentation constants are summarized in Table II and Fig. 2.

TABLE II

OCTOPUS BLOOD, SEDIMENTATION VELOCITY MEASUREMENTS IN BUFFER SOLUTIONS

Experimental conditions as in Table I

Solvent	Total molar	P_H of soln.	$s_{20} \times 10^{13}$ A	B
HAc	0.2	2.8	..	5.3
HAc, NaAc	.2	3.5	..	9.9
HAc, NaAc	.2	4.0	..	12.9
HAc, NaAc	.2	4.2	..	14.3
HAc, NaAc	.2	4.5	..	21.5
HAc, NaAc	.2	5.0	..	30.7
HAc, NaAc	.2	5.2	50.2	26.8
Na_2HPO_4, KH_2PO_4	.2	5.3	47.6	31.7
Na_2HPO_4, KH_2PO_4	.2	5.5	48.0	30.4
Na_2HPO_4, KH_2PO_4	.2	5.7	..	33.1
Na_2HPO_4, KH_2PO_4	.2	5.7	47.6	21.6
Na_2HPO_4, KH_2PO_4	.2	6.2	44.2	..
Na_2HPO_4, KH_2PO_4	.2	6.2	47.5	..
Na_2HPO_4, KH_2PO_4	.2	6.2	44.9	..
Na_2HPO_4, KH_2PO_4	.2	6.8	43.6	..
Na_2HPO_4, KH_2PO_4	.2	7.1	42.0	17.5
Na_2HPO_4, KH_2PO_4	.2	7.2	40.7	15.8
Na_2HPO_4, KH_2PO_4	.2	7.4	40.5	20.3
Na_2HPO_4, KH_2PO_4	.2	8.0	44.1	..
Na_2HPO_4	.2	8.4	44.9	..
Na_2HPO_4, NaOH	.2	8.7	45.1	9.3
Na_2HPO_4, NaOH	.2	9.1	45.3	..
Na_2HPO_4, NaOH	.2	10.2	..	9.9
Na_2HPO_4, NaOH	.2	11.1	..	9.2

A third series of measurements of the sedimentation velocity was made on untreated octopus blood at different protein concentrations, using 1% sodium chloride as diluting agent. The determinations are given in Table III and in Fig. 3. The mean of the six last determinations (1.0–0.5%) is also represented by a point in the diagram Fig. 2 (at P_H 7.9).

The values given in Tables I, II and III and in Figs. 1 and 2 show that solutions of *o*-hemocyanin contain two components. The sedimentation constant of one of them, A, is practically independent of P_H within the range 4.3–9.7 and has a mean value of 43.2×10^{-13}. The sedimentation

[7] In cases where more than one determination was carried out at the same P_H the mean value has been used for the diagram.

constant of the other component, B, varies strongly with P_H. The ratio of the two components changes with P_H in a very peculiar way.[8] There is

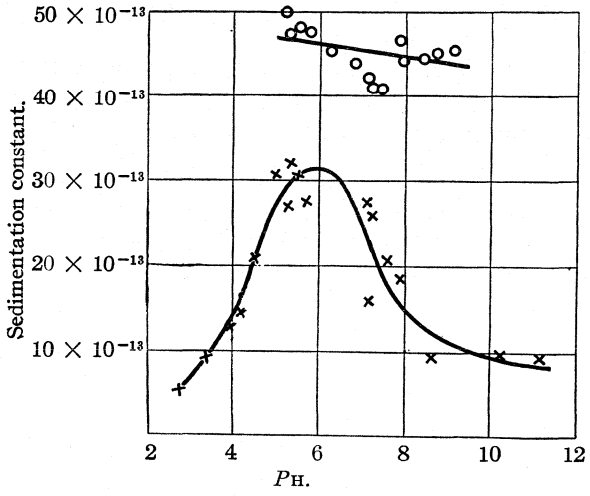


Fig. 2.

one acid region, P_H 4.3–4.5, and one alkaline region, P_H 7.9–9.7, where the component A predominates and a middle region, P_H 5.0–7.2, where com-

TABLE III

OCTOPUS BLOOD, SEDIMENTATION VELOCITY MEASUREMENTS AT DIFFERENT DILUTIONS

Experimental conditions as in Tables I and II

State of the blood	P_H of soln.	Concn. of protein	$s_{20} \times 10^{13}$ A	B
Oxygenated, undiluted	...	10.0	11.7	..
Oxygenated, diluted 1% NaCl	...	7.0	18.4	..
Oxygenated, diluted 1% NaCl	...	4.0	30.4	..
Oxygenated, diluted 1% NaCl	...	2.0	40.7	..
Oxygenated, diluted 1% NaCl	...	1.5	44.2	..
Oxygenated, diluted 1% NaCl	...	1.0	48.1	..
Oxygenated, diluted 1% NaCl	7.9	0.7	47.3	18.6
Oxygenated, diluted 1% NaCl	7.9	0.5	45.8	..
Reduced by bact., dil. 1% NaCl	7.9	0.7	44.5	..
Reduced by evac. and H_2, dil. 1% NaCl	7.9	0.7	49.7	..
Reduced by evac. and N_2, dil. 1% NaCl	7.9	0.7	49.5	..

[8] Percentage values were calculated from the microphotometric records on the assumption that the light absorptions of the two components are identical at the wave length used (366 mμ). A comparison of two solutions of the same protein concentration, one of them containing practically only component A and the other practically only component B, showed that the light absorption of B is somewhat higher than that of A. There seems to be some other factor except the P_H which also influences the ratio between the components, occasionally giving rise to irregular results. We have not been able to locate this factor and therefore refrain from giving numerical values of the ratio A:B.

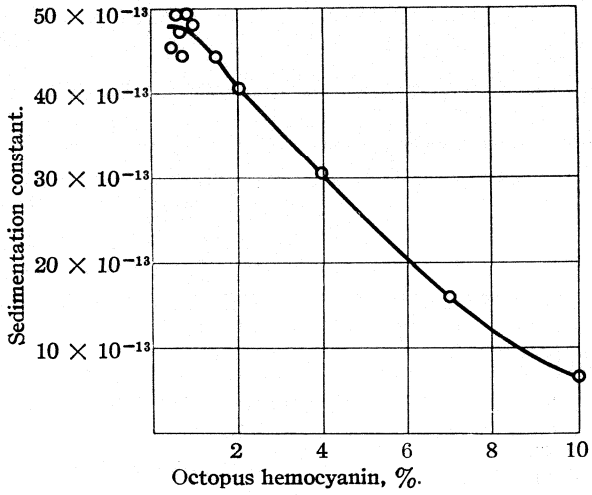


Fig. 3.

ponent A is fairly abundant. In the two regions P_H 4.5–5.0 and 7.2–7.9 the concentration of A is practically zero. The two components A and B are not two different proteins but represent two different kinds of aggregation in equilibrium. Only component A which has a sedimentation constant (and accordingly a molecular weight) practically independent of P_H over a certain P_H range should be termed a distinct molecular species like *h*-hemocyanin and *l*-hemocyanin. The change from A to B and from B to A is reversible. This fact is borne out by the following determinations. A solution at P_H 6.8 containing only about 5% of the high molecular component was brought to P_H 8.4 and showed there a content of 73%. When the P_H was lowered to 7.3, the high molecular component disappeared completely. To illustrate the striking change in constitution of the *o*-hemocyanin brought about by a shift in the P_H, the sedimentation pictures of runs at 6.5, 7.3 and 8.0 are given in Fig. 4. At P_H 6.5 (Fig. 4, A)

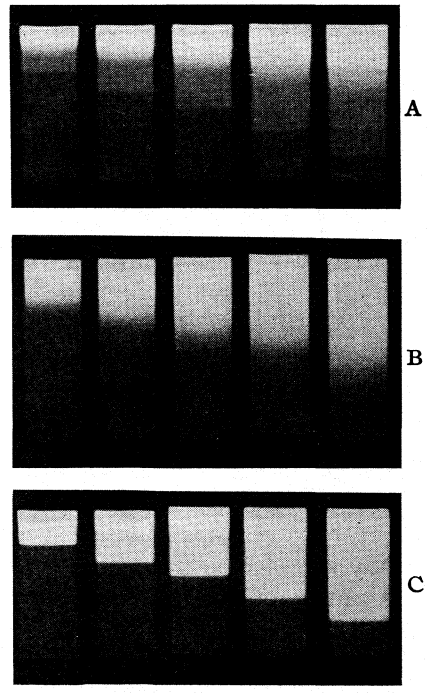


Fig. 4.

the sedimentation boundaries of the two components moving with different velocities are clearly seen, while at P_H 7.3 (Fig. 4, B) only one boundary corresponding to the movement of the low molecular component is visible. At P_H 8.0 the high molecular component predominates and the picture shows—in reproduction—only that boundary (Fig. 4, C). Owing to the slower diffusion and probably also to a higher degree of homogeneity the boundary of the high molecular component is much sharper than that of the low molecular component. The centrifugal field was about the same in the three runs, *viz.*, a little over 100,000 times gravity, but the time between the exposures was ten minutes in Expt. B against only five minutes in Expts. A and C so as to allow the low molecular component to sediment sufficiently. The curves giving the relation between distance from meniscus and relative concentration for the three runs are reproduced in Fig. 5, A, B, C. A small amount of the low molecular component is present in the third run, as borne out by the microphotometric curves in Fig. 5, C although not visible in the reproduction Fig. 4, C.

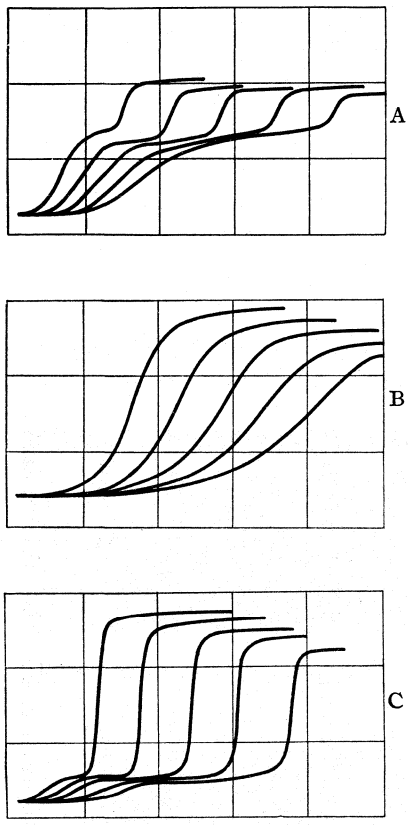


Fig. 5.

In order to find out whether the ratio of the two components depends on the total protein concentration runs were made with solutions of crystallized *o*-hemocyanin containing 1, 2 and 3% at P_H 6.8 where component B predominates. One would expect the formation of component A which has the higher sedimentation constant (and the higher molecular weight) to be favored by an increase in the total protein concentration. No such effect, however, was noticed the concentration of component A being practically zero also in these concentrated solutions.

