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THE REACTIONS OF H AND D ATOMS WITH CYCLIC AND PARAFFIN HYDROCARBONS[1]

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Abstract

The reactions of H and D atoms, produced by the discharge method, with benzene, four cycloalkanes, and the corresponding normal paraffins have been investigated at room temperature. Methane is the major product of each reaction. Collision yields have been calculated on the basis of hydrocarbon disappearance and exchange. Of the cycloalkanes, cyclopropane is the most inert with cyclopentane the most reactive. Cyclopropane and cyclobutane do not exchange with D atoms but benzene, cyclopentane, and cyclohexane undergo considerable exchange. In the case of the normal paraffins the degree of exchange increases with increasing molecular weight.

It is concluded that the initial reaction

$$H + RH \rightarrow R + H_2$$

is responsible for the products formed in the reactions but other primary processes may be responsible for the exchange of these hydrocarbons.

The discharge method of producing H atoms has been widely used to study the primary processes in reactions of H atoms with hydrocarbons. The consensus of opinion at present is that H atoms react with paraffins by hydrogen abstraction to produce hydrocarbon radicals which then undergo rapid "atomic cracking" reactions. This belief is largely based on the appearance of methane as the major product in all such reactions. It seemed of some interest therefore to investigate the reaction of H atoms with benzene and with some of the cycloalkanes.

Materials

Cylinder hydrogen was freed from oxygen by passage over copper wool at 300°C., and through two traps cooled in liquid nitrogen. About 0.6% nitrogen still remained as an impurity.

Deuterium was obtained under pressure by reacting 99.6% D_2O with specially purified calcium turnings at 260°C. in an autoclave; traces of NH_3 formed from the Ca_3N_2 present in the calcium were readily frozen out. Analysis showed the deuterium contained no H_2 and not more than 10% HD for which appropriate corrections were made in the calculations.

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Cyclopropane was obtained from the Ohio Chemical Company and was rated as 99.5% pure. It was freed from noncondensable gases and subjected to several trap-to-trap distillations, the middle 1/3 fraction being retained.

Cyclobutane was prepared from cyclobutanone by the method of Roberts and Sauer (9). The cyclobutanone was obtained from the reaction of diazomethane with ketene. The cyclobutane was tested for impurities by carefully fractionating a sample in a modified Ward still (10) and analyzing the fractions in the mass spectrometer. Cyclopentane, the largest impurity, was present to the extent of 0.6 mole %; lighter hydrocarbons amounted to less than 0.07 mole %. An infrared spectrum of the gas was found to agree well with published spectra except for the presence of an absorption maximum at 1810 cm.$^{-1}$ for which no explanation has as yet been found.

National Bureau of Standards standard samples of cyclopentane and cyclohexane were dried by passage over phosphorus pentoxide and used without further purification.

Carefully purified and freshly distilled benzene was provided for us by Dr. L. Marion of this laboratory and was thoroughly degassed and dried over phosphorus pentoxide before use.

The normal paraffins were Phillip's "Research Grade" materials rated as 99.88% pure. These were degassed and subjected to several trap-to-trap distillations prior to use.

Experimental Procedure

The discharge tube was of the familiar Wood–Bonhoeffer type described in previous communications from this laboratory (11, 15). The hydrogen pressure was reduced from atmospheric to about 0.35 mm., and its flow rate (58 cc. at N.T.P. per min.) was controlled by a capillary leak at the inlet end and a throttle at the pump end of the system; throttling at the pump end was found to be necessary in order to minimize pressure fluctuations. Atom concentrations were measured before and after each experiment at the top and bottom of the reaction tube by means of Wrede–Harteck gauges (5, 17) used in conjunction with a thermocouple type Pirani gauge which was frequently calibrated for hydrogen and deuterium. The average of these readings was considered to represent the average atom concentration obtaining during the experiment.

The flow rate of the hydrocarbon was controlled by maintaining a fixed vapor pressure in a side tube of known volume. The pressure of the gas at room temperature in this volume was measured before and after each experiment; the difference then gave a measure of the total amount of hydrocarbon used in the experiment, from which the flow rate could be calculated. The reactant gases were mixed at a distance of 20 cm. from the discharge and flowed together down a cylindrical reaction tube; hydrogen atoms leaving the tube recom-

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bined on platinum gauze. From the flow rates of the gases, their partial pressures, and the volume of the reaction tube it was possible to calculate the average time spent by a molecule in the tube; this reaction time was of the order of 0.6 sec.

The condensable products were trapped out at liquid nitrogen temperature, their volume measured at room temperature, and their composition determined by separation in a Ward still followed by mass spectrometer analysis of the various fractions.

The noncondensable products passed through a "Leybold" diffusion pump and were adsorbed on silica gel at liquid nitrogen temperature. After an experiment the silica gel was maintained at liquid nitrogen temperature and opened to a "megavac" oil pump for 15 min. in order to desorb most of the hydrogen. "Davco" technical grade silica gel was found to be the most suitable material for this purpose since the use of a more "active" gel made the desorption exceedingly slow. The amounts of methane and ethane lost by this procedure were shown to be negligible by blank experiments made with known gas mixtures and by the excellent material balances obtained in all the experiments. The trap was then warmed to room temperature and the gas toeplered into a gas burette where its volume was measured. An aliquot was isolated in a sample bulb for subsequent mass spectrometer analysis. From the amount of hydrocarbon which had undergone reaction (subsequently referred to as the amount decomposed) and the reaction time it was possible to calculate the rate of the initial process.

There are several objections frequently raised against this method of calculating the rate of the initial reaction. First the concentration of H atoms decreases down the reaction tube as the reaction takes place; calculated corrections for this effect are complicated and generally inaccurate. However, the use of the mass spectrometer and other improved analytical procedures has made it possible to work with very small quantities of hydrocarbon gases. Consequently, we were able to reduce the flow rate of the hydrocarbon to less than 1/50th that of the H atoms, thereby greatly minimizing this source of error.

The practice of equating the rate of disappearance of the hydrocarbon to the rate of the primary step can also be criticized. A secondary reaction which could regenerate the hydrocarbon, such as the combination of an atom with the hydrocarbon radical would, of course, vitiate this procedure. This objection may be overcome by the use of deuterium in place of hydrogen; the amount of hydrocarbon which has been exchanged can then be determined by means of a mass spectrometer and added to the amount decomposed in order to calculate the true rate of the initial step. In order to interpret the mass spectra it was necessary to assume that the ion sensitivity (ion current per centimeter partial pressure) for the parent peak of a hydrocarbon does not change appreciably when the hydrocarbon is deuterated; evidence from work on methane

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and ethane indicates that this assumption is reasonably valid. Corrections were made for the contributions to each parent peak from the cracking in the mass spectrometer of more deuterated hydrocarbon molecules, and for the C^{13} isotope. This involves the additional assumption that all the deuterated hydrocarbons have similar cracking patterns, but since these corrections were always small for the hydrocarbons investigated, this assumption does not introduce a serious error. It should be emphasized that the use of the mass spectrometer provides a much more positive and sensitive test for deuteration than any other method. The amount of each isotopic species of the compound can be measured independently and added together to give a true value of the percentage of the hydrocarbon which has undergone exchange, whereas the procedure of combusting the hydrocarbon and analyzing the resultant water gives only the over-all deuterium content of the sample. Further, there is no possibility of error arising from the presence of deuterium or deuterated reaction products in the sample.

Products of the Reactions

Methane was by far the most important product in the reactions of H and D atoms with all the hydrocarbons. Analysis of the methane produced in experiments with D atoms showed it to be over 80% CD_4, with the remainder being mainly CD_3H.

Methane was found to be the only product of the reaction of H or D atoms with cyclopropane. This is neither in agreement with Gunning and Steacie (4), who found no evidence for reaction of cyclopropane with H atoms produced by mercury photosensitization, nor with Dingle and LeRoy (3) who found no reaction with H atoms produced by the thermal dissociation of H_2. It was necessary, therefore, to investigate the reaction in detail to ensure that the methane in our experiments did not arise from any extraneous sources. Blank experiments, conducted in the absence of cyclopropane, produced some methane by the reaction of H atoms with the "apiezon" grease on the standard taper joints connecting the Wrede gauges and the hydrocarbon inlet tube with the reaction vessel. These joints were, therefore, eliminated from the apparatus and subsequent blank experiments produced no appreciable amounts of methane.

As previously mentioned, the hydrogen contained about 0.6% nitrogen which formed ammonia in the discharge tube. To eliminate any possible effect of this impurity one experiment was conducted by first passing the hydrogen through a long, thin glass helix immersed in liquid hydrogen. This was found to remove the nitrogen but had no effect on the amount of methane produced.

To ensure that no cyclopropane was diffusing back into the discharge the hydrocarbon inlet tube was bent away from the discharge and experiments were conducted over a considerable range of cyclopropane flow rates; in each case the amount of methane produced was the same percentage of the cyclopropane used.

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It was later discovered that small methane peaks were present in the mass spectra of tank hydrogen even after the hydrogen had been purified by passage through a palladium tube. Presumably, the methane was formed in some way in the mass spectrometer itself. To correct this, a standard hydrogen sample was measured in the mass spectrometer before each analysis at a pressure equal to the partial hydrogen pressure in the sample to be analyzed. The height of the mass 16 peak obtained from the hydrogen spectrum was then taken as the residual peak height to be subtracted from the sample spectrum.

Finally, to test whether the methane was formed from any impurity present in the cyclopropane, unreacted cyclopropane was recovered from one experiment and used in a subsequent experiment; the percentage of methane formed was found to be the same in each case. We can safely conclude, therefore, that methane is a true product of the reaction of H atoms with cyclopropane under our experiment conditions. No deuterated cyclopropane was recovered from any of the deuterium experiments.

In the case of cyclobutane, methane was again the sole product of the reaction with H and D atoms, while no measurable amount of deuterated cyclobutane could be detected.

With cyclopentane and cyclohexane, methane accounted for over 90% of the reaction products, with small amounts of other light hydrocarbons also being formed. To illustrate the order of magnitude of these products, the results of the mass spectrometer analyses of the products of the H atom-cyclopentane reaction are reported in Table I. In the deuterium experiments considerable exchange was found to occur. It was found, however, that the ratio of the amount of hydrocarbon decomposed to the amount exchanged was not constant but increased with increasing D atom concentration.

The green fluorescence reported by Bonhoeffer and Harteck (1) for the reaction of H atoms with benzene was observed in several of our experiments. About 85% of the decomposed benzene appeared as methane, the other 15% being comprised of all the straight chain hydrocarbons containing six carbon

TABLE I

PRODUCTS OF THE H ATOM – CYCLOPENTANE REACTION

Cyclopentane flow, cc. per min. N.T.P.	H atom flow, cc. per min. N.T.P.	% Cyclopentane which reacted to form							Cyclopentane unreacted	Mass balance
		CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}		
0.692	14.8	26.8	1.3	...	0.70	0.4	0.05	...	74.0	103
0.373	16.6	23.9	2.9	.05	0.68	1.4	0.3	...	74.0	103
0.508	13.3	14.3	0.4	...	0.29	0.7	0.15	.04	78.2	94
0.518	10.1	11.4	0.2	...	0.23	0.8	0.2	...	81.3	94
0.201	20.1	33.0	1.2	...	0.32	0.9	0.2	...	63.6	99
0.060	10.2	42.6	2.8	.02	1.09	1.5	0.3	.30	52.0	101
0.042	11.8	36.6	0.50	...	1.15	0.5	0.03	...	51.7	90
0.173	14.7	29.0	0.80	...	1.30	0.2	0.15	...	66.0	98

atoms or less. This is a good indication of the complexity of the secondary reactions involved; apparently once the hydrocarbon radical is formed, it undergoes rapid atomic cracking and hydrogenation reactions until the relatively inert methane molecule is formed. There was no evidence for the formation of any cyclohexane or cyclohexene, which might have been expected in the event of hydrogenation of the benzene without ring split. The benzene recovered after reaction with D atoms was found to have undergone exchange to a considerable extent.

Single experiments were made with each of the normal paraffins for comparison purposes. The reaction products were almost exclusively methane in each case. All the normal paraffins were found to be partially exchanged in the deuterium experiments.