An attempt was also made to study the influence of high dilution upon the ratio of the two components by using chlorine and bromine filters when taking the sedimentation pictures. Owing to the presence of some low-molecular substance of high light-absorbing power in the short ultraviolet, however, this experiment failed.

The rapid fall of the sedimentation velocity with increasing protein concentration is demonstrated by Fig. 3. Determinations of the change of viscosity with concentration showed that the phenomenon is not merely a viscosity effect but is largely due to an interaction between the protein molecules similar to the effect already observed in solutions of *h*-hemocyanin.[1]

As shown by the diagrams in Figs. 1 and 2 the sedimentation velocity values found for diluted octopus blood agree well with those found for dilute solutions of crystallized *o*-hemocyanin. The maximum of the curve for component B is shifted slightly in the alkaline direction and is not quite so high as for the crystallized product. The mean value of the sedimentation constant of all the determinations on diluted blood (1.0–0.4%) for component A is 45.8×10^{-13} against 43.2×10^{-13} for the same component in the solutions of the crystallized product, which is probably within the limits of experimental error. The *o*-hemocyanin therefore exists in the blood with the same molecular weight as in the purified product. From the data of Table III it follows that the sedimentation and, accordingly, the molecular weight is the same in the oxygenated and the reduced state.

The peculiar behavior of the *o*-hemocyanin with regard to its dependence on P_H is without any parallel in the other proteins so far investigated by means of the ultracentrifugal technique. The phenomenon seems at first sight very difficult to explain but may perhaps be correlated with some interesting facts found by Roche[9,10] when studying the titration curves of the hemocyanins. The hemocyanin from helix[10] gave a curve with one inflection point at a P_H corresponding to that of the isoelectric point 5.2. The hemocyanin from octopus,[9] however, gave a titration curve with three inflection points, one at P_H 4.8, the isoelectric point, one at 6.3 and one at 7.5. The first and third inflection points are characterized by great change in P_H when the amount of acid or alkali present is but slightly changed. The affinity of the *o*-hemocyanin to an acid or a base is low at these points. Now these two minima of reactivity found by Roche correspond very nearly with the two regions where the concentration of component A is practically zero. It does not seem unlikely that the power of forming the huge molecules of this component is lost when the protein has become electrochemically saturated.

Molecular Weight and Molecular Symmetry.—Four sedimentation equilibrium runs, one on crystallized *o*-hemocyanin and three on diluted octopus blood, were carried out at a P_H of 8.4 where the solution consists almost entirely of component A. In Table IV the results are given.

From the mean of all the sedimentation constant measurements in dilute solutions, 44.7×10^{-13}, and the mean molecular weight, 2,050,000, we get for the molar frictional constant $f = M(1 - V\rho)/s$ the value $11.9 \times$

[9] Roche, *Arch. de physique biol.*, **7**, 207 (1930).

[10] Roche, *Compt. rend. de sc. de la soc. de biol. de Lyon*, **107**, 1145 (1931).

TABLE IV

OCTOPUS HEMOCYANIN, SEDIMENTATION EQUILIBRIUM MEASUREMENTS

Solvent, 0.15–0.20 M Na_2HPO_4; P_H of soln., 8.4; concn. of protein, 0.5% at start

Nature of soln.	Mean speed	Mol. wt.
Cryst. *o*-hemocyanin	1600	1,700,000
Diluted octopus blood	1500	2,000,000
Diluted octopus blood	1530	2,200,000
Diluted octopus blood	1530	2,300,000
		Mean 2,050,000

10^{16}. A spherical molecule of the same specific volume would have a frictional constant $f_s = 6\pi\eta Nr$ equal to 9.6×10^{16}, where η is the viscosity, N the Avogadro constant and r the radius which is expressed by $(3MV/4\pi N)^{1/3}$. The *o*-hemocyanin molecule therefore deviates markedly from the spherical shape (dissymmetry number $f/f_s = 1.24$).

The expenses connected with this investigation have been defrayed by grants from the Nobel Fund of Chemistry, from the Rockefeller Foundation and from the Foundation "Therese och Johan Anderssons Minne."

Summary

1. The sedimentation constant, the P_H stability range and the molecular weight of octopus hemocyanin (called *o*-hemocyanin) have been determined by means of the ultracentrifugal methods.

2. Within the range P_H 4.3–9.7 solutions of crystallized *o*-hemocyanin contain two components, one of high molecular weight, A, and one of lower molecular weight, B. The sedimentation constant of A is almost independent of P_H and has a mean value of 43.2×10^{-13}, that of B varies strongly with P_H, showing a maximum at about P_H 5.2. Component A predominates in the regions P_H 4.3–4.5 and 7.9–9.7; it is less abundant in the region P_H 5.0–7.2 and has a very low concentration in the regions P_H 4.5–5.0 and 7.2–7.9. The change from one component to the other is reversible. On the acid side of P_H 4.3 and on the alkaline side of P_H 9.7 only component B exists.

3. A similar series of determinations on octopus blood gave analogous results. The mean value 45.8×10^{-13} was obtained for the sedimentation constant of component A.

4. Only component A, the sedimentation constant of which is independent of P_H, should be termed a molecular species like *Helix* hemocyanin and *Limulus* hemocyanin. From sedimentation equilibrium measurements a molecular weight of about 2,000,000 was derived.

5. The molecule of *o*-hemocyanin (component A) is not spherical in shape. The dissymmetry number is 1.24.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

A CONDENSATION OF ACETOPHENONE WITH ISATIN BY THE KNOEVENAGEL METHOD[1]

BY H. G. LINDWALL AND J. S. MACLENNAN

RECEIVED JULY 9, 1932 PUBLISHED DECEMBER 13, 1932

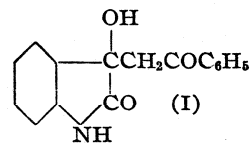
The Pfitzinger[2] method of synthesis of substituted cinchoninic acids, like cinchophen, from isatin and methyl ketones with concentrated potash, serves as a convenient reaction when no alkali-sensitive groups are present. The desirability of a more gentle method suggested the Knoevenagel[3] catalysts in place of the alkali.

When an alcoholic solution of isatin and acetophenone containing a small quantity of diethylamine is allowed to stand overnight a copious yield of a product (I) is obtained. The product is not cinchophen but is, according to its empirical formula, an addition product

$$\underset{\text{Isatin}}{C_8H_5O_2N} + \underset{\text{Acetophenone}}{C_8H_8O} = \underset{\text{(I)}}{C_{16}H_{13}O_3N}$$

The same product (I) is obtained by the use of piperidine or low concentrations of potash. Furthermore, repetition of the procedure described in German Patent 301,591, using cold dilute ammonia, yields (I) ($C_{16}H_{13}O_3N$) again, proving it to be identical with the product described in that patent.[4]

The product is evidently the result of interaction of the beta carbonyl of isatin with the methyl group of acetophenone and its structure is 3-hydroxy-3-phenacyloxindole (I). This structure is postulated on the basis of the following facts. (1) Linkage of acetophenone to the nitrogen of isatin is not a possibility since N-methylisatin also condenses, like isatin, to yield a product with similar chemical properties. (2) Linkage to the alpha carbonyl is decidedly unusual in isatin condensations. Furthermore, isatin-β-anil and isatin-β-bispiperidyl give no product with these catalysts and methods, indicating that the α-carbonyl is not involved in this type of condensation. (3) The chemical properties of the compound favor the structure shown above.



(I)

It has proved difficult to obtain a sharp melting point for (I). Heating the compound at its approximate melting point resulted in its decomposition to isatin and acetophenone, through a reversal of the aldol-like condensation. This behavior is similar to that noted by Kohler and Corson[5]

[1] Abstract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University.

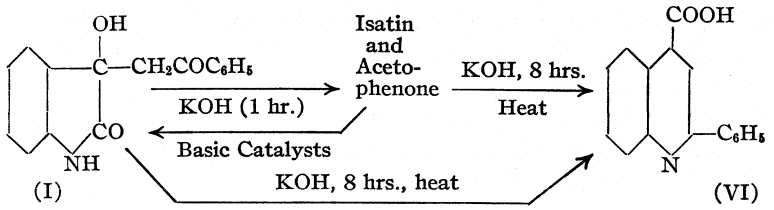
[2] Pfitzinger, *J. prakt. Chem.*, **33**, 100 (1886); **38**, 583 (1888); **56**, 283 (1897).

[3] Knoevenagel, *Ann.*, **281**, 25 (1894); *Ann.*, **288**, 321 (1895); *Ber.*, **31**, 2585, 2596 (1898); *ibid.*, **37**, 4464 (1904).

[4] *Chem. Zentr.*, I, 148 (1918).

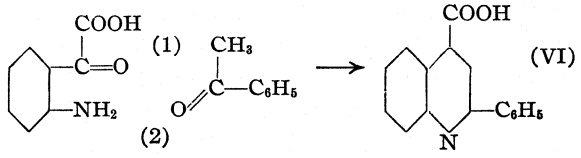
[5] Kohler and Corson, THIS JOURNAL, **45**, 1975 (1923).

for their condensation product of methyl benzoyl formate and methyl cyanoacetate. This same decomposition was noted when the product (I) was treated with potash solution with a short period of warming. Using potash under the more strenuous Pfitzinger conditions resulted in the formation of cinchophen—not, apparently, through any rearrangement of (I), but rather through its decomposition into isatin and acetophenone followed by condensation of these two, after ring opening of the isatin.

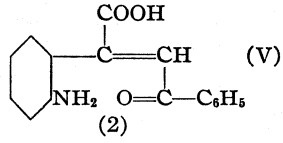


Treatment of the 3-hydroxy-3-phenacyloxindole with acid resulted in its dehydration to yield 3-phenacylideneoxindole (II).

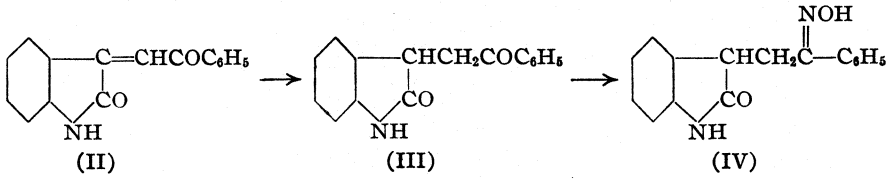
The Pfitzinger reaction for the formation of cinchophen (VI) is ordinarily conceived to take place in the following fashion



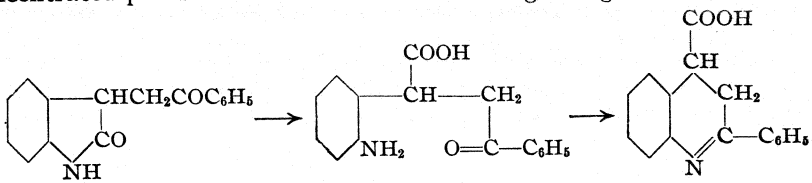
If condensation occurs first at position (1) to yield (V) as an intermediate



it might be assumed that compound (II) would, upon ring opening by hydrolysis with potash also yield (V) and subsequently, through reaction of the groups at (2), yield cinchophen. This assumption is contrary to the experimental result. No cinchophen could be isolated from the hydrolysis reaction mixture. It is possible that (V) is a "trans" isomer and will not form the quinoline derivative for this reason. This point has not yet been investigated.



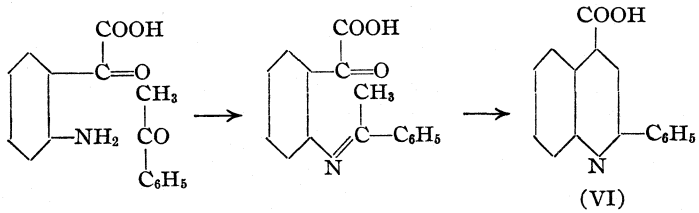
3-Phenacylideneoxindole (II) upon reduction yielded 3-phenacyloxindole (III). Again in this case it might be assumed that treatment with concentrated potash would lead to the following changes



(III)

Compound (III) proved surprisingly stable, being returned unchanged from the concentrated potash solution after several hours of heating. Oxime (IV) formation attested to the ketone structure of (III).

Compound (II) cannot, therefore, be an intermediate in the course of the Pfitzinger synthesis of substituted cinchoninic acids. It would seem probable that the Pfitzinger reaction proceeds through reaction *first* of the ketone carbonyl with the amino group of the *o*-aminobenzoylformic acid.



(VI)

In the case of the products (described in the Experimental Part) formed through the interaction of isatin or N-methylisatin with acetophenone or para-(Br, Cl, CH_3, OCH_3)-substituted acetophenones, the reactions and general properties are completely analogous to those described above.

Experimental Part

3-Hydroxy-3-phenacyloxindole (I) and Derivatives

(A) By the Action of Diethylamine.—Five grams of isatin and an equimolecular amount of acetophenone were dissolved in 100 cc. of absolute alcohol and diethylamine (10 drops) was added. The mixture was allowed to stand overnight at room temperature. The yellow needles which formed were separated by filtration and were recrystallized from alcohol. This procedure was also followed in the reactions of N-methylisatin with acetophenone and of isatin with para-(methoxy, chloro, bromo)-acetophenones (Table I). Piperidine may be substituted for diethylamine, giving comparable yields.

(B) By the Action of Other Catalysts.—Variations of Method "A" were tried in the condensation of isatin and acetophenone, substituting other catalysts for diethylamine. *Ammonia* gave a slightly improved yield of product (72%). The reaction was carried out at room temperature, using 2 cc. of concentrated ammonium hydroxide in 15 cc. of 33% ethyl alcohol per gram of isatin. *Potassium hydroxide* was tried in various amounts. The concentration for the optimum yield (85%) was found to be 15 cc. of 60% ethyl alcohol, containing 0.16% of potash, per gram of isatin.

Decomposition of 3-Hydroxy-3-phenacyloxindole (I) into Isatin and Acetophenone

(A) **By Heat.**—A 2-g. sample of (I) was heated slowly in a bath of sulfuric acid until the melting range of the material was reached. Evident decomposition resulted with a marked odor of acetophenone. Fractional crystallization of the residue yielded a small quantity (0.2 g.) of isatin.

(B) **By the Action of Potash.**—One gram of (I) was dissolved in 10 cc. of 95% ethyl alcohol, and to this was added 10 cc. of 10% alcoholic potash. The mixture was heated on a steam-bath for one hour. Isatin (0.3 g.) was isolated from the reaction mixture.

TABLE I

Products by method "A"	Formula	Yield, %	Corr. m. p., °C.	Analyses	Calcd.	Found	
3-Hydroxy-3-phenacyl-oxindole	$C_{16}H_{13}O_3N$	63	169–172 dec.	C,	71.92	72.33	72.44
				H,	4.87	4.81	4.93
				N,	5.20	5.05	
3-Hydroxy-1-methyl-3-phenacyloxindole	$C_{17}H_{15}O_3N$	72	168–170 dec.	C,	72.6	73.0	
				H,	5.34	5.40	
3-Hydroxy-3(4′-chlorophenacyl)-oxindole	$C_{16}H_{12}O_3NCl$	87	175–176	Cl,	11.82	11.79	
3-Hydroxy-3(4′-bromophenacyl)-oxindole	$C_{16}H_{12}O_3NBr$	87	178–181	Br,	23.09	23.05	
3-Hydroxy-3(4′-methylphenacyl)-oxindole	$C_{17}H_{15}O_3N$	85	185–186	N,	4.98	4.90	
3-Hydroxy-3-(4′-methoxyphenacyl)-oxindole	$C_{17}H_{15}O_4N$	86	186–187	N,	4.71	4.67	

Cinchophen (2-Phenylquinoline-4-acid) from 3-Hydroxy-3-phenacyloxindole (I).—A 5-g. sample of (I) was dissolved in 24 cc. of 95% alcohol and 33% potash solution (12 cc.) was added. The mixture was heated on a steam-bath for eight hours. Acidification resulted in the precipitation of a white solid which was recrystallized from alcohol. Cinchophen (60% yield) was identified by its melting point and a mixed melting point with a commercial sample.

TABLE II

Dehydrating agent plus: -oxindole	Product, -oxindole	Formula	M. p., °C. (corr.)	Yield, %	Analyses	Calcd.	Found
3-Hydroxy-3-phenacyl-	3-Phenacylidene-	$C_{16}H_{11}O_2N$	193–194	92	C,	77.10	76.74
					H,	4.42	4.39
					N,	5.61	5.50
3-Hydroxy-1-methyl-3-phenacyl-	1-Methyl-3-phenacylidene-	$C_{17}H_{13}O_2N$	127–128	76	C,	77.55	77.70
					H,	4.94	4.96
3-Hydroxy-3-(4′-chlorophenacyl)-	3-(4′-Chlorophenacylidene)-	$C_{16}H_{10}O_2NCl$	209–210	95	Cl,	12.52	12.65
3-Hydroxy-3-(4′-bromophenacyl)-	3-(4′-Bromophenacylidene)-	$C_{16}H_{10}O_2NBr$	218–219	85	Br,	24.35	24.06
3-Hydroxy-3-(4′-methylphenacyl)-	3-(4′-Methylphenacylidene)-	$C_{17}H_{13}O_2N$	182–183	85	N,	5.32	5.30
3-Hydroxy-3-(4′-methoxyphenacyl)-	3-(4′-Methoxyphenacylidene)-	$C_{17}H_{13}O_3N$	201	89	N,	5.01	4.95

Dehydration of 3-Hydroxy-3-phenacyloxindole (I) and Derivatives

(A) By Aqueous Alcoholic Hydrochloric Acid.—A mixture containing 8 g. of (I), 25 cc. of alcohol and 50 cc. of concd. hydrochloric acid (or 50 cc. of 20% sulfuric acid) was allowed to stand overnight (or was heated for one-half hour at 100°). Fine orange-red needles formed. The product was recrystallized from ethyl alcohol. This procedure was also used in the case of certain derivatives of (I) (Table II).

(B) By Hydrochloric Acid in Acetic Acid.—When a mixture containing 2 g. of (I), 0.5 cc. of concd. hydrochloric acid and 20 cc. of glacial acetic acid, was warmed on the steam-bath for fifteen minutes and then cooled, the same product formed as in "A."

Reduction of 3-Phenacylideneoxindole and Derivatives

By Sodium Hydrosulfite.—3-Phenacylideneoxindole (5 g.) was partially dissolved in 75 cc. of 95% ethyl alcohol. To this was added 5 g. of sodium hyposulfite ($Na_2S_2O_4$) dissolved in 25 cc. of water. At room temperature, reduction was complete in about two hours; at steam-bath temperature, in twenty minutes. Upon thorough cooling of this solution, white crystals were formed. The product was purified by recrystallization from ethyl alcohol (Table III).

TABLE III

$Na_2S_2O_4$ plus: -oxindole	Product, -oxindole	Formula	M. p., °C. (corr.)	Yield, %	Analyses	Calcd.	Found
3-Phenacylidene-	3-Phenacyl-	$C_{16}H_{13}O_2N$	177	89	C,	76.51	76.30
					H,	5.18	5.13
1-Methyl-3-phenacylidene-	1-Methyl-3-phenacyl-	$C_{17}H_{15}O_2N$	134–135	65	N,	5.20	5.28
3-(4′-Chlorophenacylidene)-	3-(4′-Chlorophenacyl)-	$C_{16}H_{12}O_2NCl$	182–183	84	Cl,	12.44	12.47
3-(4′-Bromophenacylidene)-	3-(4′-Bromophenacyl)-	$C_{16}H_{12}O_2NBr$	191–192	90	Br,	24.21	24.19
3-(4′-Methylphenacylidene)-	3-(4′-Methylphenacyl)-	$C_{17}H_{15}O_2N$	145–146	78	N,	5.28	5.24
3-(4′-Methoxyphenacylidene)-	3-(4′-Methoxyphenacyl)-	$C_{17}H_{15}O_3N$	164–165	76	N,	4.98	4.92

3-Phenacyloxindole Oxime.—3-Phenacyloxindole (5 g.) was dissolved in 100 cc. of 95% ethyl alcohol and to this was added an aqueous solution of hydroxylamine, prepared by adding 12.5 cc. of 10% sodium hydroxide to 2.5 g. of hydroxylamine hydrochloride in 10 cc. of water. The mixture was heated on a steam-bath for one hour and on cooling the oxime crystallized from solution. It was recrystallized from ethyl alcohol; yield 85%, m. p. 198–199°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 72.18; H, 5.26. Found: C, 71.95; H, 5.22.

Attempted Rearrangement of 3-Phenacylideneoxindole to Cinchophen.—A mixture of 3-phenacylideneoxindole (2.7 g.) in 12 cc. of ethyl alcohol and 6 cc. of 33% potash was refluxed for three hours. The mixture was cooled and acidified with hydrochloric acid. A dark brown gummy material separated which solidified upon standing under water. No cinchophen could be obtained from this mass.

Attempted Rearrangement of 3-Phenacyloxindole to 3,4-Dihydro-2-phenylcinchoninic Acid.—3-Phenacyloxindole (5 g.) was treated with the concentrations of water, alcohol and potash mentioned directly above. The mixture was refluxed for fifteen hours, then cooled and acidified. The product (4 g.), after purification, was found to be unchanged 3-phenacyloxindole.

Summary

Isatin has been condensed with acetophenone to yield 3-hydroxy-3-phenacyloxindole. Some chemical properties and derivatives of this compound are described.

3-Phenacylideneoxindole and 3-phenacyloxindole failed to rearrange to give quinoline derivatives under the experimental conditions employed. This suggested that 3-phenacylideneoxindole is not an intermediate in the Pfitzinger synthesis of cinchophen from isatin and acetophenone.