Calculation and Discussion of Collision Yields

The collision yield can be defined as:

$$\frac{\text{The rate of the primary process}}{\text{The number of collisions per cc. per sec.}}$$

The numerator is determined experimentally; the denominator, the collision number, can be calculated from kinetic theory. The values for the collision diameters used in these calculations were obtained from viscosity data (13); 2.1 Å for H, 4.2 for C_3H_8, 4.8 for C_4H_{10}, 5.2 for C_5H_{12}, 5.8 for C_6H_{14}, 4.0 for cyclo-C_3H_6, 5.2 for cyclo-C_6H_{12}, and 5.0 for C_6H_6. Values of 4.4 and 4.8 Å were obtained by interpolation for cyclo-C_4H_8 and cyclo-C_5H_{10} respectively. The details of the calculations of collision yields for the cycloalkanes are shown in Table II. The experiments marked D in column 1 of the table refer to deuterium experi-

TABLE II

CALCULATION OF COLLISION YIELDS FOR THE CYCLOALKANES

Hydrocarbon flow, cc. per min. NTP	Atom flow, cc. per min. at NTP	Partial pressure of atoms, mm. Hg	Reaction time, sec.	Z in reaction time[a]	Per cent methane formed	Per cent other products[b]	Per cent exchange	Collision yield for reaction $\times 10^7$	Collision yield exchange $\times 10^7$
Cyclopropane									
.113	38.4	.175	.59	25.8×10^3	2.50	<0.1		.097	
.430	12.9	.070	.67	11.3	0.50			.044	
.588	10.1	.056	.68	9.2	1.17			.127	
.225	9.5	.052	.68	8.4	0.90			.107	
1.092	12.1	.066	.68	11.0	1.32			.120	
.916	20.5	.105	.64	21.8	2.05			.094	
.244	45.1	.193	.58	27.0	1.16			.043	
.635	29.0	.133	.62	19.8	2.10			.106	
.660	18.9	.098	.65	15.3	2.03			.133	
.160	11.5	.063	.68	10.7	2.76			.258	
.269	14.3	.082	.65	12.9	1.45			.112	
.252	15.1	.092	.67	14.7	1.36			.092	
.406	14.3	.089	.70	14.9	1.36			.091	
.257	19.9	.109	.62	16.3	2.30			.141	
.050(D)	20.6	.140	.88	21.0	4.4	<0.1	0	.21	0
.046(D)	4.1	.035	.97	5.8	2.9		0	.50	0
.067(D)	20.0	.137	.90	16.3	5.8		0	.36	0
.104(D)	14.5	.105	.92	21.0	4.5		0	.21	0

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TABLE III—*Continued*

Hydrocarbon flow, cc. per min. NTP	Atom flow, cc. per min. at NTP	Partial pressure of atoms, mm. Hg.	Reaction time, sec.	Z in reaction time[a]	Per cent methane formed	Per cent other products[b]	Per cent exchange	Collision yield for reaction $\times 10^7$	Collision yield exchange $\times 10^7$
Cyclobutane									
.267	16.1	.097	.67	17.9	13.4	>0.1		.75	
.253	13.5	.082	.67	15.1	12.8			.85	
.168	11.2	.068	.70	12.6	17.1			1.4	
.077	9.4	.059	.71	10.9	17.8			1.6	
.227	10.0	.065	.70	11.9	12.9			1.1	
.134	13.8	.082	.69	14.6	14.9			1.0	
.171(D)	10.0	.064	1.00	12.7	33.6	>0.1	0	2.6	0
.253(D)	9.2	.053	1.02	10.7	34.0		0	3.2	0
.043(D)	12.0	.073	.99	14.3	23.0		0	1.6	0
Cyclopentane									
.692	14.8	.049	.55	8.2	26.8	2.4			
.373	16.6	.059	.55	9.9	23.9	5.3			
.508	13.3	.041	.54	7.7	14.3	1.6			
.518	10.1	.031	.55	6.1	11.4	1.4			
.201	20.0	.066	.51	10.2	33.0	2.6			
.169	14.7	.052	.54	8.4	29.0	2.4			
.223(D)	8.30	.077	.82	14.0	47.8		26.4	3.4	1.9
.143(D)	8.30	.077	.82	14.0	55.9		34.0	4.0	2.4
.096(D)	3.87	.037	.86	7.1	41.4		35.7	5.9	5.1
.190(D)	5.46	.050	.83	9.3	33.1		41.7	3.6	4.4
.266(D)	3.75	.032	.87	6.2	24.0		51.0	3.9	8.3
.270(D)	3.36	.032	.85	6.1	24.0		50.2	3.9	8.3
.502(D)	Diffusion into Discharge								
.269(D)	1.91	.017	.79	3.8	18.6		43.8	4.9	11.6
.202(D)	2.49	.020	.77	3.7	26.0		41.8	7.0	11.2
.060(D)	1.91	.016	.82	2.6	17.4		54.2	6.2	20.9
.119(D)	3.20	.028	.77	4.8	32.0		46.0	6.7	9.5
.319(D)	1.47	.013	.77	2.1	11.8		40.7	5.6	19.4
.249(D)	1.40	.013	.77	2.1	12.4		37.5	5.9	17.5
.280(D)	1.75	.017	.75	2.8	16.9		40.2	6.0	14.4
Cyclohexane									
.381	14.0	.060	.43	9.9	11.6	1.5		1.3	
.376	14.5	.063	.43	10.5	8.9	1.1		1.0	
.390	9.3	.044	.45	7.6	5.8	0.5		0.82	
.079	5.5	.026	.46	4.6	8.7	1.0		1.80	
.092	6.4	.032	.47	5.7	10.4	0.5		1.90	
.101	4.7	.024	.46	4.3	6.5	0.4		1.61	
.108(D)	8.3	.056	.60	9.1	30.1		33.0	3.3	3.6

(a) *The number of collisions of 1 hydrocarbon molecule with H or D atoms in the reaction time.*
(b) *In the deuterium experiments other products when determined are grouped together with the methane.*

ments. The collision yields for all the hydrocarbons along with their mean deviations are shown in Table III. Column 2 of Table III gives the collision yields for the hydrogen experiments calculated from the rate of hydrocarbon disappearance. Column 4 gives the same data for the deuterium experiments,

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while column 6 gives the collision yields for the exchange process; column 7 is the sum of columns 4 and 6. The average value for the percentage of hydrocarbon which has undergone exchange is given in column 6; this will, of course, depend upon the D atom concentration. Activation energies are given in column 3 for the H atom reactions and in column 8 for the D atom reactions; the latter were calculated from the combined collision yields for exchange and decomposition. In making these calculations a value of 0.1 has been chosen for the steric factor, in the expression

$$\text{collision yield} = A.e^{-E/RT}$$

since this has been the custom in the past in dealing with H atom reactions. However, a great deal of evidence is accumulating which indicates that many free radical reactions have very low steric factors (*ca.* 10^{-4}). There appears to be no way at present of deciding if steric factors are low for H atom reactions. If they also should prove to be very low then the activation energies reported may be greatly in error. However, this has no effect on any arguments concerning relative reactivity which are based on collision yields.

The reason for the uncertainty in the case of benzene becomes apparent when the stoicheiometry of the reaction is considered. At least 18 H atoms are required to transform one molecule of benzene into methane. Since this reaction is rapid there is a serious depletion of H atoms even at the flow rates used in these experiments, which results in too low a value for the collision yield. (Robb and Melville (7) have recently reported a collision yield of 7×10^{-4} for this reaction calculated from the rate of hydrogen atom disappearance.)

It will be seen from Table III that cyclopropane is more inert than the other cycloalkanes, with cyclopentane being the most reactive. It is interesting to note that this is the same order of reactivity found by Trotman-Dickenson and Steacie (16) for the reactions of methyl radicals with the cycloalkanes. The inertness of cyclopropane may seem somewhat surprising although the rate

TABLE III

COLLISION YIELDS AND ACTIVATION ENERGIES

Hydrocarbon	H atoms		D atoms				
	Collision Yield $\times 10^7$	Activation energy, kcal.	Collision yield for reaction $\times 10^7$	Average % exchange	Collision yield for exchange $\times 10^7$	Total Collision yield $\times 10^7$	Activation energy, kcal.
Cyclopropane	0.11 ± .03	9.5	.34 ± .11	0	0	.34 ± 1.1	9.3
Cyclobutane	1.1 ± .3	8.2	2.5 ± .5	0	0	2.5 ± .5	7.7
Cyclopentane	3.0 ± .6	7.5	5.2 ± 1.1	40	10.4 ± 5.0	15.6 ± 6.1	6.6
Cyclohexane	1.4 ± .4	8.0	3.3	33	3.6	6.9	7.2
Benzene	> 5	< 7	> 5	>40	> 10	> 15	<6
Propane	0.46	8.6	1.13	6	.21	1.2	8.0
n-Butane	0.31	8.9	.65	13	.50	1.5	7.9
n-Pentane	0.59	8.5	.66	36	1.38	2.0	7.8
n-Hexane	0.22	9.1	.94	50	1.90	2.8	8.0

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determining step probably does not involve the strained ring configuration but rather the rupture of a C–H bond which could be stronger than the C–H bond in normal paraffins. With the exception of cyclopropane the cycloalkanes react somewhat more rapidly than their straight chain counterparts. The fact that the cyclic hydrocarbons possess only secondary bonds scarcely seems sufficient cause for these differences.

Since only single experiments were conducted with each of the normal paraffins no significance can be attributed to the differences in their collision yields, which are within the estimated experimental error. The collision yields compare quite favorably with previously published values.

The percentage decompositions in the deuterium experiments are all somewhat larger than for the corresponding H atom experiments. Since the atoms do not possess zero point energies the differences, if real, must be attributed to the energy differences in the activated complexes. However, these differences may be largely superficial since it was noted during blank experiments that the D atom concentrations decreased more slowly with time than did the H atom concentrations. Hence the procedure of using the average of the atom concentrations measured before and after each experiment may involve errors sufficiently large to account for the different rates.* The main point of interest in the deuterium experiments lies in the degree to which the hydrocarbons are exchanged. In the case of cyclopropane and cyclobutane no exchange occurs, while cyclopentane, cyclohexane, and benzene undergo considerable exchange. In the case of the normal paraffins it will be seen that the degree of exchange increases with increasing molecular weight. This appears to be in disagreement with the work of Steacie and Parlee (12) who found that C_3H_8 does not exchange with D atoms at room temperature, and with Trenner, Morikawa, and Taylor (14) who found no exchange with either C_3H_8 or n–C_4H_{10}. However, we have already mentioned that the mass spectrometer method is much more positive and sensitive a test than those employed by these workers. Thus the 6% exchange which we observed in the case of propane (which was mainly C_3H_7D) would correspond to less than 1% deuterium content by the method of Steacie and Parlee.

The exchange of a hydrocarbon may be conceived to occur by one of the following mechanisms:

$$\begin{aligned}
&\text{A.}\quad RH + D \rightarrow R + HD && (1)\\
&\qquad R + D_2 \rightarrow RD + D && (2)\\
&\text{B.}\quad RH + D \rightarrow R + HD && (1)\\
&\qquad R + D \rightarrow RD^* && (2)\\
&\qquad RD^* + M \rightarrow RD + M && (3)\\
&\text{C.}\quad RH + D \rightarrow (H\text{–}R\text{–}D) \rightarrow RD + H
\end{aligned}$$

* *It may be argued that the reaction time is greater in the case of deuterium owing to its slower flow rate. Experimental measurements showed the relative flow rates of H_2 and D_2 to be 1.41, i.e., the inverse ratio of the square roots of their masses. From the kinetic theory of viscous flow it can be shown that this corresponds to equal collision diameters for H_2 and D_2. Since the reduced masses in the expression for the collision number are nearly in the inverse ratio of the square roots of the masses of H_2 to D_2 these effects should nearly cancel.*

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The reaction of methyl radicals with H_2 has been shown to occur with an activation energy of about 9 kcal. and a low steric factor. It is to be expected that the activation energy should probably increase and the steric factor decrease for reaction A (2) with more complicated hydrocarbon radicals. Hence mechanism A would not be expected to play a very important part in exchange processes at room temperature. However, the increase in the ratio of hydrocarbon decomposed to hydrocarbon exchanged with increasing atom concentration observed in the case of cyclopentane suggests that this mechanism may contribute slightly to the exchange process.

The radical recombination mechanism B provides an alternate fate for the hydrocarbon radical to that of "atomic cracking". It is similar to the mechanism first proposed by Taylor (14) to explain the high degree of deuteration of the methane formed in D atom reactions:

$$CH_3 + D \rightarrow CH_3D^* \rightarrow CH_2D + H \text{ etc.}$$

The quasi-deuteromethane can be stabilized only by collision with the wall or some other third body. The lifetime of the quasi-molecule is probably quite small and so there is a good probability of the splitting off of an H atom. This process recurs until there are only CD_3 radicals reacting with a large excess of D atoms and eventually a three body collision will occur to produce a stable CD_4 molecule.

Trenner, Morikawa, and Taylor (14) suggest that the three body restriction is also important for the combination of D atoms with propyl and butyl radicals, although their experimental evidence is not very clear. If exchange does occur by mechanism B then our results show that the three body restriction is much less important for the compounds investigated. Fig. 1 represents a typical mass spectrum of the cyclohexane recovered after reaction with D atoms. Mass 84 is the parent peak of cyclohexane and so the subsequent peaks will be nearly proportional to the amount of each deuterated cyclohexane present. We see that they decrease regularly from $C_6H_{11}D$ to C_6D_{12}, the reverse order to that observed for the deuteromethanes formed from this reaction. On the basis of mechanism B this simply means that for so complex a molecule sufficient degrees of freedom exist for the sharing of the excess energy that the collision time exceeds the average lifetime of the quasi-molecule, and the amounts of the various deuterocyclohexanes are those expected on a probability basis. The absence of deuteration in pairs also suggests that the excess energy does not remain localized at any single carbon atom in the molecule. Completely analogous spectra were obtained from the other hydrocarbons reacted with D atoms.

The reason for the absence of deuteration in the cases of cyclopropane and cyclobutane may lie in the strained structures of these compounds. Thus if the cyclopropyl and cyclobutyl radicals possess strain energy then they may be expected to decompose upon collision with a D atom with little likelihood of being stabilized. Cyclopentyl and cyclohexyl radicals on the other hand are relatively free from strain and could be readily stabilized.