NEW YORK, N. Y.

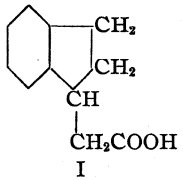
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE INDENE FROM ALPHA, GAMMA-BISDIPHENYLENE-BETA-PHENYLALLYL ALCOHOL

BY C. FREDERICK KOELSCH[1]

RECEIVED JULY 11, 1932 PUBLISHED DECEMBER 13, 1932

A molecule whose structure involves two fused five membered rings adjacent to each other on a benzene nucleus is, as mechanical models show, so highly strained that it is generally regarded as being incapable of existence. Several unsuccessful attempts to obtain such a molecule have been recorded. V. Braun and Reutter[2] were unable to convert hydrindene-1-acetic acid (I) into the tricyclic ketone (II), while the homologous hydrindene-1-β-propionic acid (III) and tetralin-1-acetic acid (V) were readily cyclized to the ketones (IV) and (VI).



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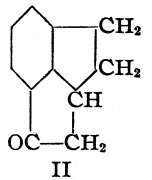
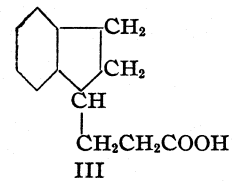


II



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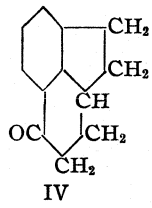

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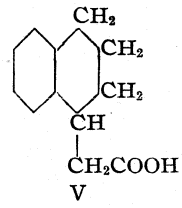

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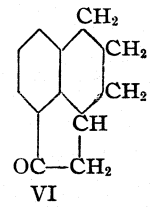


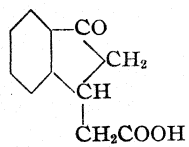
VI

Similarly Jackson and Kenner[3] were unable to convert 1-ketohydrindene-3-acetic acid (VII) or indoxylacetic acid (VIII) into the tricyclic compounds (IX) and (X).

[1] National Research Fellow in Chemistry.

[2] V. Braun and Reutter, *Ber.*, **59**, 1922 (1926).

[3] Jackson and Kenner, *J. Chem. Soc.*, 573 (1928).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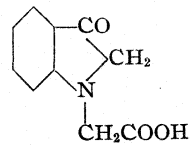
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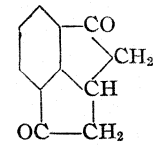
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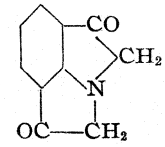
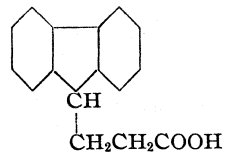

X

V. Braun and Anton[4] showed that while fluorene-9-propionic acid (XI) could be cyclized to (XII), fluorene-9-acetic acid (XIII) could not be converted into (XIV). They also showed that fluoranthene did not have the previously accepted formula $C_{15}H_{10}$ and the structure (XV), but had the formula $C_{16}H_{10}$ and the structure (XVI).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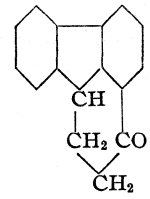
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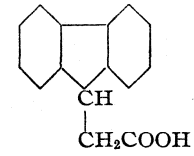
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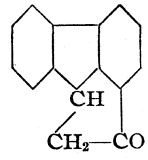
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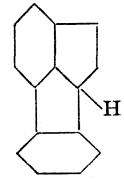
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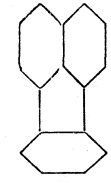
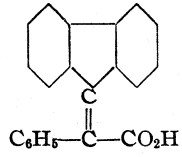

XVI

It has recently been shown[5] that α-phenyl-β-diphenyleneacrylic acid (XVII) was not cyclized under conditions which led to the formation of 2,3-diphenylindone (XIX) from α,β,β-triphenylacrylic acid (XVIII). And although pentaphenylallyl alcohol (XX) was converted into tetraphenylindene (XXI) by even a trace of acid, α,γ-bisdiphenylene-β-phenylallyl alcohol (XXII) gave a fairly stable chloride when treated with hydrogen chloride.[6]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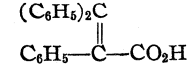
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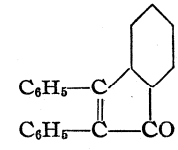
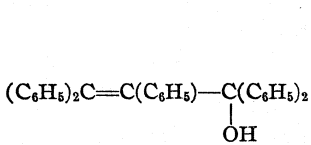

XIX

[4] V. Braun and Anton, *Ber.*, **62**, 145 (1929).

[5] Koelsch, THIS JOURNAL, **54**, 3384 (1932).

[6] Data to be published soon.



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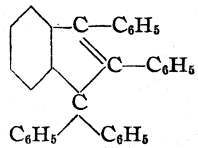
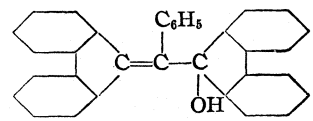
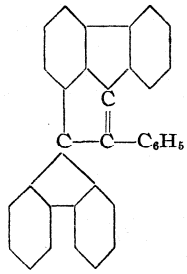


XXI

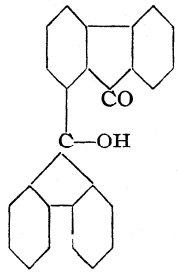


XXII

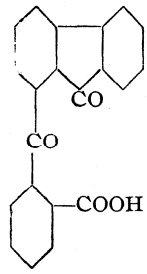
The acetic acid solution of the halochromic sulfate of α,γ-bisdiphenylene-β-phenylallyl alcohol slowly loses its color, and a yellow hydrocarbon $C_{33}H_{20}$ is formed. In the present paper it is shown that this hydrocarbon contains the structure hitherto considered impossible and is 1-diphenylene-2-phenyl-3,4-phenyleneindene (XXIII).



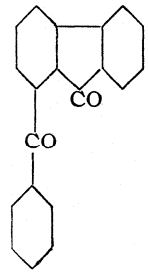
XXIII



XXIV



XXV



XXVI

On oxidation it gives benzoic acid and 1-diphenyleneoxymethylfluorenone (XXIV) whose functional groups are shown to be carbonyl and hydroxyl by its reaction with phenylmagnesium bromide to form 1-diphenyleneoxymethyl-9-oxy-9-phenylfluorene and its reaction with thionyl chloride to form 1-diphenylenechloromethylfluorenone.

Further oxidation of the oxy-oxo compound gives *o*-(fluorenone-1-carboyl)-benzoic acid (XXV). This acid exists in two interconvertible forms, one yellow and the other orange. It is believed that the more deeply colored form is an inner oxonium salt as Hantzsch[7] showed to be the case with fluorenone-1-carboxylic acid, which is orange in the solid state or in highly polar solvents and yellow, as are its salts, chloride and esters, in other solvents.

Decarboxylation of *o*-(fluorenone-1-carboyl)-benzoic acid gives 1-benzoylfluorenone (XXVI), which is identical with the compound prepared from the chloride of fluorenone-1-carboxylic acid, benzene and aluminum chloride.

A new synthesis of *o,m'*-ditolyl, from which fluorenone-1-carboxylic acid is obtained by oxidation to *iso*-diphenic acid and subsequent cyclization of this, is described.

Experimental

α,γ-Bisdiphenylene-β-phenylallyl Alcohol.—A mixture of 70 g. of α-phenyl-β-diphenylenevinyl bromide,[5] 5 g. of magnesium, a small crystal of iodine and 500 ml. of

[7] Hantzsch, *Ber.*, **49**, 226 (1916).

ether is refluxed with stirring. Heating is stopped after the reaction starts and is resumed when necessary and continued until the magnesium is completely dissolved. A saturated solution of fluorenone (35 g.) in toluene is added slowly. Stirring and refluxing are continued for one hour, and the mixture is then allowed to stand for ten hours. The magnesium compound is filtered off, washed well with ether and decomposed with iced ammonium chloride. The adhering ether is removed by gentle warming, and the solid residue is washed with water, dried and crystallized from toluene (150 ml.). The first crop of crystals weighs 23.5 g. and from the mother liquor by adding an equal volume of petroleum ether is obtained an additional 15 g.

The product crystallizes in yellow prisms that melt at 192–193.5°. With concd. sulfuric acid it gives a deep violet color; its solution in acetic acid is colored violet by sulfuric acid and red-brown by hydrochloric acid.

Anal. Calcd. for $C_{33}H_{22}O$: C, 91.3; H, 5.1. Found: C, 91.4; H, 5.4.

A solution of 0.6 g. of the alcohol in 35 ml. of acetic acid treated with 0.6 g. of chromic acid in a little water and boiled for a short time gives 0.15 g. of crude benzoic acid and 0.25 g. of steam distilled fluorenone.

1-Diphenylene-2-phenyl-3,4-phenyleneindene (XXIII).—A solution of 14.5 g. of α,γ-bisdiphenylene-β-phenylallyl alcohol in 250 ml. of hot acetic acid is cooled and before crystallization starts, 5 ml. of sulfuric acid in 10 ml. of acetic acid is added. The deep violet solution is allowed to stand for thirty minutes or until it has become light brown. The product is filtered off and crystallized from toluene and petroleum ether. There is obtained 12.2 g. of yellow prisms that melt at 196–197°.

Anal. Calcd. for $C_{33}H_{22}$: C, 95.2; H, 4.8. Found: C, 95.1; H, 5.0.

The hydrocarbon reacts readily with 40% sodium amalgam in dry ether to form a black sodium compound whose hydrolysis gives an amorphous substance. An amorphous product is also obtained by reduction with sodium in boiling amyl alcohol.

When the indene (1 g.) is warmed with an excess of undiluted bromine, hydrogen bromide is evolved and a heptabromo derivative is formed (2.3 g.). Crystallized from benzene and petroleum ether, the compound forms yellow needles that melt at 328–331°. It is quite resistant to chromic acid in acetic acid and when attacked is apparently completely oxidized.

Anal. Calcd. for $C_{33}H_{13}Br_7$: C, 40.9; H, 1.3. Found: C, 41.1; H, 1.5.

1-Diphenyleneoxymethylfluorenone (XXIV).—To a suspension of 6 g. of $C_{33}H_{20}$ in 50 ml. of hot acetic acid is added slowly a solution of 6 g. of chromic acid in a little water and 30 ml. of acetic acid. When the reaction is over, the solution is boiled for a few minutes, cooled and poured into water. The products are taken up in ether, from which solution sodium carbonate removes benzoic acid (0.5 g. after recrystallization). The ether is evaporated to a small volume, and the product which separates is recrystallized from benzene and petroleum ether; yield, 2.3 g. of yellow prisms that melt at 222–224°.

Anal. Calcd. for $C_{26}H_{16}O_2$: C, 86.6; H, 4.4. Found: C, 86.4; H, 4.6.