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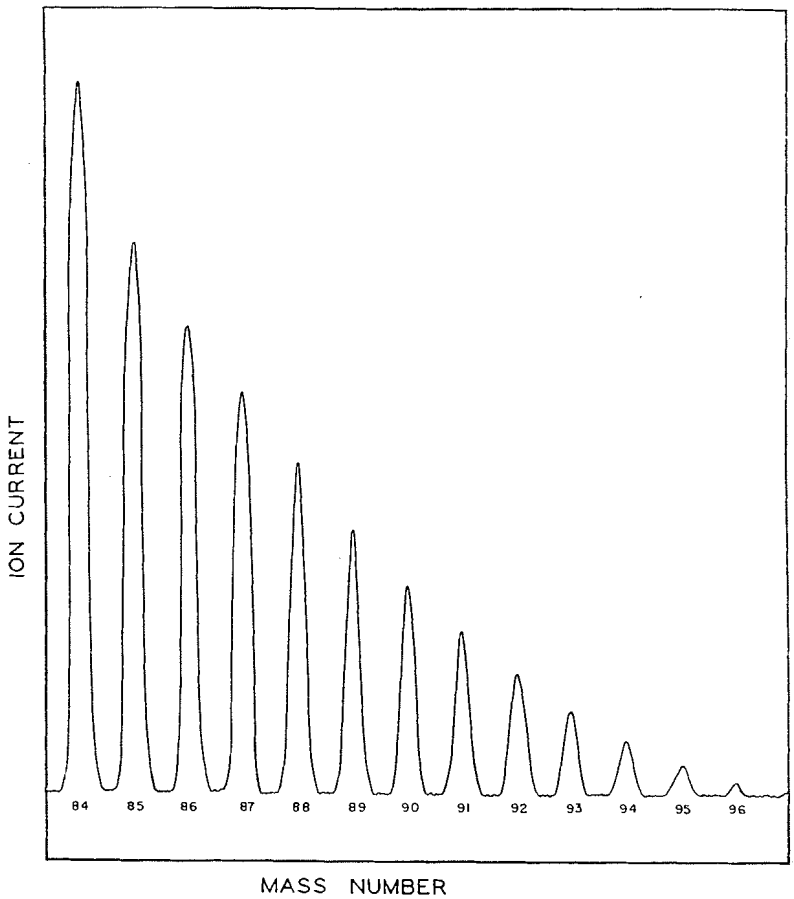

FIG. 1.

In the case of the normal paraffins, mechanism B suggests that as the number of degrees of freedom increases, the average lifetime of the quasi-molecule should also increase. This predicts increased deuteration up the series which is in accord with experimental observation. However, we would expect the amount of exchange to increase at the expense of the amount decomposed if the rates of the initial process were the same for all the normal paraffins. Experimentally, the amount decomposed remains essentially constant throughout the series. To be tenable, mechanism B therefore requires an increasing rate for the initial process equal to the increasing rate of exchange. If this is so, then the collision yields for exchange reaction must be added to the collision yield for the decomposition reaction in order to obtain the collision yield of the primary process.

If mechanism C is operative then the collision yields should not be added since they represent different initial steps. The absence of exchange with cyclopropane and cyclobutane must be attributed to the inability of the strained

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structures to undergo the Walden type inversion, whereas the increasing degree of exchange in the normal paraffins require the inversion to occur more readily the greater the number of degrees of freedom in the molecule. According to this mechanism deuteration need not occur at the expense of the decomposition reaction. It will also be unnecessary to invoke the concept of the three-body collision in this case to explain the mass spectra of the deuterated hydrocarbons. A comparison of our results with the two experiments of Robb and Melville (6) with *n*-hexane and cyclohexane lends support to this mechanism. They calculated collision yields from the rate of disappearance of H atoms which are in fair agreement with our collision yields calculated on the basis of decomposition alone, if the same values for collision diameters are used in both calculations. There is considerable disagreement, however, when their results are compared with the sum of our collision yields for decomposition and exchange. The use of mechanism C removes this discrepancy since there is no net decrease in atom concentration as a result of the exchange process.

Summing up then we may say that the reaction

$$H + RH \rightarrow R + H_2$$

followed by "atomic cracking" reactions is undoubtedly responsible for the products formed in the reactions of H and D atoms with benzene and the cycloalkanes as well as with normal paraffins. Other initial processes, however, may be responsible for the exchange of these hydrocarbons with D atoms.

Acknowledgments

The authors are indebted to Dr. L. Leitch for the preparation of the cyclobutane and the deuterium used in this research, to Dr. A. Cole for the infrared spectrum analysis of cyclobutane, and to Dr. F. P. Lossing and Miss Frances Gauthier for the mass spectrometer analyses of the reaction products.

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THE PAPILIONACEOUS ALKALOIDS

VIII. THE STRUCTURE OF THERMOPSINE[1]

By William F. Cockburn[2] and Léo Marion

Abstract

Thermopsine, an isomer of anagyrine, is associated with the latter in nature, but differs from it in chemical reactivity. Evidence, both chemical and from the infrared spectra, indicates that the molecule of thermopsine contains an α-pyridone ring, and possesses a structure closely related to that of anagyrine. Catalytic reduction of the alkaloid yields α-isosparteine, a stereoisomer of sparteine. It is therefore suggested that thermopsine is a stereoisomer of anagyrine, to which it bears the same relationship as α-isosparteine to sparteine. The stereochemistry of these bases is discussed.

Thermopsine, one of the Lupin alkaloids, was first isolated, in its levorotatory form, from *Thermopsis lanceolata* R. Br. by Orechov (10), who made a preliminary study of its properties. It was subsequently identified in *T. rhombifolia* (Nutt.) Richards by Manske and Marion (5), while more recently its optical enantiomorph, *d*-thermopsine,[3] has been found in one of the *Lupinus* species by Marion and coworkers (8).

The early structural investigation by Orechov (10) showed the alkaloid to be a strong, monoacidic tertiary base of empirical formula $C_{15}H_{20}N_2O$, with an optical rotation of $[\alpha]_D^{20} = -159.6°$ in ethanol, and having no active hydrogen in the molecule. The second nitrogen atom and the oxygen atom were found to be neutral, indicating the presence of an amide group, although the base, like lupanine, is stable to acids and alkalies. It rapidly decolorized potassium permanganate, and could be catalytically hydrogenated to give a crystalline tetrahydro derivative isomeric but not identical with lupanine. Since no active hydrogen was detected in this product, it was concluded that thermopsine contained two double bonds. Electrochemical reduction of thermopsine gave a crystalline solid in poor yield, having the empirical formula $C_{15}H_{28}N_2O$. It had a melting point of 112–113°C., $[\alpha]_D = +55.9°$, and was found to contain one active hydrogen. Orechov (9) concluded from the analytical results that this derivative had been formed by ring cleavage, and assumed, on the basis of a weak Liebermann test with nitrous acid, that it contained a secondary

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[2] *National Research Council of Canada Postdoctorate Fellowship holder.*

[3] *dl-Thermopsine, made by mixing equal weights of the d- and l-base, crystallized from acetone in prisms, m.p. 171–173°C. (corr.). The picrate crystallized from methanol–acetone, in both needles and square plates. The melting point was 250–251°C. (corr.) if the sample was dried in vacuo, or was heated slowly, but insertion of the undried salt at any temperature over 200°C. caused immediate frothing due to loss of solvent, the sample then resolidifying and melting again at 251°C. This phenomenon was obtained only with one sample of picrate, however, and may explain the melting point 208–209°C. quoted by Orechov (10) for l-thermopsine picrate. Solvation thus apparently depends on the exact conditions of crystallization. The perchlorate crystallized from methanol in clusters of cottony needles, m.p. 260–263°C. (uncorr.).*

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nitrogen atom. Thermopsine itself failed to add cyanogen bromide, while its methiodide and that of tetrahydro thermopsine gave completely negative results with the Hofmann and Emde methods of degradation, the bases being recovered unchanged.

Thermopsine is isomeric with anagyrine, the two bases being found associated in nature (5, 11, 6). Their infrared spectra, taken in carbon disulphide solution with a rock-salt prism, although different, show a striking similarity (Fig. 1). There is also strong spectroscopic evidence for the presence in thermopsine, as in anagyrine, of an α-pyridone ring. In the table, the position of the infrared carbonyl peak for thermopsine is compared with those of several other alkaloids containing the lactam grouping (7). It is readily seen that the frequency of the thermopsine band is almost identical with those of anagyrine, cytisine, and N-methylcytisine, the only members of the series whose lactam group is incorporated in an α-pyridone ring, while differing more or less markedly from the others. Furthermore, in tetrahydrothermopsine, the peak is shifted from 1653 cm.$^{-1}$ to 1613 cm.$^{-1}$, this value being close to that for lupanine, which contains an α-piperidone ring, and is the hydrogenation product of anagyrine. The difference of nine wave numbers may be attributable to greater susceptibility to deformation of the piperidone ring as compared with the more rigid pyridone ring. The above evidence is reinforced by the fact that thermopsine gives a red color with aqueous ferric chloride, a reaction given by other compounds containing an α-pyridone ring.

The two double bonds and the neutral oxygen and nitrogen atoms are thus accounted for, and it remains to determine the basic skeleton of the alkaloid. In spite of its obvious relationship with anagyrine, thermopsine behaves rather differently towards many of the standard chemical reagents. Since most of

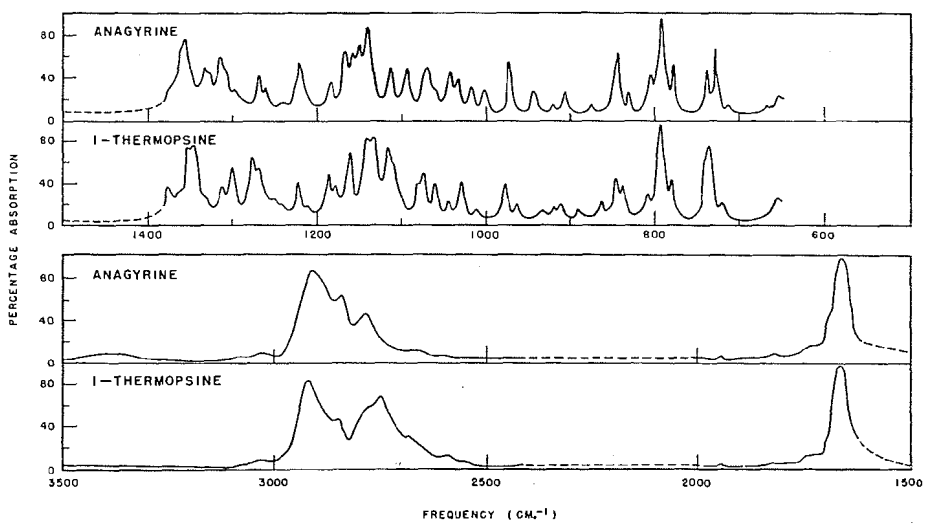

FIG. 1. *Infrared spectra measured on Perkin–Elmer spectrometer with sodium chloride prism, 1 mm. cell. Alkaloids in carbon disulphide solution, 10 mgm. per ml.*

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TABLE I

POSITION OF THE CARBONYL PEAK IN THE INFRARED SPECTRA OF ALKALOIDS CONTAINING THE LACTAM GROUP*

Alkaloid (α-Pyridones)	Wave number, $cm.^{-1}$	Alkaloid (α-Piperidones)	Wave number, $cm.^{-1}$
Thermopsine	1653	Tetrahydrothermopsine	1613
Anagyrine	1652	Lupanine	1622
Cytisine	1653	Aphyllidine	1628
N-methylcytisine	1653	Oxosparteine	1636
		Hydroxylupanine	1624

* *Spectra were taken in chloroform solution, using a calcium fluoride prism.*

these results are negative, it is not proposed to describe them in great detail here, but some may be mentioned. Whereas anagyrine is readily oxidized by barium permanganate to anagyramide (2) thermopsine is unattacked by mild oxidizing agents such as hydrogen peroxide and potassium ferricyanide, and completely broken down by permanganate and lead tetraacetate, giving only unidentified gums and oils, along with unchanged thermopsine, even after addition of 12 atoms of oxygen. Ozonolysis gave only undistillable amorphous products, again in contrast to anagyrine, while the base distilled unchanged from zinc dust at 400°C. Dehydrogenation with selenium at 300°C. gave a complex mixture of bases, which could be separated by a series of chromatograms into at least nine pure substances, all of which were still of relatively high molecular weight, and were in insufficient amount for further degradation. These compounds are listed in the experimental section.

The most useful information has come from hydrogenation with platinum oxide catalyst in hydrochloric acid solution. Using this method, Galinovsky has carried out an interesting series of reactions in the sparteine group of alkaloids, which consisted of the conversion of pyridone and piperidone rings to the fully saturated form, without causing any alteration in the basic skeleton (1). Thus *d*-lupanine was converted to *l*-sparteine, anagyrine to *d*-sparteine, and cytisine to tetrahydrodesoxy cytisine. When thermopsine was hydrogenated under these conditions, and the reaction interrupted after an uptake of two molecules of hydrogen, relatively impure[4] tetrahydrothermopsine was obtained (10). If the reaction were allowed to go to completion, however, four molecules of hydrogen were absorbed, with the formation of a fully reduced compound of empirical formula $C_{15}H_{26}N_2$, isolated as the hydrate, which was identical in its properties with the hydrate of "α-isosparteine" obtained by Winterfeld and Rauch (12) by hydrogenation of α-didehydrosparteine, and by

[4]*A purer product was obtained by carrying out the reaction in glacial acetic acid, the reaction then stopping at the tetrahydro stage. Our compound differed markedly in its properties from that described by Orechov (10), however. (See Experimental section.) While it is theoretically possible to obtain two stereoisomers on saturation of ring A, it appears that the remainder of the molecule exerts sufficient influence to give a substantially pure product.*

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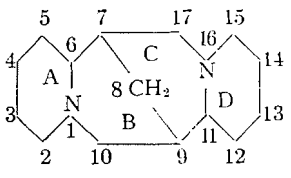
Leonard and Beyler (3) as a by-product in their synthesis of sparteine. Thus *l*-thermopsine gave *d*-α-isosparteine, while *d*-thermopsine gave *l*-α-isosparteine.[5] Identity was confirmed by direct comparison with *l*-α-isosparteine obtained from *l*-sparteine (3, 12). No sparteine was detected in the product, which again indicates that saturation of the carbon atom at position 6 with platinum oxide catalyst gives but one of the two possible configurations (cf. footnote 4).