Reaction with Thionyl Chloride.—A solution of 0.7 g. of 1-diphenyleneoxymethylfluorenone and 1 g. of thionyl chloride in a little benzene is refluxed for fifteen minutes. The solvent is distilled under reduced pressure and the residue is crystallized from ether and petroleum ether; yield, 0.6 g. 1-Diphenylenechloromethylfluorenone forms yellow crystals that melt to a red liquid at 200–203°.

Anal. Calcd. for $C_{26}H_{15}OCl$: C, 82.3; H, 4.0; Cl, 9.4. Found: C, 81.9; H, 4.4; Cl, 9.2.

Reaction with Phenylmagnesium Bromide.—A solution of 1.2 g. of 1-diphenyleneoxymethylfluorenone in 25 ml. of toluene is added to the Grignard reagent from 3 g. of

phenyl bromide. After refluxing for thirty minutes, the solution is hydrolyzed with iced ammonium chloride. The ether, diphenyl, etc., are steam distilled, and the residue is crystallized from hot ethanol (250 ml.). The product, 1-diphenyleneoxymethyl-9-oxy-9-phenylfluorene, forms white plates that melt at 260–262° and contain one molecule of alcohol which is not lost at 100°. With concd. sulfuric acid it gives a brown-orange color.

Anal. Calcd. for $C_{33}H_{22}O_2 + C_2H_6O$: C, 84.4; H, 5.8. Found: C, 84.8; H, 5.8.

The alcohol of crystallization is driven off when the substance is heated at 140° under reduced pressure for one hour.

Anal. Calcd. for $C_{33}H_{22}O_2 + C_2H_6O$: C_2H_6O, 9.5. Found: loss in weight, 9.1. Calcd. for $C_{33}H_{22}O_2$: C, 87.6; H, 5.0. Found: C, 87.6; H, 5.1.

***o*-(Fluorenone-1-carboyl)-benzoic Acid (XXV).**—When 1-diphenyleneoxymethylfluorenone (0.2 g.) is oxidized in acetic acid with 0.6 g. of chromic acid, it gives 0.1 g. of *o*-(fluorenone-1-carboyl)-benzoic acid as the sole product.

This acid is best obtained, however, by oxidizing the mixture of substances remaining in the ether mother liquor from which 1-diphenyleneoxymethylfluorenone has been crystallized. This yellow glassy substance (1.4 g. from 3 g. of $C_{33}H_{20}$) is completely freed of ether, dissolved in acetic acid and boiled while a concd. aqueous solution of chromic acid (3 g.) is added. The solution is then poured into water and the product is taken up in ether, from which it is removed with sodium carbonate solution. The crude acid is dissolved in hot acetic acid. If this solution is cooled rapidly, or if it is disturbed while cooling, the product (0.3 g.) separates in the form of bright yellow needles that melt at 208–209°.

Anal. Calcd. for $C_{21}H_{12}O_4$: C, 76.7; H, 3.7. Found: C, 76.5; H, 3.7.

If the acetic acid solution is cooled very slowly and kept free from disturbance and from seed of the yellow form, the product separates as deep orange prisms that melt at 210–212°.

Anal. Found: C, 76.6; H, 3.8.

A mixture of the two forms of the acid melts at 205–209°. The two forms are stable in the solid state, but either may be converted into the other by proper crystallization from acetic acid.

Decarboxylation of *o*-(Fluorenone-1-carboyl)-benzoic Acid.—A mixture of 0.303 g. of the orange acid with 0.02 g. of cupric carbonate is heated at 250° as long as gas is evolved (twenty minutes; loss in weight, 0.049 g.). The dark melt is boiled with acetic acid, poured into water and taken up in ether. This solution is washed with dilute sulfuric acid and with sodium carbonate and then dried with sodium sulfate. Petroleum ether is added to precipitate tarry impurities which are discarded. The mother liquor is distilled under reduced pressure, and the residue is crystallized twice from ethanol. The product, 1-benzoylfluorenone, forms yellow needles that melt at 114–116° alone or mixed with a sample synthesized as described below; yield, 0.09 g.

Anal. Calcd. for $C_{20}H_{12}O_2$: C, 83.8; H, 4.2. Found: C, 83.8; H, 4.2.

***o,m'*-Ditolyl.**—To the Grignard reagent from 13 g. of *o*-tolyl bromide is added dropwise an ether solution of 5.8 g. of 1-methylcyclohexene-1-one-3,[8] and the mixture is refluxed for thirty minutes with stirring. Hydrolysis with dilute sulfuric acid and distillation of the product gives 6 g. of 1-methyl-3-*o*-tolylcyclohexadiene-1,3 which boils at 145–148° (21 mm.).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.3; H, 8.7. Found: C, 89.9; H, 8.6.

[8] Rabe and Pollock, *Ber.*, **40**, 2926 (1912).

The unsaturated hydrocarbon (5.9 g.) is heated with sulfur (2 g.) at 250° until no more hydrogen sulfide is evolved (one hour) and then distilled. There is obtained 4.5 g. of *o,m'*-ditolyl boiling at 265–267°.

1-Benzoylfluorenone.—The *o,m'*-ditolyl (4 g.) on oxidation with potassium permanganate gives 2.3 g. of *iso*-diphenic acid (m. p. 215–216°) and this is converted into fluorenone-1-carboxylic acid (m. p. 191–193°) by treatment with sulfuric acid.[9]

Fluorenone-1-carboxylic acid (0.35 g.) is refluxed with an excess of thionyl chloride for one hour and then warmed under reduced pressure. The crystalline acid chloride remaining is dissolved in 10 ml. of benzene, and 0.5 g. of aluminum chloride is added. After it has been warmed on a water-bath for ten minutes, the mixture is hydrolyzed with ice and hydrochloric acid. The benzene solution is separated and the solvent is distilled under reduced pressure. The residue is crystallized from alcohol, when there is obtained 0.2 g. of 1-benzoylfluorenone in the form of yellow needles that melt at 114–116°. The compound gives a red-brown color with sulfuric acid.

Anal. Calcd. for $C_{20}H_{12}O_2$: C, 83.8; H, 4.2. Found: C, 84.2; H, 4.3.

Summary

The halochromic sulfate of α,γ-bisdiphenylene-β-phenylallyl alcohol decomposes in acetic acid solution to give 1-diphenylene-2-phenyl-3,4-phenyleneindene, a hydrocarbon which contains a ring system hitherto considered impossible.

The structure of this hydrocarbon is proved by its degradation through 1-diphenyleneoxymethylfluorenone and *o*-(fluorenone-1-carboyl)-benzoic acid to 1-benzoylfluorenone.

An independent synthesis of 1-benzoylfluorenone is described.

[9] Mayer and Freitag, *Ber.*, **54**, 354 (1921).

CAMBRIDGE, MASSACHUSETTS

COMMUNICATIONS TO THE EDITOR

THE PREPARATION OF *l*-ARABINOSE AND *l*-RIBOSE BY THE OXIDATION OF *l*-ARABINAL WITH BENZOIC PERACID

Sir:

By the reactions *l*-arabinose ⟶ acetobromo-*l*-arabinose ⟶ diacetyl-*l*-arabinal ⟶ *l*-arabinal, employed by Gehrke and Aicher [*Ber.*, **60**, 918 (1927)] and by Meisenheimer and Jung [*ibid.*, **60**, 1462 (1927)] we have prepared 75 g. of crystalline *l*-arabinal, with melting point 78–81° and $[\alpha]_D^{20-25}$ −192°, in chloroform. An aqueous solution of 68 g. of this *l*-arabinal was stirred with a solution of benzoic peracid in ethyl acetate according to the general procedure of Levene and Tipson [*J. Biol. Chem.*, **93**, 631 (1931)]. The titration with iodine by the directions of Goebel [*ibid.*, **72**, 801 (1927)] was then equivalent to the oxidation of 78% of the *l*-arabinal to aldopentose. The observed rotation of the solution gave, on the basis of the above yield of aldopentose, the value $[\alpha]_D^{20-25}$ +49.77°. This rotation has now been shown to be due largely to the presence of both *l*-arabinose and *l*-ribose in the reaction product.

The solution of the above reaction products was concentrated to a sirup, thinned with absolute alcohol and ether, and yielded 7 g. of crystalline *l*-arabinose. This sugar was recrystallized to 5.5 g. of pure *l*-arabinose, with m. p. 159–160° and $[\alpha]_D^{20-25}$ +104.6°, in water. The solution containing the remaining larger portion of the reaction products was again concentrated to a sirup, from which no more *l*-arabinose could be crystallized. After three weeks crystal nuclei appeared spontaneously in this sirup. These were stirred into the sirup after the addition of absolute alcohol. Refrigeration overnight resulted in the formation of 15 g. of crystalline *l*-ribose, with m. p. 81–84° and $[\alpha]_D^{20-25}$ +23.85° (seventeen hours after solution in water). One recrystallization from absolute alcohol has raised its melting point to 85–87°. From the mother liquors an additional 13 g. of *l*-ribose has been secured by direct crystallization, and 8.7 g. more by way of the *p*-bromophenylhydrazone in the method of van Ekenstein and Blanksma [*Chem. Weekblad*, **22**, 373 (1909)]. The purified *p*-bromophenylhydrazone of *l*-ribose melted at 171–172°, while the value given by Levene and Jacobs [*Ber.*, **42**, 2474 (1909)] for the same derivative of *d*-ribose was 170°.

The synthesis of both *d*- and *l*-ribose may now be accomplished by the above reactions more quickly and cheaply than by preparations from any other sources. Our studies, which were supported in part by a Grant-in-aid from the National Research Council, will be more fully described in in a future publication.

From the *l*-ribose which has thus been formed we shall undertake the preparation, by the cyanhydrin reaction, of the remaining unknown aldohexoses, *l*-allose and *l*-altrose.

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W. C. AUSTIN
FRED L. HUMOLLER

RECEIVED OCTOBER 19, 1932
PUBLISHED DECEMBER 13, 1932

THE FLUOROCHLORIDES OF SILICON

Sir:

Since 1915 this Laboratory has been engaged in the investigation of the fluorides, especially in Groups III and IV of the periodic table.[1] Unaware of any other investigators working on the problem, we have continued the studies begun in this Laboratory some time ago on the fluorination of

[1] Germann and Booth, *J. Phys. Chem.*, **21**, 92 (1917); Germann and Cleaveland, *Science*, [2] **53**, 582 (1921); Germann and Torrey, *ibid.*, **54**, 16 (1921); Germann and Booth, *J. Phys. Chem.*, **30**, 369 (1926); Booth and Starrs, *ibid.*, **35**, 3553 (1931); Booth and Carter, *ibid.*, **36**, 1359 (1932); Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932); Booth and Bixby, *ibid.*, **24**, 637 (1932); Booth, Swinehart and Morris, THIS JOURNAL, **54**, 2561 (1932).

halides and have prepared the compounds $SiFCl_3$, SiF_2Cl_2, SiF_3Cl by the direct method of the reaction of antimony trifluoride on silicon tetrachloride in the presence of either antimony pentachloride, chlorine or similar catalyst, obtaining large quantities of these products very readily along with lesser amounts of silicon tetrafluoride.

Recently in an excellent paper Schumb and Gamble[2] have obtained the last three of these compounds, that is, SiF_2Cl_2, SiF_3Cl and SiF_4 by the indirect method of the more difficult explosive reaction of chlorine on Si_2F_6 at elevated temperatures. However, our method permits ready control of the product obtained, that is, the fluorination can be made progressive by condensing the higher boiling compounds, for instance the $SiFCl_3$, and letting them run back into the generator. By this reaction we have prepared over 200 liters of $SiFCl_3$, 100 liters of SiF_2Cl_2 and 75 liters of SiF_3Cl. As would be expected, much larger quantities of the least fluorinated compound were obtained. The boiling points of SiF_2Cl_2 and SiF_3Cl observed by us agree closely with the values obtained by Schumb and Gamble.

They found a very small amount of a higher boiling material of which they say, "Because of the difficulty of purifying the small quantity of this higher boiling residue, its composition was not definitely established but it is probable that a little of the third fluorochloride, $SiFCl_3$, was contained therein." We have definitely prepared and purified large quantities of $SiFCl_3$, boiling point 12.2°, and established its composition.

The critical constants of these three gases have also been determined

For $SiFCl_3$, $T_c = 165.17 \pm 0.05°$ and $P_c = 34.34$ atm.
For SiF_2Cl_2, $T_c = 95.75 \pm 0.05°$ and $P_c = 34.57$ atm.
For SiF_2Cl_3, $T_c = 34.50 \pm 0.10°$ and $P_c = 34.42$ atm.

All these gases are completely hydrolyzed by water, yielding hydrated silica, fluosilicic and hydrochloric acids. We have found them somewhat nauseating and very irritating when inhaled. The complete data and physical and chemical properties will be reported in a subsequent article.

[2] Schumb and Gamble, THIS JOURNAL, **54**, 3943 (1932).

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
HAROLD SIMMONS BOOTH
CARL F. SWINEHART

RECEIVED OCTOBER 22, 1932
PUBLISHED DECEMBER 13, 1932

A NEW GENERAL METHOD FOR FLUORINATION OF INORGANIC HALIDES

Sir:

The fluorination of silicon chloride by antimony trifluoride with a catalyst to yield fluorochlorides and fluorides as described in the previous

note appears to be a general reaction which may be expected to proceed whenever both the fluoride and chloride (or bromide or iodide) are non-polar. With a polar fluoride it may proceed providing the mixed fluorohalide is non-polar and volatile.

It seems further that whenever the heat of this reaction is high, or when the temperature is high, fluorination tends to go to completion but where the heat of reaction is low, or the temperature is kept down, intermediate fluorohalides are obtainable, and fluorination may be made progressive by condensing the least fluorinated compound back into the generator for further reaction. The latter is characteristic of the reaction with halides of Group IV. The reaction of SbF_3 with a catalyst on $SiCl_4$ is slower than on CCl_4, on $GeCl_4$ slower than on $SiCl_4$, and slow with $SnCl_4$. Since both CCl_4 and $SiCl_4$ yield fluorochlorides and fluorides, the gases from $GeCl_4$ and $SnCl_4$ are probably likewise fluorochlorides and fluorides, especially since the reaction characteristics are precisely the same. Small amounts of gas are evolved with $TiCl_4$, but this may be due to impurities. In these cases we have found it advisable to increase the speed of the reaction by warming the reaction flask gently; in others it is necessary to diminish the speed of the reaction by cooling. It is always advisable to use excess of the liquid halide (or an inert solvent) to absorb the heat of reaction, thus controlling its speed.

The reaction with PCl_3 or PBr_3 gives a smooth evolution of gases but the reaction with PCl_5 is violent. When SbF_3 is added to solid PCl_5, reaction is delayed, begins slowly, gathers speed rapidly, and suddenly clouds of gases evolve, while the reaction mass liquefies. In solvents the violence of this reaction is diminished, and the gases evolved are phosphorus fluorochlorides with some PF_5 and PF_3.

Non-polar oxychlorides also react with SbF_3 in the presence of a catalyst to yield gases. For instance, $SeOCl_2$, SO_2Cl_2, and even $VOCl_3$ when gently warmed, evolved gases. $POCl_3$ evolves gases immediately with SbF_3 without a catalyst.

Even non-polar thiohalides react. For example, $PSCl_3$ yields gases immediately with SbF_3 without a catalyst. $SiHCl_3$ yields fluorochlorides with SbF_3 and $SbCl_5$, and probably $SiBr_4$, Si_2Cl_6, Si_3Cl_8, $SiSCl_2$, Si_2OCl_2, BCl_3, B_2Cl_4, $POCl$, $SOCl_2$, etc., will react similarly.

This is a simple, general method for preparing fluorohalides, and fluorides, many of which have been difficult to prepare heretofore. As far as we can find this is the first time in the forty years since Swarts [*Acad. Roy. de Belgique*, **24,** 309, 474 (1892)] discovered that SbF_3 and a catalyst would cause partial replacement of a halogen in an aliphatic halide that this reaction has been successfully applied to the preparation of inorganic fluorohalides and fluorides.

Investigations are now in progress in the Laboratory on all the applica-

tions of this reaction to all the non-polar inorganic halides and will be reported as rapidly as possible.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO
HAROLD SIMMONS BOOTH
CARL F. SWINEHART

RECEIVED OCTOBER 22, 1932
PUBLISHED DECEMBER 13, 1932

THE ACTION OF NITROUS ACID ON PHENYL-α-(β-NAPHTHOL)-AMINOMETHANE. A CORRECTION

Sir:

In a recent paper [Ray, THIS JOURNAL, **54,** 295 (1932)] it was reported that phenyl-α-(β-naphthol)-aminomethane on treatment with nitrous acid gave an aliphatic diazo compound. Subsequent work, the details of which are soon to appear, has shown that the reaction is much more complex than was originally supposed. The compound in question is not an aliphatic diazo compound but an N-nitroso derivative of a heterocyclic compound.

CHEMICAL LABORATORY
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO
FRANCIS EARL RAY

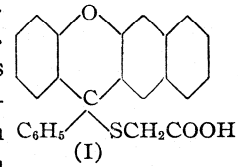
RECEIVED OCTOBER 31, 1932
PUBLISHED DECEMBER 13, 1932

THE ACTION OF SODIUM IN LIQUID AMMONIA ON DERIVATIVES OF OPTICALLY ACTIVE TRIARYLMETHANES

Sir:

In view of a recent publication by Ashley and Shriner [THIS JOURNAL, **54,** 4410 (1932)] on an attempt to prepare an optically active salt of the type $\left[\begin{matrix} & R_2 & \\ R_1 : & \ddot{C} & : R_3 \\ & \ddot{} & \end{matrix}\right]^- Na^+$ it seems advisable to place on record certain experiments which have been conducted in this Laboratory, and which were reported to the Society at its meeting in New Orleans, March 28–April 1, 1932.

In recent publications from this Laboratory a method has been described for preparing certain derivatives of optically active triarylmethanes. Investigations of such optically active compounds led us to believe that a study of their behavior toward sodium in liquid ammonia should be of special interest. For this purpose 12-phenyl-12-β-benzoxanthenethioglycolic acid (I), m. p., 187–188°, has been prepared. The pure levo modification of this compound (m. p. 184–185°) prepared by repeated crystallization of its brucine salt gave $[\alpha]_D^{20}$ in acetone −48.5°. This material in liquid ammonia was treated with metallic sodium in the absence of oxygen. The deep orange-brown sodium triarylmethyl so formed was allowed to react with a slight excess



(I)

of dry solid ammonium bromide. When these reactions were carried out under suitable conditions, the corresponding colorless trisubstituted methane was found to be optically active. In one experiment a specific rotation $[\alpha]_D^{20}$ in acetone $-11.7°$ was obtained. Since this methane derivation was obtained in an optically active condition it follows that the colored sodium triarylmethyl must have been active. Hence the three groups and the central carbon atom of the ion could not have been in a plane.

The optical stability of such an ion is being investigated further and a discussion of these results will be published at a later date.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

FREDERIC H. ADAMS
EVERETT S. WALLIS

RECEIVED NOVEMBER 10, 1932
PUBLISHED DECEMBER 13, 1932

OXIDATION COLORS DERIVED FROM 5,6-DIAMINOURACIL

Sir:

Ortho-, meta- and para-diamines differ in their behavior toward oxidizing agents, such as hydrogen peroxide, as follows. With ortho-diamines two molecules react to form a diaminophenazine. With para-diamines two or more molecules react to form a quinone-anil of the type of Bandrowski's base. Meta-diamines, however, do not react. Nevertheless, in the presence of an ortho- or para-diamine (which is capable of forming an ortho- or para-quinoid derivative on oxidation), meta-diamines do react to form deeply colored substances which have found application in fur and hair dyeing.

We find that 5,6-diaminouracil (an ortho-diaminopyrimidine) is also capable of reacting with meta-diamines, aminophenols and diphenols, in the presence of hydrogen peroxide, to form colored substances which dye animal fibers. Thus, for example, the following colors have been obtained from this pyrimidine: with *m*-phenylenediamine, purple; with *m*-aminophenol, old rose; with resorcinol, salmon.

CHEMICAL LABORATORIES
COLUMBIA UNIVERSITY
NEW YORK, N. Y.

MARSTON TAYLOR BOGERT
DAVID DAVIDSON

RECEIVED NOVEMBER 11, 1932
PUBLISHED DECEMBER 13, 1932

THE CONCENTRATION AT WHICH HEATS OF DILUTION ARE MEASURED IN THE CALORIMETRIC METHOD: A CORRECTION

Sir:

In a recent letter [THIS JOURNAL **54,** 4114 (1932)] we objected to certain of the claims made by E. Lange and A. L. Robinson based upon the extrapolation of their calorimetric data for intermediate heats of dilution

to the reference state of infinite dilution. We have since discovered that our communication was based upon an interpretation of their procedure which is erroneous, namely, that a separate extrapolation was made for each pair of solutions in order to determine the heat content of the solution at each final concentration. Instead, only the value for the lowest final concentration depends entirely upon extrapolation; the values for the heat content of all other recorded concentrations being obtainable by *alternately adding* and *subtracting* the measured values for the intermediate heats of dilution. Our objections to their procedure are consequently without foundation.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK CITY

VICTOR K. LA MER
I. A. COWPERTHWAITE

RECEIVED NOVEMBER 12, 1932
PUBLISHED DECEMBER 13, 1932

ROTENONE. XXIV. SYNTHESIS OF TETRAHYDROTUBANOL

Sir:

As has been shown recently [Haller and LaForge, THIS JOURNAL, **53,** 4460 (1931); **54,** 1988 (1932)], tubaic acid ($C_{12}H_{12}O_4$), obtained from rotenone by the action of alcoholic potash, is converted by drastic catalytic hydrogenation into tetrahydrotubaic acid ($C_{12}H_{16}O_4$). When heated to its melting point, tetrahydrotubaic acid loses carbon dioxide and yields a crystalline product, tetrahydrotubanol ($C_{11}H_{16}O_2$), which has been identified as an alkyl resorcinol. Previous work on rotenone and its derivatives indicated that the side chain is an isoamyl group. It was suggested that tetrahydrotubanol is 2,6-dihydroxy-1-isoamylbenzene. This compound has now been synthesized and found to be identical with tetrahydrotubanol. The synthesis was accomplished by the following set of reactions. 2,6-Dimethoxybenzonitrile [Lobry de Bruyn, *Rec. trav. chim.*, **2,** 210 (1883)] was allowed to react with isobutylmagnesium bromide and the resulting ketimine was hydrolyzed to 2,6-dimethoxyphenyl isobutyl ketone. The ketone was reduced to 2,6-dimethoxy-1-isoamylbenzene, which on demethylation yielded 2,6-dihydroxy-1-isoamylbenzene. A comparison of its physical and optical properties with those of tetrahydrotubanol showed them to be identical. Experimental details will be presented in an early paper.