The relationship between thermopsine and anagyrine must therefore be similar to that between α-isosparteine and sparteine, and the problem becomes one of stereochemistry. Thus sparteine and α-isosparteine can be represented by formula I, lupanine and tetrahydrothermopsine (or "α-isolupanine") by II, and anagyrine and thermopsine (or "isoanagyrine")[6] by III.



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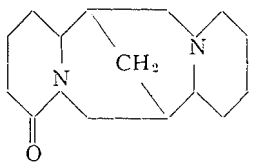
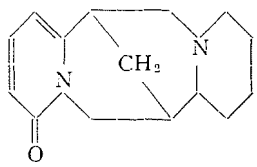


II



III

The stereochemistry of the sparteines has been discussed fully by Leonard and Beyler (3). Of the four asymmetric carbon atoms in the molecule, Nos. 7 and 9 are fixed by the rigid methylene bridge, leaving only Nos. 6 and 11 to be considered; and the relationship between these depends on whether the attached hydrogen atoms are *cis* or *trans* to the C_8 methylene bridge. There are thus four modifications possible for the lupanine skeleton (II), each capable of existence as *d*- or *l*-isomers, but only three for sparteine, which possesses a twofold axis of symmetry through carbon atom No. 8. Since the α-pyridone alkaloids (III) possess no hydrogen atom on carbon atom No. 6, however, we only have to consider the configuration on No. 11; and there are thus only twe pairs of enantiomorphs possible, one in which the hydrogen atom is *cis*, and the other *trans*. It is impossible on present evidence, however, to assign these structures finally between thermopsine and anagyrine. Both *d*- and *l*-thermopsine, and *l*-anagyrine are now known, and only *d*-anagyrine remains to be found in nature.

Experimental[7]

Oxidation

(1) Thermopsine, 0.244 gm. (0.001 mole), was dissolved in 20 ml. water at room temperature, and 1 ml. of 30% hydrogen peroxide added. No reaction was observed, the base being recovered unchanged even after several weeks. (2)

[5]*It is almost certain that the "ring-cleavage product" obtained by Orechov (9) by electrochemical reduction of thermopsine was d-α-isosparteine hydrate.*

[6]*Because of the presence of an α-pyridone ring in the molecule, only one "isoanagyrine" is possible, and the "α" can be discarded.*

[7]*All melting points are corrected, unless otherwise stated.*

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Thermopsine, 0.976 gm. (0.004 mole), was dissolved completely in 100 ml. of water, and the solution treated at room temperature with 5.264 gm. (0.016 mole) of potassium ferricyanide and 0.8 gm. (0.020 mole) of sodium hydroxide in 20 ml. of water. The mixture was examined after standing for 60 hr., when 0.723 gm. of thermopsine was recovered unchanged, along with a small quantity of unidentified oils. (3) Thermopsine, 0.488 gm. (0.002 mole), in 50 ml. water was treated gradually with 10% aqueous barium permanganate (0.5 gm.) at 25°C. After filtration from manganese dioxide, the aqueous solution was examined for products, but only starting material could be identified. (4) A solution of thermopsine in acetone containing 5–10% water was treated with varying amounts of powdered potassium permanganate, the reaction being kept approximately neutral by the addition of glacial acetic acid. The precipitated manganese dioxide was converted to manganese sulphate by means of gaseous sulphur dioxide, and removed by filtration. The acetone solution yielded a variety of unidentified oily products, along with unchanged starting material. (5) Thermopsine, 0.244 gm. (0.001 mole), was dissolved in dry benzene, and treated with solid lead tetraacetate until a positive test was obtained with starch–iodide paper. The end point was indefinite, but the reaction was stopped after the addition of 1.700 gm. (0.004 mole) of reagent. After filtration, the clear yellow solution was examined for products, but only a small amount of unchanged base could be identified.

Ozonolysis

A solution of 0.488 gm. (0.002 mole) of thermopsine in carbon tetrachloride was treated with 0.2 gm. (0.004 mole) of ozone, with the formation of a greenish-white flocculent precipitate. Water was added, and the carbon tetrachloride distilled off on the steam bath, leaving a red aqueous solution. Some sodium bisulphite was added, followed by excess ammonium hydroxide, and the solution extracted with chloroform, giving a pale amber solution. Removal of the solvent yielded a brown gummy residue which failed to give rise to derivatives, and could not be distilled up to 210°C. at 0.1 mm. pressure.

Zinc Dust Distillation

Powdered thermopsine was mixed intimately with 25 times its weight of zinc dust, and placed in a Pyrex tube between plugs of pure zinc dust. Provision was made for trapping the emergent gases in "Dry Ice". A slow stream of dry nitrogen was passed through the apparatus and the tube heated in an electric oven to 400–430°C. The bulk of the material was found to distill unchanged.

Dehydrogenation with Selenium

Thermopsine (2.84 gm.) was heated with 8 gm. of black selenium in a slow stream of nitrogen, at 300°C. for five hours, provision being made for trapping the escaping vapors in "Dry Ice". After cooling, the reaction mixture was triturated with hot benzene, until nothing further would dissolve. The yellow

benzene solution was extracted with dilute hydrochloric acid, the aqueous solution basified, and exhausted first with ether, then with chloroform. The latter extract was concentrated, and the residual oil distilled in vacuum, giving a yellow oil and a yellow solid. The oil failed to form derivatives but the solid could be recrystallized from benzene – petroleum ether in cream-colored needles, m.p. 143°C. Calc. for $C_{15}H_{18}N_2O$: C, 74.35; H, 7.49; N, 11.57. Found: C, 74.47; H, 7.18; N, 11.59. The infrared spectrum was taken in chloroform with a calcium fluoride prism, and showed peaks at 1653 cm.$^{-1}$ (probably α-pyridone carbonyl), 1613 cm.$^{-1}$, and 3385 cm.$^{-1}$ (probably NH).

The ether extract above was concentrated to an oil, and the mixture of bases separated by repeated chromatography on alumina of activity II into eight pure substances and several fractions which could not be characterized. None of these was obtained in sufficient quantity for further study, and, in most cases, only the picrate was isolated, the free base being oily. These compounds are listed briefly below:—

1. Bright yellow needles, m.p. 137-138°C. Calc. for $C_{15}H_{12}N_2O$: C, 76.22; H, 5.12; N, 11.86. Found: C, 76.57, 76.63; H, 4.96, 4.79; N, 12.50. The infrared spectrum was taken in chloroform with a calcium fluoride prism, and showed peaks at 1633 cm.$^{-1}$, 1661 cm.$^{-1}$ (probably carbonyl), and 1590 cm.$^{-1}$ (probably aromatic heterocyclic nucleus) with smaller peaks at 1552 cm.$^{-1}$ and 3593 cm.$^{-1}$. This compound formed orange-red salts, possibly indicating a mesomeric distribution of the ionic charge between the two nitrogen atoms, a type of behavior reminiscent of the quinolinoquinolines (4).

Perchlorate. Red-orange rectangular plates, m.p. 244°C. Calc. for $C_{15}H_{12}N_2O.HClO_4$: C, 53.52; H, 3.89, N, 8.33. Found: C, 53.06; H, 3.88; N, 7.70.

Picrate. Orange flocculent needles, m.p. 213–216°C. (dec.).

Hydrochloride. Orange clusters of needles, m.p. 200–205°C. (dec.).

2. Picrate only. Yellow feathery needles, which melted at 192–193°C., then resolidified and melted again at 216–217°C. Calc. for $C_{15}H_{20}N_2.2C_6H_3N_3O_7$: C, 47.24; H, 3.82; N, 16.32. Found: C, 47.56, 47.72; H, 3.73, 3.72, N, 16.14.

3. Picrate only, yellow parallelogram-shaped prisms, m.p. 219–221°C. Calc. for $C_{15}H_{16}N_2.2C_6H_3N_3O_7$: C, 47.51; H, 3.25; N, 16.43. Found: C, 47.48, 47.51; H, 3.23, 3.18; N, 16.33, 16.15.

4. Picrate only, yellow spear-shaped needles, m.p. 174–175°C. Calc. for $C_{14}H_{16}N_2.C_6H_3N_3O_7$: C, 54.43; H, 4.34; N, 15.87. Found: C, 54.40, 54.26; H, 4.50, 4.33; N, 15.45, 15.66.

5. Perchlorate only, long colorless prismatic needles, m.p. 187–188°C. Calc. for $C_{14}H_{17}N.HClO_4$: C, 56.10; H, 6.05; N, 4.67. Found: C, 56.25; H, 6.37; N, 4.57.

6. White crystalline solid, m.p. 101–102°C. Calc. for $C_{14}H_{11}N$: C, 87.02; H, 5.74. Found: C, 87.28; H, 5.20.

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Picrate. Pale yellow needles, m.p. 238–239°C. Calc. for $C_{14}H_{11}N.C_6H_3N_3O_7$: C, 56.89; H, 3.34; N, 13.27. Found: C, 57.58, 57.38; H, 3.28, 3.15; N, 13.03, 12.83.

Perchlorate, very fine needles, m.p. 290–295°C. (dec.).

7. Picrate only. Long yellow needles, m.p. 197–199°C. Calc. for $C_{13}H_{12}N_2.C_6H_3N_3O_7$: C, 53.65; H, 3.55; N, 16.46. Found: C, 53.81, 53.94; H, 3.81, 3.90, N, 16.73.

8. Picrate only. Long yellow needles, m.p. 233–234°C. Insufficient for analysis.

Hydrogenation

(*1*) *Tetrahydrothermopsine*

l-Thermopsine, 0.488 gm. (0.002 mole) was dissolved in 20 ml. glacial acetic acid plus 500 mgm. of platinum oxide catalyst and hydrogenated at slightly increased pressure at 25°C. Absorption of hydrogen after three hours was 170 ml. Saturation of two double bonds requires 103 ml., plus approximately 90 ml. to activate the catalyst. The solution was filtered from the catalyst, and the acetic acid removed by vacuum distillation. The oily residue was dissolved in 25 ml. of water, and 25% sodium hydroxide solution slowly added dropwise, yielding a crystalline precipitate which was filtered off. The base was dissolved in ethanol, and treated with fuming hydriodic acid, whereupon a yellowish hydriodide separated in sheaves of needles. After one recrystallization, this salt melted at 293°C. (uncorr.) with decomposition. (Orechov reports a m.p. of 295–296°C. for this compound (10).) On treatment with alkali, extraction with ether, and distillation, 330 mgm. of the hydriodide yielded 206.5 mgm. of free base in a pure condition, or 62.6% by weight of the salt, compared with a theoretical 66% for the monohydriodide. If the formula were $C_{15}H_{24}N_2O.2HI.3CH_3OH$ as claimed by Orechov, the proportion of free base would be only 41.3%. An elementary analysis has not yet been obtained of this salt, however, and the matter must remain in doubt. The free base was crystallized twice from petroleum ether (b.p. 65°C.), being obtained in rectangular plates, m.p. 74–75°C. Orechov reports this as 75.5–76.5°C. (10). Cooling the mother liquors in the refrigerator yielded a further crop with a m.p. 73–80°C., which changed on standing at room temperature for some weeks to 74–75°. This is apparently due to the existence of isomorphous forms of the free base. Calc. for $C_{15}H_{24}N_2O$: C, 72.52; H, 9.74; N, 11.29. Found: C, 72.08, 71.90; H, 10.17, 10.00; N, 10.98. $[\alpha]_D^{26} = -64.3°$ (*c*, 2.44 in ethanol). The rotation given by Orechov (10) for tetrahydrothermopsine is $[\alpha]_D = -52.23°$ (*c*, 8.5 in ethanol). The infrared spectrum was taken in chloroform solution using a calcium fluoride prism, and showed a large peak at 1613 $cm.^{-1}$

The picrate was made by addition of one equivalent of picric acid in ethanol, and purified by recrystallization from the same solvent. Yellow needles, m.p. 196–198°C. (dec.). Calc. for $C_{15}H_{24}N_2O.C_6H_3N_3O_7$: C, 52.82; H, 5.70.

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Found: C, 52.90, 53.06; H, 5.67, 5.87. Orechov reports a m.p. of 143–144°C. for his picrate but gives no analytical data.

The perchlorate was obtained in prismatic needles, m.p. 237°C. (uncorr.) with decomposition, when introduced into the bath at 220°C. The hydrobromide was prepared in methanol, being obtained in flat, spearlike needles, but its melting point was subject to great variation, depending on the exact technique employed, and was useless as a means of characterization.

(*2*) *α-Isosparteine*

l-Thermopsine, 0.488 gm. (0.002 mole), was dissolved in 30 ml. of *N* hydrochloric acid, plus 300 mgm. of platinum oxide catalyst, and hydrogenated at slightly increased pressure and 25°C. (8). The absorption of gas in five hours was 248 ml., as compared with a theoretical value of 203 ml. for four molecules of hydrogen, plus 50 ml. for activation of the catalyst. The solution was filtered, basified with ammonium hydroxide, and extracted thoroughly with ether. The ether solution was dried with potassium carbonate, and the solvent removed by distillation, leaving an oily residue. This was dissolved in 15 ml. ethanol, the solution concentrated, and water added dropwise in the hot to incipient turbidity. On cooling, the solution deposited flat colorless needles, m.p. 98–114°C., this figure being unaltered by recrystallization from aqueous ethanol. (Reported for *l*-α-isosparteine, 98–115°C. (3).) Calc. for $C_{15}H_{26}N_2.H_2O$: C, 71.38; H, 11.18; N, 11.10. Found: C, 71,57, 71.44; H, 11.48, 11.30; N, 11.37. $[\alpha]_D^{24} = +55.6°$(*c*, 3.290 in methanol). (Reported for *l*-α-isosparteine $[\alpha]_D^{30} = -55.8°$ (*c*, 7.216 in methanol (3)).)