INSECTICIDE DIVISION
BUREAU OF CHEMISTRY AND SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

H. L. HALLER

RECEIVED NOVEMBER 23, 1932
PUBLISHED DECEMBER 13, 1932

THE THERMAL INTERCONVERSION OF MIXED BENZOINS

Sir:

The appearance of a paper by E. Margaret Luis [*J. Chem. Soc.*, 2547 (1932)] on the "Interconversion of Mixed Benzoins," and of an article by Buck and Ide [THIS JOURNAL, **54,** 4359 (1932)] in which they describe attempts to effect the same interconversion, induce us to report that, in the course of certain of our experiments on the reaction of arylamines with α-hydroxy and α-bromo ketones, we have been able to effect the partial transformation of anisbenzoin, p-$CH_3OC_6H_4CHOHCOC_6H_5$, into benzanisoin, p-$CH_3OC_6H_4COCHOHC_6H_5$, by simply heating the former above its melting point. The same transformation is effected quantitatively by distillation of anisbenzoin in vacuum (1 mm.).

We have found that anisbenzoin, which we have prepared both by the method of Asahina and Terasaka [*J. Pharm. Soc. Japan*, **494,** 219 (1923)] as well as by the method of McKenzie, Luis, Tiffeneau and Weill, *Bull. soc. chim.*, **45,** 414 (1929)], melts at 89° when pure. This melting point was given by Asahina and Terasaka, while McKenzie and his collaborators give 100–101° as the melting point. The crystals melting at 89° have been examined by us under the microscope and seem to be perfectly pure. We have found that through slow heating, and then subsequent cooling, of the anisbenzoin (m. p. 89°) its melting point can be altered. After a number of such treatments, its melting point rises to a value approximating the melting point given by McKenzie and his collaborators. We are therefore of the opinion that the 101° compound of McKenzie and his co-workers is already a mixture of the benzanisoin (m. p. 106°) and the anisbenzoin (m. p. 89°).

DEPARTMENT OF CHEMISTRY
HOWARD UNIVERSITY
WASHINGTON, D. C.

PERCY L. JULIAN
WALTER PASSLER

RECEIVED NOVEMBER 25, 1932
PUBLISHED DECEMBER 13, 1932

NEW BOOKS

Chemical Analysis by X-Rays and its Application. By GEORG VON HEVESY. The George Fisher Baker Non-Resident Lectures in Chemistry at Cornell University, 1931. The McGraw-Hill Book Company, Inc., 330 West 42d Street, New York, 1932. 333 pp. Price, $3.00.

This volume contains the lectures delivered by Professor Georg von Hevesy at Cornell University in the winter of 1931–32 during his tenure of the George Fisher Baker Non-Resident Lectureship at that institution.

The introductory lecture is entitled "The Age of the Earth." This is followed by three series of lectures, the subjects of each series being as follows: the first series, of ten lectures, "Analysis by Means of X-Rays";

the second series, of four lectures, "The Discovery and Properties of Hafnium"; the third series, of six lectures, "The Chemical Composition of the Earth and the Cosmic Abundance of the Elements."

Professor von Hevesy has himself investigated all of these subjects with conspicuous success and he presents them here in a clear, lively and authoritative fashion. This volume, therefore, like its predecessors in this Series, affords not only a useful and interesting survey of timely subjects, but also a valuable summary of the important contributions which its author has made to them.

ARTHUR B. LAMB

Analytical Chemistry. Based on the German Text of F. P. Treadwell. Translated and Revised by WILLIAM T. HALL, S.B., Associate Professor of Analytical Chemistry, Massachusetts Institute of Technology. Vol. I. **Qualitative Analysis.** Eighth English Edition. John Wiley and Sons, Inc., 440 Fourth Ave., New York, 1932. xi + 640 pp. Illustrated. 15 × 23.5 cm. Price, $4.50.

That a new edition of the classic Treadwell–Hall Volume I should appear two years after the last is a tribute to its value. The increase in size is mainly accounted for by the addition of the syllabus of a course given at Massachusetts Institute of Technology. There have been some changes. A new "acidic group of the earth acids" containing tantalum and columbium (niobium) from the ammonium sulfide group, and tungsten from the hydrogen sulfide group has been formed. Thallium, indium, gallium and vanadium have been transferred from the hydrogen sulfide to the ammonium sulfide group. The book seems quite free from typographical errors, although one has been noted: isomorphous on p. 114 has been misspelled. The reviewer, perhaps unreasonably, feels that the section on "electrolytical dissociation" should be modernized, as should that on "solubility product."

LOUIS WALDBAUER

L'Azéotropisme. La Tension de Vapeur des Mélanges de Liquides. Bibliographie. (Azeotropism. The Vapor Pressure of Liquid Mixtures. A Bibliography.) By Prof. Dr. MAURICE LECAT. Maurice Lamertin, Éditeur, Rue Coudenberg, 58–62, Brussels, Belgium, 1932. viii + 135 pp. 16 × 24.5 cm. Price, 15 belgas.

This Bibliography covers not only the literature relative to azeotropic mixtures but also that dealing with the vapor pressure of liquid mixtures in general. It is to be followed, in the near future, according to a statement of the author in the Preface, by a large quarto volume containing tables of azeotropic binary mixtures, whose references to the literature will be based on the present volume.

This Bibliography contains three lists: in the first or main list the articles are arranged alphabetically according to the authors' names; in the second list, the authors' names are arranged chronologically, with cross

references to the main list; in the third list, the names of the sources, chiefly scientific journals, are arranged alphabetically, also with cross references to the main list.

In the main list are given not only the name of the author but also the title of the article, its date of receipt and publication, and in many instances the place and date of the author's birth. Unfortunately, when there are two or more authors of one article, one or more of the authors' names has frequently been omitted from the list. This may result in some inconvenience to the reader and some oversights.

This volume, particularly in conjunction with the promised tables, should be of value to any one concerned with azeotropic mixtures, and doubly so since Professor Lecat's earlier tabulation of azeotropic mixtures is now out of print. The Preface to this volume, in addition to its normal content, is enlivened with a stirring invective against war.

ARTHUR B. LAMB

The Biochemistry of Muscle. By DOROTHY MOYLE NEEDHAM, M.A., Ph.D., Biochemical Laboratory, Cambridge. E. P. Dutton and Company, Inc., 286–302 Fourth Avenue, New York, 1932. viii + 166 pp. 11 × 17.5 cm. Price, $1.25.

This is one of a series of "Monographs on Biological Subjects" and is a most excellent critical survey of the subject.

The views of the mechanism of muscle contraction have undergone a complete revolution within the past three or four years. Those who have not followed all of the recent literature, and whose field of interest lies in physiology or biochemistry, cannot afford not to read this little volume, for it presents the older theories, the new discoveries and the present status of the problem in a condensed but lucid manner. Literature citations appear to be very complete, as is attested by a bibliography of 300 citations. Fortunately the author has herself done excellent research work in this field and is thoroughly competent to evaluate critically the data.

The book, of a size which easily slips in one's coat pocket, is divided into eight chapters, *i. e.*, "Lactic Acid Metabolism," "The Energy Production during Contraction," "The Part Played by Phosphate in the Mechanism of Carbohydrate Breakdown," "Adenylic Acid, Pyrophosphoric Acid and Phosphagen," "Contraction without Lactic Acid," "Respiration," "Inorganic Factors and Rigor Mortis" and "The Muscle as a Machine."

The readers should not be limited to those interested only in muscle physiology or biochemistry, for related data concerning the physiology and biochemistry of yeast, tumor and brain tissues, kidney, liver, fermentation, respiration, etc., are correlated with those directly relating to either "white" or "red" muscle. A glossary of technical terms is appended.

The book is highly recommended. The author and publisher are both

to be congratulated on its excellence. It will unquestionably stimulate further research, for numerous problems still unsolved are pointed out, and will be a boon to the teacher who can accept this summary as a clear-cut statement of the present status of the problem.

ROSS AIKEN GORTNER

BOOKS RECEIVED

October 15, 1932–November 15, 1932

KENNETH C. BAILEY, Editor. "The Elder Pliny's Chapters on Chemical Subjects." Part II. Edward Arnold and Co., London. Longmans, Green and Co., 55 Fifth Ave., New York. 299 pp. $5.00

GEORGE BARGER. "Organic Chemistry for Medical Students." Gurney and Jackson, 33 Paternoster Row, London E. C., England. 252 pp. 12s. 6d., net.

KLAUS CLUSIUS. "Kettenreaktionen." Fortschritte der Chemie, Physik und physikalischen Chemie. Band 21, Heft 5, Serie B. Verlag von Gebrüder Borntraeger, W 35, Schöneberger Ufer 12a, Berlin, Germany. 73 pp. Subscribers, RM. 9.60; separately, RM. 12.80.

WILHELM EITEL, Editor. "Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikatforschung in Berlin-Dahlem." Vol. V. Verlag von Friedr. Vieweg & Sohn Akt.-Ges., Braunschweig, Germany. 212 pp. RM. 28.

HAVEN EMERSON, Editor. "Alcohol and Man. The Effects of Alcohol on Man in Health and Disease." The Macmillan Company, 60 Fifth Ave., New York. 451 pp. $3.50.

A. GRÜTZNER. "Eisen- und Stahllegierungen. Patentsammlung geordnet nach Legierungssystemen." Zugleich Anhang zur Metallurgie des Eisens in Gmelins Handbuch der anorganischen Chemie. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 308 pp. Mk. 32, to subscribers.

PAUL GÜNTHER. "Wilhelm Ostwald, 1853–1932." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 24 pp. Mk. 1.

OTTO JORDAN. "Chemische Technologie der Lösungsmittel." Verlag von Julius Springer, Linkstrasse 23–24, Berlin W 9, Germany. 322 pp. RM. 26.50.