The hydrate was slowly sublimed along a Pyrex tube at 50°C. (0.2 mm.), and the tube sealed. The anhydrous base was obtained in colorless plates, m.p. 65°C. An analysis could not be obtained, however, owing to rapid formation of the hydrate in air.

Dipicrate.—The hydrate (76 mgm.) in ethanol was treated with 138 mgm. of picric acid and the solution boiled. On cooling, 147 mgm. of small yellow rhombic crystals separated, which, after one recrystallization from aqueous ethanol, melted with decomposition at 222°C., with previous darkening at 210°C. (Reported 221° (dec.)(3).) Calc. for $C_{15}H_{26}N_2.2C_6H_3N_3O_7$: C, 46.82; H, 4.66. Found: C, 46.71; H, 5.06.

Monopicrate.—The hydrate (76 mgm.) in ethanol was treated with 69 mgm. of picric acid, and the solution cooled slowly, giving starlike clusters of very fine needles, which, after two recrystallizations from ethanol had a m.p. of 118–119°C. Calc. for $C_{15}H_{26}N_2.C_6H_3N_3O_7$: C, 54.42, H, 6.30. Found: C, 54.15, 54.33; H, 6.43, 6.57.

Diperchlorate.—Concentrated aqueous perchloric acid was added dropwise to an ethanolic solution of the hydrate until the solution was acid to Congo red. The salt was obtained in feathery colorless crystals, which after recrystallization from methanol, had a m.p. of 252–255°C. (uncorr.). Calc.

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for $C_{15}H_{26}N_2.2HClO_4$: C, 41.38; H, 6.48. Found: C, 41.57, 41.51; H, 6.21, 6.34.

Bisulphate.—This was prepared by the addition of methanolic sulphuric acid to an ethanolic solution of the hydrate. After recrystallization from ethanol, the m.p. was 263°C. (uncorr.) (Reported 267°C. (dec.)(3).)

The same treatment of *d*-thermopsine yielded *l*-α-isosparteine, m.p. 98–114° C. $[\alpha]_D^{26} = -55.2°$ (*c*, 3.425 in methanol). *l*-α-Isosparteine was also prepared from *l*-sparteine (10, 11), and obtained in flat white needles, m.p. 97–115°C. $[\alpha]_D^{26} = -55.3°$ (*c*, 4.975 in methanol). A mixture of the two samples melted at 98–115°C. The dipicrates of both were prepared, and melted, either alone or in admixture, at 222°C. (dec.).

Acknowledgment

The absorption spectra were taken by Dr. R. N. Jones and Mr. R. Lauzon, of these laboratories, whose courtesy is gratefully acknowledged.

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THE PAPILIONACEOUS ALKALOIDS

IX. NATURAL OCCURRENCE OF THE ALKALOIDS OF THE α-ISOSPARTEINE GROUP[1]

By Léo Marion, François Turcotte, and Jacques Ouellet

Abstract

The species of *Lupinus* under investigation has been found to contain five alkaloids: *l*-α-isosparteine, *d*-α-isolupanine, *d*-thermopsine, *l*-sparteine and *d*-lupanine. The first three had not heretofore been reported as occurring in nature. Both *d*-α-isolupanine and *d*-thermopsine can be converted by hydrogenation into *l*-α-isosparteine and are both structurally related to this stereoisomer of sparteine.

In his investigation of *Lupinus caudatus* Kellogg, Couch (4) reported the occurrence of only one alkaloid, monolupine, which has since been shown by two of us to be identical with anagyrine (8). It was of interest to reinvestigate this plant in order to obtain a supply of monolupine (anagyrine) and also to ascertain whether other alkaloids might not be found as well. The plant collected for us through the kindness of S. B. Penick Inc. was identified as *Lupinus caudatus* Kellogg. It was not possible, however, to isolate any anagyrine from this plant,[2] but it was found to contain five alkaloids, three of which were of very marked interest because of their structural relationship. Of the five alkaloids two, *l*-sparteine and *d*-lupanine were well known. The remaining three, however, alkaloids P5, P6, P7, had not heretofore been reported as occurring in nature.

Winterfeld and Rauch (11) have described a stereoisomer of sparteine that they called α-isosparteine and that they obtained from *l*-sparteine by dehydrogenation followed by catalytic hydrogenation. Later, Leonard and Beyler (6) obtained the racemic α-isosparteine as a by-product in their synthesis of sparteine and they discussed the stereochemical relationship of the two compounds. It is probable that the base obtained by Sorm and Keil (10) by the electrolytic reduction of their higher melting synthetic dioxosparteine and isolated as a dipicrate melting at 222°C., was also racemic α-isosparteine. Alkaloid P5 is a levorotatory crystalline base forming a picrate and a perchlorate shown by melting point and mixed melting point to be identical with *l*-α-isosparteine prepared from *l*-sparteine by the method of Winterfeld and Rauch (11).

Alkaloid P6 is a crystalline dextrorotatory base forming a crystalline picrate and crystalline perchlorate. *l*-Thermopsine, previously isolated from *Thermopsis lanceolata* R. Br. (9) and *Thermopsis rhombifolia* (Nutt.) Richards (7),

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[2] *Since this plant was collected in the autumn and was very much withered, it is possible that the botanical identification may not have been definite. Hence, for the present, the identity of the plant investigated must, unfortunately, remain uncertain.*

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and its picrate and perchlorate have the same melting points as alkaloid P6 and its corresponding salts. Furthermore, the optical rotation of the two bases are identical numerically, but of opposite signs. That alkaloid P6 is *d*-thermopsine, the optical antipode of *l*-thermopsine was confirmed by a comparison of the infrared absorption spectra (Fig. 2) of the two bases: these are superposable. Recently, the structure of thermopsine has been established and it has been shown that this base is related to α-isosparteine in the same way that anagyrine is related to sparteine (3) so that *d*-thermopsine could be termed *d*-isoanagyrine.[3]

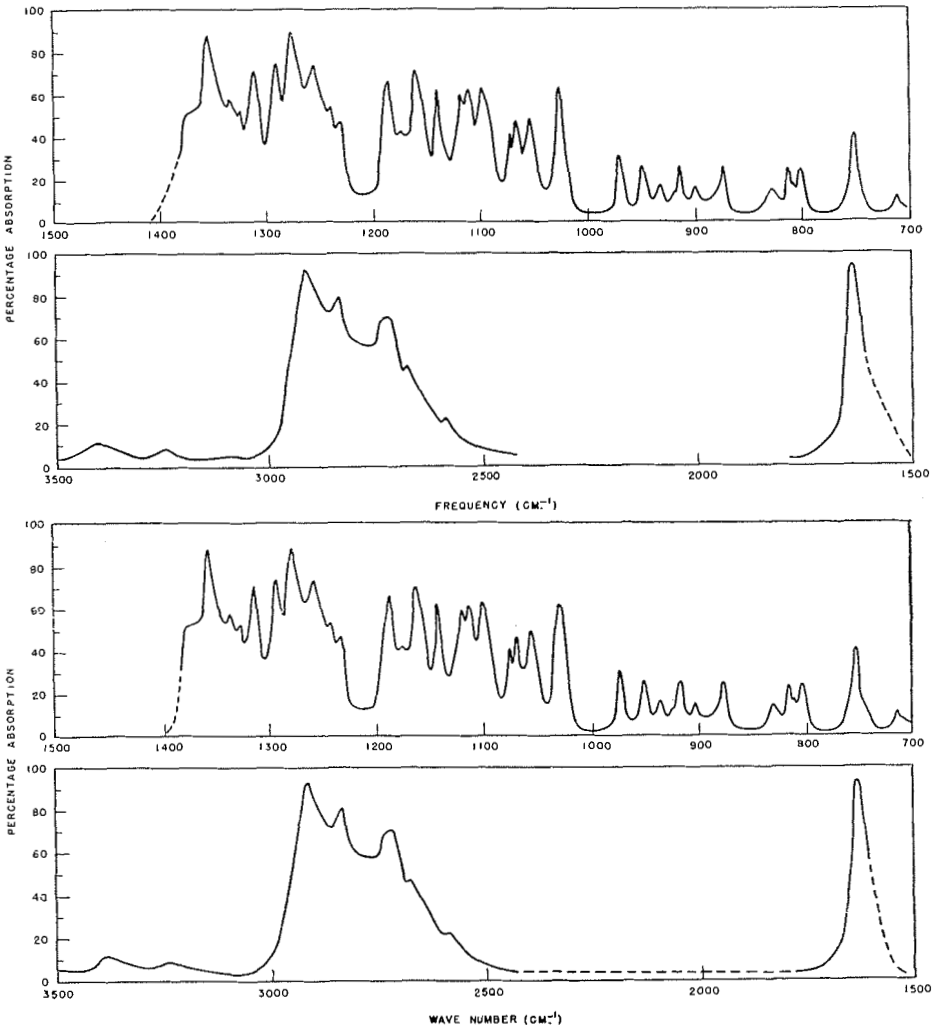

FIG. 1. *Infrared spectra of l-tetrahydrothermopsine (top) and d-α-isolupanine (bottom), measured on a Perkin–Elmer 12B single beam spectrometer with sodium chloride prism, 1 mm. cell. The alkaloids were in carbon disulphide solution, 10 mgm. per ml.*

[3]*Since one of the end rings in anagyrine is an α-pyridone, only one enantiomorph of the iso series is possible. Hence d-thermopsine need not be termed d-α-isoanagyrine.*

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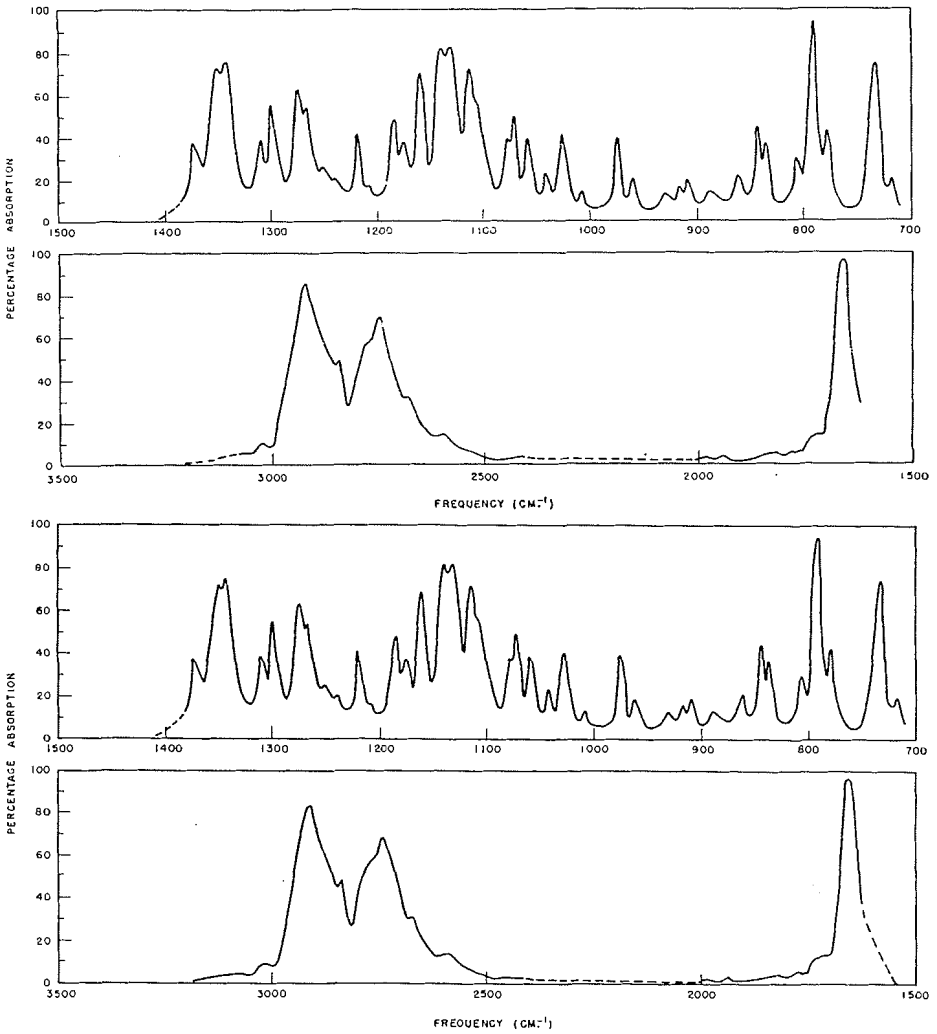

FIG. 2. *Infrared spectra of l-thermopsine (top) and d-thermopsine (bottom), measured in carbon disulphide solution (10 mgm. per ml.) on a Perkin–Elmer 12B single beam spectrometer with sodium chloride prism, 1 mm. cell.*

It has further been shown by the same authors (3) that catalytic hydrogenation converts *l*-thermopsine into *l*-tetrahydrothermopsine ($C_{15}H_{24}ON_2$), an isomer of lupanine. The infrared absorption spectrum of this reduction product was identical with that of the new alkaloid, P7, (Fig. 1) and the melting points of the bases were identical. The melting points of the picrates and perchlorates of both bases were also identical. However, whereas our sample of tetrahydrothermopsine was levorotatory, alkaloid P7 was dextrorotatory. Hence, alkaloid P7 is the optical antipode of *l*-tetrahydrothermopsine. This conclusion was further confirmed by the fact that whereas the catalytic hydrogenation of *l*-thermopsine in 2*N* hydrochloric acid gave rise to *d*-α-iso-

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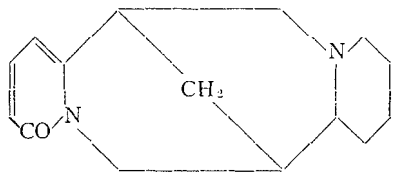
sparteine (3), the reduction of alkaloid P7 with lithium aluminum hydride gave rise to *l*-α-isosparteine, identical with alkaloid P5. The elucidation of the structure of thermopsine (I) together with the fact that *l*-tetrahydrothermopsine is the optical antipode of alkaloid P7 locates the oxygen in this base which must be represented by II. It is proposed to name alkaloid P7, *d*-α-isolupanine,[4] which indicates its relationship to *l*-α-isosparteine.