W. MCCARTNEY. Gattermann's "Laboratory Methods of Organic Chemistry." Translated from the Twenty-Second German Edition as Revised by Heinrich Wieland. The Macmillan Company, 60 Fifth Ave., New York. 416 pp. $3.50.

L. F. MAREK AND DOROTHY A. HAHN. "The Catalytic Oxidation of Organic Compounds in the Vapor Phase." American Chemical Society Monograph. The Chemical Catalog Co., Inc., 419 Fourth Ave., New York. 486 pp. $9.00.

ERICH MÜLLER. "Die elektrometrische (potentiometrische) Massanalyse." Fifth edition. Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 276 pp. RM. 14.50; bound, RM. 16.

GEORGE SUTTON PARKS AND HUGH MARTIN HUFFMAN. "The Free Energies of Some Organic Compounds." American Chemical Society Monograph. The Chemical Catalog Co., Inc., 419 Fourth Ave., New York. 251 pp. $4.50.

HEINRICH PINCASS. "Die industrielle Herstellung von Wasserstoff." Verlag von Theodor Steinkopff, Residenzstrasse 32, Dresden-Blasewitz, Germany. 82 pp. RM. 6.50; bound, RM. 7.30.

ROBERT ROBINSON. "Versuch einer Elektronentheorie organisch-chemischen Reaktionen." Translated from the English by M. Wreschner. Verlag von Ferdinand Enke, Stuttgart, Germany. 76 pp. RM. 7.

ELLA M. SALMONSEN, Compiler. "Bibliographical Survey of Vitamins, 1650–1930." With a Section on Patents, by Mark H. Wodlinger. Published by Mark H. Wodlinger, 86 East Randolph St., Chicago, Ill. 334 pp.

E. SCHIEBOLD. "Methoden der Kristallstrukturbestimmung mit Röntgenstrahlen. I Band. Die Lauemethode." Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany. 173 pp. M. 12; bound, M. 13.

J. L. SIMONSEN. "The Terpenes." Vol. II. The Dicyclic Terpenes, Sesquiterpenes and Their Derivatives." The Macmillan Company, 60 Fifth Ave., New York. 627 pp. $7.00.

LYNDON F. SMALL AND ROBERT E. LUTZ. "Chemistry of the Opium Alkaloids." Supplement No. 103 to the Public Health Reports. Superintendent of Documents, Government Printing Office, Washington, D. C. 375 pp.

PAUL WALDEN. "Goethe als Chemiker und Techniker." Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 87 pp. Mk. 2.

"Gmelins Handbuch der anorganischen Chemie." 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 59, Eisen. Teil A, Lieferung 4. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany. 260 pp. Mk. 41; subscribers, Mk. 35.50.

"Measurement of Oil in Bulk. Part I. Standard Weights and Measures." By Standardization Sub-Committee 10, Institution of Petroleum Technologists. Published by The Institute of Petroleum Technologists, Aldine House, Bedford St., London W. C. 2, England. 30 pp. 2s. 6d., net.

"Prout's Hypothesis." Papers by William Prout, J. S. Stas and C. Marignac. Alembic Club Reprint No. 20. Gurney and Jackson, 33 Paternoster Row, London E. C. 4, England. 58 pp. $0.65.

"Publications of the Department of Chemistry. Research Studies and Chemical Education. January 1, 1931–June 30, 1932." The Ohio State University, Columbus, Ohio. Reprints of 39 Papers.

ADDITIONS AND CORRECTIONS

NOTICE TO READERS.—For the convenience of those who may wish to cut out the corrections and attach them to the margins of the articles corrected, they have been printed only upon one side of the page.

1918. VOL. 40

The Reaction between Acid Chlorides and Aldehydes. I. By Roger Adams and E. H. Vollweiler.

Page 1744. In the fifth line from the bottom of the page, for "benzylidine benzoate" read "benzylidine acetate."

In the third line from the bottom of the page, for "silver benzoate" read "silver acetate."—ROGER ADAMS.

1930. VOL. 52

Studies in Gaseous Oxidations. I. The Homogeneous Uncatalyzed Reaction between Oxygen and Acetylene. By George B. Kistiakowsky and Sam Lenher.

The authors wish to state that in discussing the work of Professor William A. Bone, on page 3794, they incorrectly attributed to him views and statements which he does not maintain and has not maintained.—GEORGE B. KISTIAKOWSKY AND SAMUEL LENHER.

1931. VOL. 53

Diffusion in Alkaline Copper Systems. By V. L. Ricketts and J. L. Culbertson.

Pages 4004–4005. In the column of equations headed "Equation for Quantity."

Line 1, the exponent of e should read $-kt(2n + 1)^2\pi^2/4a^2$.

Line 6, the part of the equation after the large sigma's should read

$$\frac{1}{a^2\alpha_m^2(2n + 1)^2}\, e^{-kT\{\alpha_m^2 + [(2n + 1)^2\pi^2/h^2]\}}$$

Line 7, the exponent of e at the end of the formula should be $-n^2\pi^2kt/a^2$.—VERNON L. RICKETTS.

1932. VOL. 54

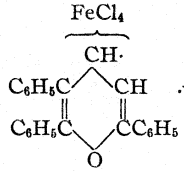
The 4-*n*-Alkyl-guaiacols. By Norine Hower Howells and Henry P. Howells.

Page 401. In line 2 the date in the reference should be 1930.

The Preparation of Iodine-free Bromine. By George M. Karns and H. C. Donaldson.

Page 443. In line 9, for "0.1%" read "approximately 0.01%."—GEORGE M. KARNS.

Addition Reactions of Vinyl Phenyl Ketone. II. Desoxybenzoin. By C. F. H. Allen and W. E. Barker.

Page 737. Formula VIII should be  .—C. F. H. ALLEN

The Photochemical Reaction between Quinine and Dichromic Acid. I. Quantum Yields. By George S. Forbes, Lawrence J. Heidt and Charles G. Boissonnas.

Page 960. The correct spelling of the name of the third author is Charles G. Boissonnas.

Page 967. In the last line of footnote 27, the numerical value should be "405 mμ" instead of "450 mμ."—GEORGE S. FORBES.

Bactericidal Properties of Monoethers of Dihydric Phenols. III. The Monoethers of Pyrocatechol. Comparative Notes on the Three Series of Monoethers. By Emil Klarmann, Louis W. Gates and Vladimir A. Shternov.

Page 1210. In the section headed (b) Bacteriological, the last two sentences of the second paragraph should be replaced by the statement: "However, not more than 15% of alcohol was present in most of the final dilutions. The *n*-heptyl and the phenylpropyl monoethers required 30% of alcohol in the test with *Staphylococcus aureus*, the phenylethyl, 25%."—E. KLARMANN.

Calcium Nitrate. III. Heats of Hydration and of Solution of the Binary System Calcium Nitrate–Water. By Warren W. Ewing, Alfred N. Rogers, John Z. Miller and Edward McGovern.

Page 1339. At the bottom of the page, the ΔH values for strontium nitrate tetrahydrate should be plus instead of minus.—WARREN W. EWING.

The Isolation of Pure, Anhydrous Ethyl Alcohol from Non-Alcoholic Human and Animal Tissues. By Alexander O. Gettler, Joseph B. Niederl and A. A. Benedetti-Pichler.

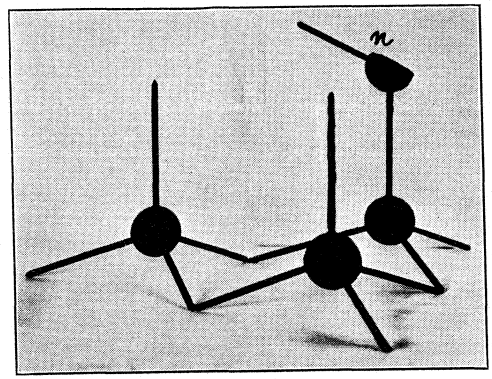
Page 1484. In Table II the heading of the fourth column should read "Ethyl alcohol in mg. per 1000 g."—ALEXANDER O. GETTLER.

Mass, Zahl und Gewicht in der Chemie der Vergangenheit. Ein Kapitel aus der Vorgeschichte des sogenannten Quantitativen Zeitalters der Chemie. By Paul Walden.

Page 1700. In paragraph one, lines 7 and 8, for "appear as our Troy and avoirdupois pounds of today," read "appear as the older Dutch Troy pound and our avoirdupois pound of today."—ARTHUR B. LAMB.

The Existence of Neutrons in the Atomic Nucleus. By Wendell M. Latimer.

Page 2125. Through an unfortunate oversight during the process of publication, there was omitted from the text of this Communication to the Editor the diagram mentioned therein and shown herewith.—THE EDITOR.



The Pinacol-Pinacolone Rearrangement. The Examination of Some Ortho-Substituted Benzopinacols. By Colin H. Beale and Harold H. Hatt.

Page 2405. In line 3 of footnote 5, for "*sym.*-2,2'-dimethoxybenzopinacol" read "*sym.*-3,3'-dimethylbenzopinacol."—H. H. HATT.

The Interaction of Diarylarsyl Iodides, Diarylstibyl Iodides and Phenyldihaloarsines with the Piperidine Salt of N-Pentamethylenedithiocarbamic acid. By F. F. Blicke and U. O. Oakdale.

Page 2994. In line 15 the word "from" should read "to form."

Page 2996. In line 2 the melting point should be "183–184°."—F. F. BLICKE.

Dehydration of Diethylcarbinol. By F. A. Karnatz and Frank C. Whitmore.

Page 3461. For "diethylcarbinol" read "diethylcarbincarbinol (2-ethylbutanol-1)."—FRANK C. WHITMORE.

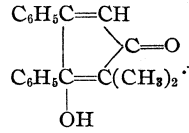
New Books. Page 3465. The price of **Microchemical Laboratory Manual,** by Friedrich Emich, translated by Frank Schneider, should be $3.00.

Further Studies in the Rare Gases. I. By Wm. D. Urry.

Pages 3892–3893. Twelve lines of p. 3892 beginning "and hence. . . " to foot of page should follow Equation (2), and five lines of large type on page 3893 after Equation (2) should follow Equation (8).—WM. D. URRY.

New Books. Page 4123. The price of **An Introduction to Organic Chemistry,** by Ira D. Garard should be $2.75.

The Reactions of Anhydracetonebenzil with Certain Halogen Compounds. By C. F. H. Allen and E. W. Spanagel.

Page 4342. Formula for XX should read  .—C. F. H. ALLEN.

Communication to the Editor. By Wallace E. Duncan and Emil Ott.

Page 4463. Title of the Communication to read, **"The Formation of Basic Lead Polysulfides by the Reaction between Basic Lead Mercaptides and Sulfur."**—EMIL OTT.

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[1] This index was prepared in the Editorial Offices of *Chemical Abstracts* through the courtesy of Dr. E. J. Crane and under his direction.

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