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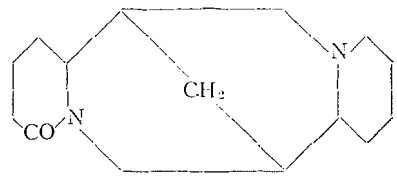

II

The three new alkaloids isolated from this plant, i.e., *l*-α-isosparteine, *d*-α-isolupanine and *d*-thermopsine bear the same relationship to each other as *l*-sparteine, *d*-lupanine and *d*-anagyrine. It is interesting to note that α-isosparteine was obtained synthetically (6) before its present isolation from a plant.

Experimental

The plant material used was collected in October when it was already wilted (cf. footnote 2). The dried and ground plant weighed 4252 gm. It was extracted in Soxhlets with methanol and the extract evaporated on the steam bath until the solvent was largely removed. Water was added to the concentrated extract, the mixture made acid to Congo red with hydrochloric acid and heated on the steam bath for 12 hr. It was cooled first to room temperature, then in the refrigerator and filtered on a Büchner funnel. The insoluble filter cake was heated once more with dilute hydrochloric acid, cooled, and filtered. The combined filtrates were extracted with ether (discarded), alkalized with ammonia, and extracted repeatedly with chloroform. On evaporation, the chloroform extract left a gummy basic residue (wt. 13.5 gm.).

The basic residue was dissolved in warm 2*N* hydrochloric acid, the solution filtered through charcoal to remove a quantity of insoluble material, and the filtrate extracted thoroughly with ether. The aqueous solution was alkalized with ammonia and extracted with chloroform in a continuous liquid–liquid extractor. Evaporation of the extract on the steam bath under reduced pressure left a brown, oily, basic residue (wt. 8.58 gm.) that partly crystallized on standing. This residue was triturated with 25 ml. portions of cold acetone until all the acetone-soluble material had been removed. The acetone-insoluble

[4]*Clemo and Leitch (1) have used the term "isolupanine" to designate an isomer of lupanine that they obtained by reduction of an oxidation product of lupanine. However, since this isolupanine was subsequently shown to be identical with oxosparteine, the oxidation product of sparteine, the term was abandoned (2). It seems legitimate, therefore, to revive it to designate alkaloid P7, to which it fits so well. An alkaloid (m.p. 75.5–76°,* $[\alpha]_D^{15}$ *+ 34.6°, aurichloride, m.p. 190°, dec.), isomeric with lupanine was isolated from* Lupinus angustifolius *by Kneuer (5a). This alkaloid, named lupanidine, may possibly be identical with α-isolupanine.*

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residue contained only resinous substances that did not distill at 220°C. (0.1 mm.). When concentrated and cooled, the acetone solution deposited a small quantity of crystals that were filtered and will be described further on.

The mother liquor from which the crystals had been filtered was evaporated to dryness and the residual bases fractionated *in vacuo*. Three main fractions were obtained: fraction I, b.p. 70–85°C. (0.1 mm.), a colorless oil that crystallized on standing, wt. 0.585 gm.; fraction II, b.p. 115–130°C. (0.1 mm.), a viscous oil, wt. 1.02 gm.; fraction III, b.p. 160–170°C. (0.1 mm.), a white sublimate accompanied by a yellow oil, wt. 1.762 gm.

l-α-Isosparteine

Fraction I was crystallized from boiling acetone from which the base separated on cooling as colorless flat needles melting at 108–110°C. In admixture with *l-α*-isosparteine prepared from *l*-sparteine as described by Winterfeld and Rauch (11) and by Leonard and Beyler (6), the melting point was undepressed. Calc. for $C_{15}H_{26}N_2.H_2O$: C, 71.38; H, 11.11; N, 11.11%. Found: C, 70.99, 71.05; H, 11.07, 11.20; N, 10.74, 10.81%. $[\alpha]_D^{22}$ −51.3° (c = 0.696 in absolute ethanol). Leonard and Beyler (6) report $[\alpha]_D$ −55.3° in methanol.

Some of the base (110 mgm.) was dissolved in methanol and added to a solution of picric acid (190 mgm.) in methanol. A picrate separated immediately which, after three recrystallizations from acetone–methanol, melted at 220–221°C. either alone or in admixture with *l-α*-isosparteine dipicrate. Calc. for $C_{15}H_{26}N_2.2C_6H_3O_7N_3$: C, 46.80; H, 4.62; N, 16.18%. Found: C, 46.46, 46.50; H, 3.87, 4.03; N, 16.01%.

A further quantity of the base (100 mgm.) was dissolved in methanol and the solution made just acid to Congo red by the dropwise addition of 65% perchloric acid. Crystallization of the salt was initiated by dilution of the solution with ether. It sintered at 250–255°C. and melted at 262–263°C., either alone or after admixture with *l-α*-isosparteine diperchlorate. Calc. for $C_{15}H_{26}N_2.2HClO_4$: C, 41.38; H, 6.43; N, 6.43%. Found: C, 41.24, 41.36; H, 6.42, 6.49; N, 6.45, 6.24%.

d-α-Isolupanine

Fraction II was dissolved in methanol and the solution made just acid to Congo red by the cautious addition of 65% perchloric acid. Ether was added to incipient turbidity and the crystalline salt that separated was filtered. After several recrystallizations from methanol–ether and finally from methanol, the perchlorate melted at 248–249°C. Calc. for $C_{15}H_{24}ON_2.HClO_4$: C, 51.64; H, 7.22; N, 8.03%. Found: C, 51.65, 51.71; H, 7.23, 7.03; N, 7.91, 7.92%.

A small quantity of the pure perchlorate was dissolved in water, the solution alkalized with ammonia and extracted with chloroform. Evaporation of the chloroform extract left a residue which was distilled, b.p. 110–120°C. (0.1 mm.), and crystallized from petroleum ether. The free base thus obtained consisted

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of colorless rectangular plates, m.p. 83–84°C. (It is noteworthy that *l*-tetrahydrothermopsine (3), the optical antipode of *d*-α-isolupanine, melted at 75–76°C. After keeping for some time *d*-α-isolupanine no longer melted at 83–84°C., but at 75–76°C. This behavior is probably due to isomorphism). $[\alpha]_D^{23}$ + 65.9° (c = 1.495 in absolute ethanol). Calc. for $C_{15}H_{24}ON_2$: C, 72.57; H, 9.67; N, 11.30%. Found: C, 72.25, 72.44; H, 8.96, 9.11; N, 11.33, 11.50%. The picrate of the base was prepared in ethanol; after recrystallization from the same solvent it consisted of long, yellow needles, m.p. 197–198°C. The infrared absorption spectrum of the base which contains a carbonyl absorption band, is identical with that of *l*-tetrahydrothermopsine (3), Fig. 1.

Reduction of α-Isolupanine

In a dry apparatus containing a solution of *d*-α-isolupanine (62 mgm.) in anhydrous ether (5 ml.) under a slight pressure of nitrogen, a 2% solution (1.5 ml.) of lithium aluminum hydride in anhydrous ether was added dropwise. A flocculent white precipitate formed immediately and the mixture was refluxed for 90 min. To the cooled reaction mixture, moist ether and then water were cautiously added and the aqueous layer separated and extracted four times with ether. The combined ether extract was dried over anhydrous sodium sulphate, evaporated to remove the solvent and the remaining residue was distilled *in vacuo*. An oil distilled at 70–80°C. (0.1 mm.) (wt. 8 mgm.) which crystallized from moist acetone as flat needles, melting at 102–104°C. and in admixture with *l*-α-isosparteine at 106°C. The picrate of the reduced base was prepared in methanol, and after five recrystallizations in acetone–methanol melted at 212–214°C., while in admixture with the dipicrate of *l*-α-isosparteine it melted at 214–216°C.

The residue left after the distillation of *l*-α-isosparteine yielded 20 mgm. of unchanged α-isolupanine.

d-Lupanine

The mother liquor from which the perchlorate of *d*-α-isolupanine had crystallized was evaporated to a small volume and allowed to stand. After two weeks a small quantity of impure crystals had separated. After two recrystallizations from methanol this perchlorate melted at 211°C. and did not depress the melting point of *d*-lupanine perchlorate on admixture. The base liberated from its perchlorate, boiled at 110–120°C. (0.1 mm.) and had $[\alpha]_D^{22}$ + 80.0° (c = 2.04 in absolute ethanol) in agreement with the value given in the literature (5) for *d*-lupanine.

The base (150 mgm.) was dissolved in methanol and added to an aqueous solution of ammonium thiocyanate (48 mgm.). The solution was evaporated to dryness on the steam bath and the residue crystallized from boiling acetone. The base thiocyanate sintered at 146°C. and melted at 183°C., either alone or in admixture with an authentic sample of *d*-lupanine thiocyanate.

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l-Sparteine

Fraction II, after separation of *d*-lupanine and *d*-α-isolupanine, still contained 250 mgm. of basic material. This was dissolved in benzene and chromatographed on a column of alumina. The benzene eluate yielded 86 mgm. of a mobile oil, b.p. 100–105°C. (0.1 mm.), that formed a picrate crystallizing from methanol in long yellow needles. After two recrystallizations the picrate melted at 207°C. either alone or in admixture with an authentic sample of *l*-sparteine dipicrate. Calc. for $C_{15}H_{26}N_2.2C_6H_3O_7N_3$: C, 46.80; H, 4.62%. Found: C, 46.79; H, 4.57%.

The base was liberated by shaking a suspension of the picrate in ether with 15% hydrochloric acid. The aqueous solution was freed of picric acid by repeated extraction with ether, alkalized with ammonia and extracted with chloroform. Evaporation of the chloroform left the base as an oily residue which after distillation *in vacuo* had $[\alpha]_D^{22} - 17.4°$ (c = 1.86 in absolute ethanol).

The 95% benzene – 5% ether eluate yielded a further 37 mgm. of *d*-lupanine characterized as its perchlorate. The 50% benzene – 50% ether eluate gave 53 mgm. of a mixture of *d*-lupanine and *d*-α-isolupanine, while the ether eluate yielded 44 mgm. of pure *d*-α-isolupanine, characterized as its perchlorate, m.p. 249°C.

d-Thermopsine

Fraction III, which was almost entirely crystalline, was dissolved in boiling acetone. On cooling, the solution deposited crystals consisting, after three recrystallizations from acetone, of colorless prisms, m.p. 207°C. This base was identical with the substance that had crystallized from the original acetone solution of the crude bases. $[\alpha]_D + 154.4°$ (c = 0.8 in absolute ethanol). A sample dried at 100° *in vacuo* was used for the analysis. Calc. for $C_{15}H_{20}ON_2$: C, 73.77; H, 8.20; N, 11.48%. Found: C, 73.92; H, 8.01; N, 11.56, 11.50%. The infrared absorption spectrum of this base was identical with that of *l*-thermopsine (Fig. 2) and therefore the base is the optical antipode of the latter.

A small quantity of the base was dissolved in methanol and the solution neutralized to Congo red by the dropwise addition of 70% perchloric acid. The perchlorate that separated crystallized from methanol as long, colorless needles, m.p. 289°C. Calc. for $C_{15}H_{20}ON_2.HClO_4$: C, 52.25; H, 6.10; N, 8.13%. Found: C, 52.14, 52.01; H, 6.20, 6.04; N, 8.05, 8.14%.

The base formed a picrate that crystallized from methanol as yellow needles, m.p. 253°C. Calc. for $C_{15}H_{20}ON_2.C_6H_3O_7N_3$: C, 53.28; H, 4.86; N, 14.80%. Found: C, 52.70, 52.86; H, 5.34, 5.32; N, 14.11, 14.21%. The melting points of the picrate and of the perchlorate were identical with those of the corresponding salts of *l*-thermopsine (7, 9).

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THE BIOGENESIS OF ALKALOIDS

II. THE ORIGIN OF THE METHYL GROUPS OF HORDENINE AND CHOLINE[1]

By Sam Kirkwood[2] and Léo Marion

Abstract

Potassium formate labeled with C^{14} was fed to sprouting barley, and choline and hordenine (N-dimethyltyramine) were isolated from the roots. Both of these substances bore the labeled carbon largely, if not entirely, in the methyl groups, as shown by means of degradation experiments. This indicates that the N-methyl groups of these compounds originate from formate ions.

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Introduction

The origin of the N-methyl groups of alkaloids is as yet obscure. It has been postulated that they arise from formaldehyde (1, 14), but there has been no direct experimental evidence for this route. The formaldehyde hypothesis undoubtedly had its origin in von Baeyer's theory of the biogenesis of glucose, coupled with the ease with which the Eschweiler reaction proceeds *in vitro* (5, 12). It has also been postulated that the N-methyl groups of alkaloids may arise by a process of transmethylation (14) analogous to that known to occur in animals (2). However, as Robinson has pointed out (14), this process would not, even if it were substantiated, be the primal origin of the groups. It would merely shift the problem back one step.

There is abundant evidence in the recent literature that formate is an extremely important intermediate in the metabolic processes of the higher animals (18, 19) and bacteria (3, 17). If one is prepared to accept the recent evidence that the folic acid group of vitamins functions as a carrier of formate (11) then it would follow that formate is an important metabolic intermediate in most, if not all, living cells. It has been shown that the methyl groups of methionine and choline are oxidized to carbon dioxide via formate in rat liver slices (18) and that formate is reduced to the methyl group of methionine both *in vivo* and *in vitro* (18, 19). Siekivitz and Greenberg (18) have postulated that the formation of formaldehyde may in some cases precede that of formate in biological oxidations; however, a great deal more experimental work is required to clarify the status of formaldehyde in these reactions.

Recent studies (8) have indicated that the synthesis of the alkaloid hordenine in barley roots proceeds by a stepwise methylation of tyramine entirely analogous to the synthesis of choline from ethanolamine by the mold *Neurospora crassa*. Since the recently established synthesis of "labile methyl" in the rat proceeds by way of formate (19) one would expect that the methyl groups of

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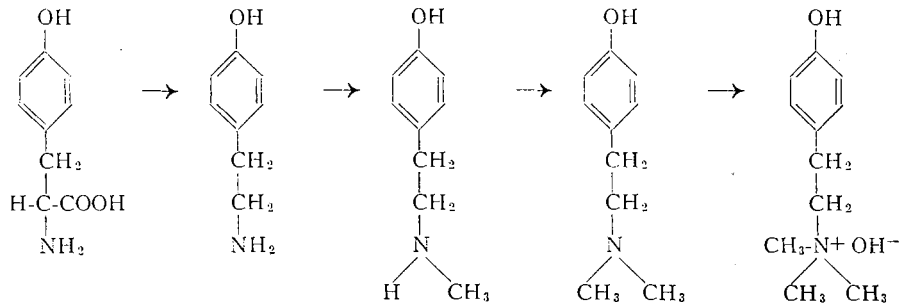
choline and hordenine in the barley plant might arise from the same source. If this proved to be the case one would have reasonable evidence for postulating the following route for the biosynthesis of the alkaloids N-methyltyramine (8), hordenine (12), and candicine (13).



With this in mind, we have studied the incorporation of labeled formate carbon into the methyl groups of both choline and hordenine by barley roots.

Experimental

Technique of Growing Barley and Administering Tracer

A 720 gm. sample of Charlottetown #80 barley was evenly divided among twelve 20 × 25 cm. Pyrex glass trays. Distilled water (50 ml.) was added to each tray and they were stored in a closed germination cabinet. The barley was watered daily by spraying with an atomizer. On the sixth day of sprouting a solution of 36 mgm. of potassium formate containing a total of 5.0×10^7 counts per minute of C^{14} was fed to the barley[3] (total solution 240 ml., 20 ml. per tray).

The barley was harvested on the 11th day of sprouting and the roots worked up as described previously (8). Although Charlottetown #80 produced hordenine and not N-methyltyramine, the procedure for the isolation of the alkaloid was identical to that described for N-methyltyramine. An investigation of the stem fraction showed that it contained a very small fraction of the total activity in the plant, and the choline isolated from the stems had a negligible activity so that the stems were not further investigated.

Isolation of Choline from the Root Fraction

The choline in this fraction would be expected to appear at two places in the isolation procedure for hordenine. The free choline would be in the aqueous residue of the first continuous ether extract. The choline combined in the phospholipid fraction would appear in the acid ether extract of the methanol-soluble residue. Consequently, these two fractions were worked up separately and the choline obtained from them was pooled.

[3]*An aliquot of the potassium formate solution was dried on a dish and counted as an infinitely thin layer, the total activity being computed from this figure.*

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(a) *Free Choline*

The aqueous residue of the first continuous ether extract in the hordenine isolation procedure was treated with one sixth of its volume of methanol to prevent foaming, and the methanol and ammonia were removed under reduced pressure. The residue was made definitely acid with concentrated hydrochloric acid and filtered through a filter cel pad on a Büchner funnel. The filter cel pad was then washed thoroughly with water. The filtrate and washings were combined (total volume, 1500 ml.) and treated with a solution of 12.0 gms. of ammonium reineckate in 300 ml. of 0.5*N* hydrochloric acid. A heavy amorphous precipitate resulted and the supernatant liquor showed a definite excess of ammonium reineckate. The mixture was allowed to stand in the refrigerator for 12 hr. and the precipitate was filtered off. It was washed thoroughly with water and ethanol, dissolved in acetone, and the solution was filtered, evaporated to dryness *in vacuo*. The reineckate was taken up in 75 ml. of acetone and decomposed by the method of Kapfhammer and Bischoff (7). The ammonium reineckate precipitation was repeated twice more. On the third precipitation a beautifully crystalline precipitate separated. This was filtered off, washed as described above and combined with the reineckate obtained from the phospholipid fraction.

(b) *Phospholipid Choline*

The acid ether extract of the methanol-soluble residue was evaporated to dryness under reduced pressure. The residue was taken up in a 1*N* solution of potassium hydroxide in 30% ethanol, and the mixture refluxed on a steam bath for four hours. The solution was made distinctly acid with concentrated hydrochloric acid and extracted twice with its own volume of petroleum ether. The aqueous liquor was filtered through a pad of filter cel and treated with an excess of ammonium reineckate in 0.5*N* hydrochloric acid, as described above, and the precipitate filtered, washed, and decomposed. This procedure was repeated twice more as described for the free choline. The third precipitate was beautifully crystalline and was combined with that obtained from the free choline fraction.

Determination of the Activity and Identity of the Isolated Choline Reineckate

The combined reineckates were dissolved in acetone, decomposed, and reprecipitated with ammonium reineckate. The yield of dry choline reineckate was 1.1 gm. Since the analyses of reineckates are unreliable, no attempt was made to analyze this specimen, but its identity was established by analysis of the chloroplatinate prepared from it. Choline reineckate was counted as an infinitely thick layer in a Radiation Counters Laboratory "Nucleometer". Its specific activity was 1.36×10^4 counts per millimole per minute.

The above sample of choline reineckate was decomposed and the final filtrate was evaporated to dryness under reduced pressure. The residual choline chloride crystallized. It was taken up in absolute ethanol, the solution filtered,

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TABLE I

LOCATION OF ACTIVITY IN CHOLINE AND HORDENINE

Compound	Activity per millimole base per min.
Choline reineckate	1.36×10^4
Choline chloroplatinate	1.47×10^4
Trimethylamine chloroplatinate	1.39×10^4
Hordenine methiodide	1.40×10^5
Chloroplatinate of above base	1.29×10^5
Trimethylamine chloroplatinate	1.36×10^5

and excess ethanolic chloroplatinic acid added. The precipitate was allowed to stand at room temperature overnight, centrifuged off, and washed three times with absolute ethanol. This sample when counted as an infinitely thick layer in the Nucleometer had a specific activity of 1.47×10^4 counts per millimole per minute.

The yield was quantitative. Found: Pt, 31.74%. Calc. for $C_{10}H_{28}O_2N_2PtCl_6$: Pt, 31.68%.

Degradation of Labeled Choline Chloroplatinate

To determine the location of the labeled carbon in the choline molecule, the salt was degraded by the method of Lintzel and Monasterio (10) to trimethyl amine. The extent of labeling in the methyl groups as compared to the rest of the molecule could then be determined by comparing the activity per millimole of the trimethylamine to that of the choline from which it was obtained.

The labeled choline chloroplatinate (0.500 gm.) was degraded by the procedure of Lintzel and Monasterio (10) and the contents of the traps were evaporated to dryness under reduced pressure. The residue crystallized readily; it was taken up in absolute alcohol, filtered, and treated with excess chloroplatinic acid in ethanol. The precipitate was centrifuged, washed twice with absolute ethanol, and dried in a vacuum desiccator. The yield was 0.333 gm. or 77% of theory. Found: Pt, 36.89%. Calc. for $C_6H_{20}N_2PtCl_6$: Pt, 36.96%. This sample when counted as an infinitely thick layer had a specific activity of 1.39×10^4 counts per millimole per minute.

Determination of the Location of Labeled Carbon in Hordenine

To determine the location of the tagged atom in hordenine, it was first converted to the methiodide and to the chloroplatinate which was then degraded by the method of Lintzel and Monasterio (10). It was first determined that no appreciable exchange occurred between methyl iodide and a sample of methyl-labeled hordenine methiodide. The method of Lintzel and Monasterio was found to be readily applicable to hordenine chloroplatinate, giving good yields of trimethylamine.

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(a) *Conversion of Hordenine to the Methiodide*

Hordenine was isolated from the root fraction by the method previously described for N-methyltyramine. The sample was sublimed twice and the yield (from 720 gm. of barley) was 350 mgm. To this was added 2.00 gm. of synthetic hordenine as a carrier and the whole was resublimed.

A quantity of this sample of hordenine (2.29 gm.) was dissolved in 20 ml. of ethanol in a three necked flask to which had been added 0.5 gm. of finely powdered sodium bicarbonate.[4] The mixture was stirred with a propeller stirrer inserted through the center neck while the other two necks bore a reflux condenser and a dropping funnel. The flask was fitted with a heating mantle controlled by a variac. Methyl iodide (2.2 gm.) in 20 ml. of ethanol was added slowly under stirring (period of addition, 30 min.). While the methyl iodide was being added the mixture was kept slowly refluxing. As soon as all the methyl iodide was added the heat was turned off and the stirring continued for three hours. The hordenine methiodide was obtained by repeated extraction of the bicarbonate with boiling ethyl alcohol. The combined filtered extracts were evaporated until crystallization commenced. The yield of crystalline hordenine methiodide was practically quantitative. This salt, counted as an infinitely thick layer in the Nucleometer, resulted in a specific activity for the carrier-free material of 1.40×10^5 counts per millimole per minute.

(b) *Conversion of Methiodide to Chloroplatinate*

The above methiodide (1.000 gm.) was dissolved in 30 ml. of water and 0.544 gm. of silver acetate added. The mixture was warmed on a steam bath for 15 min. with constant stirring, the precipitated silver iodide filtered and washed with water. The filtrate was combined with the washings and evaporated to dryness under reduced pressure. The residue was then taken up in absolute alcohol, the solution filtered, and excess alcoholic chloroplatinic acid was added. After standing an hour at room temperature the precipitated chloroplatinate was centrifuged, washed twice with absolute ethanol, and dried in a vacuum desiccator. The yield was quantitative. This material, counted as an infinitely thick layer in the Nucleometer, resulted in a specific activity for the carrier-free material of 1.29×10^5 counts per millimole per minute.

(c) *Degradation of Quaternary Base Chloroplatinate*

The chloroplatinate (0.858 gm.) was degraded by the method of Lintzel and Monasterio (10) and worked up as described above for the choline sample. There was obtained 0.379 gm. of trimethylamine chloroplatinate (64%). This material, counted as an infinitely thick layer in the Nucleometer, resulted in a specific activity for the carrier-free material of 1.36×10^5 counts per millimole per minute.

[4]*It has been shown that strains of barley that produce hordenine also produce small amounts of its precursor N-methyltyramine (9). The bicarbonate ensures that this N-methyltyramine will be quantitatively methylated to hordenine methiodide.*

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Discussion

It is evident from the above experiments that when potassium formate, labeled with C^{14}, is fed to sprouting barley the labeled carbon is incorporated into both hordenine and choline and the activity is largely, if not entirely, in the N-methyl groups of these substances (see table). The difference in the activities of these two compounds is very probably a reflection of their rates of metabolism. The choline is apparently metabolized faster and hence its activity is less than that of hordenine owing to the greater dilution arising from the higher rate of metabolism.

The experimental results indicate that the synthesis of choline in barley proceeds by a route similar to that used in the synthesis of this material by the rat (19). They also give strong evidence that the N-methyl groups of the alkaloid hordenine arise through a similar series of reactions. It may be argued that the synthesis of the alkaloid methyls, in the present experiment, proceeds from carbon dioxide produced from the formate fed rather than by formylation followed by reduction, which appears to be the route in the rat (18, 19). However, preliminary experiments in this laboratory (9) showed that when methyl-labeled choline, of comparable activity to the formate used in these experiments, was fed to barley the hordenine isolated had a negligible radioactivity, in spite of the fact that the barley could rapidly oxidize these methyls to carbon dioxide. In the authors' opinion this experiment not only disposes of carbon dioxide as an intermediate but also shows that the N-methyl groups of hordenine do not arise by transmethylation from the choline–methionine system. It further indicates that the oxidation of choline methyl to carbon dioxide in the barley plant does not proceed via formate as has been shown to occur in the rat (16). This problem is under active study in our laboratory at the present time.

It would seem likely, therefore, that at least in barley and probably in the higher plants in general the synthesis of choline methyl proceeds by a route similar to that known to occur in the rat (6, 15, 19). Further, the N-methyl groups of the alkaloid hordenine appear to arise by an analogous series of reactions. It seems possible then that the formylation of amines followed by reduction is a general route for the synthesis of N-methyl groups in nature. The folic acid group of vitamins has been shown to act as a carrier of formate in processes involving this substance in rats and in bacteria (4, 11), and one would expect that they function in a similar fashion in the higher plants. This possibility is also under study in our laboratory.

Acknowledgment

The authors are indebted to Mr. R. B. MacLaren of the Experimental Station, Charlottetown, P.E.I., for supplying the barley used in these experiments.

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GELSEMINE

III. REDUCTION WITH LITHIUM ALUMINUM HYDRIDE[1, 2]

By Morris Kates[3] and Léo Marion

Abstract

The infrared absorption spectrum of gelsemine indicates the presence of a carbonyl group. Reduction of the alkaloid with lithium aluminum hydride converts the carbonyl not to a secondary alcohol, but to a methylene group, thus indicating that the carbonyl is present in a lactamic grouping. The reduced base shows the properties of a substituted aniline. Since gelsemine has been shown to yield 3-ethylindole on dehydrogenation with selenium and since the N-atom involved in the lactamic group cannot be the strongly basic nitrogen, gelsemine must contain an oxindole grouping. Furthermore, 3-monosubstituted oxindoles are converted by lithium aluminum hydride to 3-substituted indoles, whereas gelsemine under the same conditions gives rise to a dihydroindole. Therefore, the alkaloid must contain a 3, 3-disubstituted oxindole grouping.

Gelsemine ($C_{20}H_{22}O_2N_2$) is a strong monoacidic tertiary base that has been shown to be an indole derivative (5, 8). The indole nature of the alkaloid is further supported by the isolation, herein reported, of anthranilic acid on fusion of gelsemine with potassium hydroxide and of picric acid on oxidation of the base with fuming nitric acid.

Our knowledge of the nature of the oxygen atoms in gelsemine has so far been obscure. It was claimed by Moore (7) that gelsemine contained a free hydroxyl group which could be acetylated with acetic anhydride. However, all attempts to prepare O-acetylgelsemine have failed in our hands, and other investigators (2, 3) have been similarly unsuccessful. Indeed, Moore's claim is untenable in view of the facts that gelsemine contains only one active hydrogen (Zerewitinow) and that its infrared absorption spectrum shows a sharp absorption band at 3443 cm.$^{-1}$ indicative of an imino group, but no absorption in the hydroxyl region. Since gelsemine is an indole alkaloid (5, 8) and since the basic nitrogen is known to be tertiary, it follows that the one active hydrogen in the base must be attributed to the indole imino group.

The infrared absorption spectra of both gelsemine and dihydrogelsemine (Table I) show a strong absorption band at 1720 cm.$^{-1}$ and 1722 cm.$^{-1}$ respectively in the region of carbonyl absorption, indicating the presence of a carbonyl group in these substances. However, it has been reported (3) that gelsemine and dihydrogelsemine are unaffected by reagents known generally to react with ketonic groups, such as hydroxylamine and *n*-butylmagnesium bromide, and that they are recovered unchanged after boiling with strong

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[2] *A preliminary report of this work, considered as Part II of this series, has been published in J. Am. Chem. Soc. 72: 2308, 1950, and has been presented at the meeting of the Canadian Institute of Chemistry at Toronto, June 1950.*

[3] *National Research Council of Canada Postdoctorate Fellowship holder.*

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TABLE I

MAJOR INFRARED ABSORPTION BANDS OF THE COMPOUNDS DISCUSSED*

	NH band, cm.$^{-1}$	CO band, cm.$^{-1}$	'Benzene ring' band, cm.$^{-1}$
Gelsemine	3443	1720	1619
Dihydrogelsemine	3438	1722	1620
3, 3-Dimethyloxindole	3438	1718	1618
Dihydrodesoxygelsemine	3411	–	1606
Tetrahydrodesoxygelsemine	3414	–	1607
3, 3-Dimethyldihydroindole	3418	–	1607
N-Acetyltetrahydrodesoxygelsemine	–	1650	1594

* *The infrared absorption spectra were measured in chloroform solution at a concentration of 3 mgm. per ml., using a calcium fluoride prism.*

alkali and after treatment in boiling cyclohexanol with sodium. It seemed desirable, therefore, to investigate the action of lithium aluminum hydride on gelsemine and dihydrogelsemine.

To avoid complications which might arise from possible reaction at the double bond, the reduction of dihydrogelsemine was undertaken first. In a preliminary experiment, dihydrogelsemine was recovered unchanged after treatment with lithium aluminum hydride in boiling ether. However, when the reaction was carried out in boiling dioxane with excess reducing agent, there was obtained, in good yield, a crystalline substance which gave analytical figures corresponding to tetrahydrodesoxygelsemine ($C_{20}H_{26}ON_2$). Electrometric titration showed the new base to be diacidic, with one strongly basic group and one weakly basic group. It contained one active hydrogen (Zerewitinow) and its infrared absorption spectrum (Table I) showed no absorption in the carbonyl region but contained an absorption band at 3414 cm.$^{-1}$ indicative of a weakly associated imino group. Acetylation of tetrahydrodesoxygelsemine with boiling acetic anhydride yielded a crystalline monoacetyl derivative. This derivative was an N-acetyl compound since titration showed it to be a strong monoacidic base, whereas the parent base was diacidic, and since its infrared absorption spectrum (Table I) contained no N–H absorption band, but contained a carbonyl band at 1650 cm.$^{-1}$, attributable to the N-acetyl group (6). Finally, tetrahydrodesoxygelsemine coupled with diazotized sulphanilic acid to form a methyl orange indicator, thus revealing the presence of a basic nitrogen atom directly attached to an aromatic nucleus with a free and reactive *para* position.

Similar results were obtained in the reduction of gelsemine with lithium aluminum hydride. The reduction product, dihydrodesoxygelsemine ($C_{20}H_{24}$

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ON_2), was a diacidic base and its infrared absorption spectrum showed no absorption in the carbonyl region but contained an absorption band at 3411 cm.$^{-1}$ indicative of an imino group. The presence of the weakly basic imino group was confirmed by the formation of a N-nitroso derivative which gave a positive Lieberman test. Furthermore, catalytic hydrogenation of dihydrodesoxygelsemine gave rise to tetrahydrodesoxygelsemine identical with that directly obtainable by the action of lithium aluminum hydride on dihydrogelsemine.

The formation of a weakly basic secondary amino group, together with the replacement of one oxygen atom by two hydrogens through the action of lithium aluminum hydride, lead to the conclusion that the desoxy bases arise from the reduction of a lactam group. Since the nitrogen involved in the lactam is of necessity the same nitrogen present in the 3-ethylindole obtainable by degradation of the alkaloid with selenium, it follows that gelsemine and dihydrogelsemine contain an oxindole group, while the corresponding desoxy bases contain a dihydroindole group. It is well known that oxindoles containing a hydrogen in the 3-position give two active hydrogens in the Zerewitinow determination while gelsemine shows only one. Furthermore, it has been reported (4) that oxindoles which still contain a hydrogen atom in the 3-position are reduced by lithium aluminum hydride to the corresponding indoles and, therefore, it must be assumed that the oxindole system in gelsemine is disubstituted in the 3-position.

To test the postulate of a 3, 3-disubstituted oxindole grouping, the model compound 3, 3-dimethyloxindole was synthesized according to the method of Brünner (1) and its properties were compared with those of gelsemine and dihydrogelsemine. The model compound was found to have an ultraviolet absorption spectrum very similar to that of gelsemine in the concentration range of $1 \times 10^{-4}M$ to $2 \times 10^{-4}M$ in the region of 220 to 300 mμ (Fig. 1), although the fact that the spectrum of gelsemine varies with concentration while that of 3, 3-dimethyloxindole does not, makes the comparison difficult. The infrared absorption spectrum (Table I) of 3, 3-dimethyloxindole shows three sharp absorption bands (an NH-band at 3438 cm.$^{-1}$, a carbonyl band at 1718 cm.$^{-1}$ and a benzene ring band (6) at 1618 cm.$^{-1}$) the wave numbers of which are identical with those of the corresponding absorption peaks in the spectra of both gelsemine and dihydrogelsemine. Reduction of 3,3-dimethyloxindole with lithium aluminum hydride in boiling dioxane solution gave an excellent yield of 3, 3-dimethyldihydroindole, the infrared absorption spectrum of which showed no absorption in the carbonyl region, but contained an absorption peak in both the NH- and benzene ring regions at the same wave numbers as the corresponding absorption peaks in the spectra of dihydrodesoxygelsemine and tetrahydrodesoxygelsemine. It is worth mentioning that this result is contrary to the literature statement that N-unsubstituted oxindoles are virtually unaffected by lithium aluminum hydride (4).

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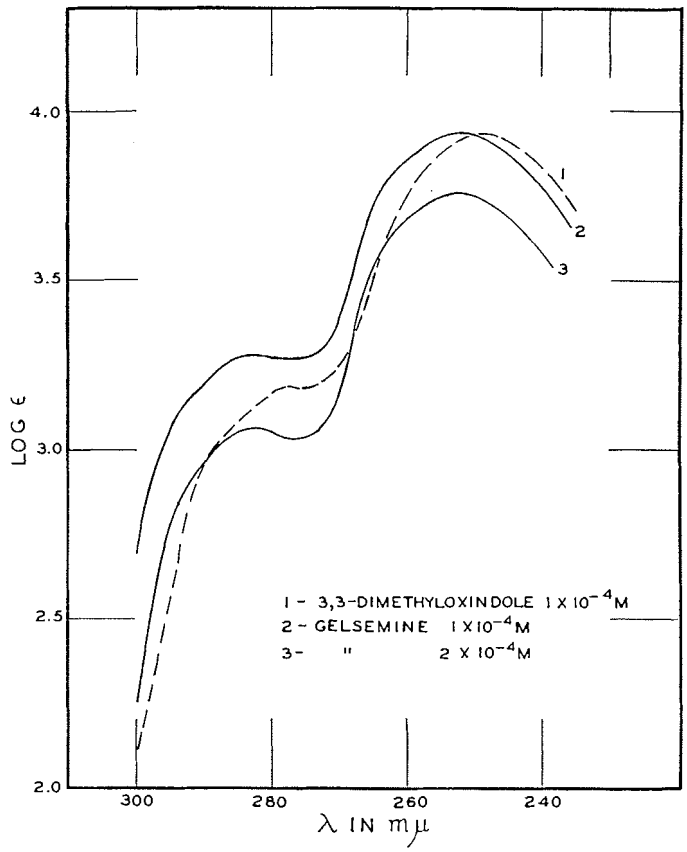
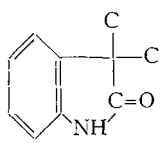


FIG. 1. *Ultraviolet absorption spectra taken in 95% ethanol solution with a Beckman quartz spectrophotometer.*



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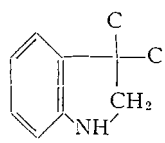

II

It may be concluded that gelsemine and dihydrogelsemine contain a 3, 3-disubstituted oxindole system represented by the partial formula I, and that it is the reduction of the oxindole group to a dihydroindole group which gives rise to the desoxy bases in which partial structure II is present.

Experimental[1]

Alkaline Fusion of Gelsemine

Gelsemine (2.5 gm.) was added gradually with stirring to fused potassium hydroxide (15 gm.) kept in a nickel crucible at 320–330°C. The melt was vigor-

[1]*All melting points are corrected unless otherwise stated.*

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ously stirred until on interruption of the stirring no frothing took place (*ca.* 15 min.). After cooling, the melt was dissolved in water and the solution extracted with ether. The aqueous solution was acidified with hydrochloric acid and extracted repeatedly with ether. This second ether extract was dried over sodium chloride and distilled to dryness on the steam bath. There remained a black resinous residue (1.0 gm.) which was no longer completely soluble in ether. The ether-soluble portion was distilled *in vacuo*; it yielded a sublimate at 120–130°C. at 0.5 mm., which after two recrystallizations from absolute ether – hexane, consisted of small rectangular plates, m.p. 147°C. either alone or in admixture with an authentic specimen of anthranilic acid. Calc. for $C_7H_7O_2N$: C, 61.32; H, 5.11%. Found: C, 61.26, 61.48; H, 5.51, 5.46%.

Oxidation of Gelsemine

Gelsemine (2.0 gm.) was refluxed gently with 20% nitric acid (80 cc.) for 72 hr. The solution when evaporated left a gum which largely dissolved when boiled with water (50 ml.). The liquor was decanted from the insoluble residue and evaporated to dryness. Concentrated nitric acid (3 ml.) was added to the gummy residue and the mixture heated one hour on the steam bath and a further half-hour over a free flame. The hot solution was diluted with water (2 ml.) and evaporated to dryness. Addition of water (2 ml.) followed by evaporation to dryness was repeated several times. Finally, the residue was dissolved in water (2 ml.), the solution filtered to remove a small quantity of insoluble material and evaporated to *ca.* 0.5 ml. This solution on cooling deposited yellow tabular prisms that were collected on a filter and washed with two drops of water, wt. 9 mgm. The crystalline product melted at 119°C. and in admixture with picric acid at 120°C. The filtrate from the crystallization of picric acid was evaporated to dryness and the residue dissolved in methanol (1 ml.). Quinoline (one drop) was added to the solution which was subsequently evaporated to half its volume. On standing this deposited small yellow warts that were filtered and dissolved in methanol. The solution was filtered through charcoal and evaporated to a small volume which on cooling deposited clusters of lemon-yellow crystals melting at 204°C. either alone or in admixture with an authentic sample of quinoline picrate, wt. 10 mgm.

Dihydrogelsemine

Gelsemine (4.0 gm., with acetone of crystallization) was hydrogenated in absolute methanol (30–35 ml.) over palladium black (0.4 gm.) at room temperature and atmospheric pressure. Yield of dihydrogelsemine (needles with acetone of crystallization), 86% (3.46 gm.). After recrystallization from acetone–methanol (10: 1), it melted at 222–223°C. (cf. (2) and (3)).

Tetrahydrodesoxygelsemine

To a solution of 2.0 gm. of acetone-free dihydrogelsemine in 40 ml. of anhydrous dioxane was added, under nitrogen, 10 ml. of a 2% solution of lithium

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aluminum hydride in absolute ether, and the mixture refluxed for two hours. More of the lithium aluminum hydride solution (1.5 ml.) was added and the refluxing was continued for one hour. To the cooled reaction mixture was added 5 ml. of methanol–water (10: 1) and the precipitate was centrifuged and washed several times with ether. The combined supernatants were concentrated *in vacuo* to a small volume which was diluted with water and extracted with ether. The dried ether solution, on concentration *in vacuo*, left a crystalline residue which was recrystallized from ethyl acetate – absolute ether (1: 1) to give 1.07 gm. of tetrahydrodesoxygelsemine (prisms), melting at 140–141.5°C. From the mother liquors there was obtained a further 0.61 gm. of material, making a total yield of 88%. After two recrystallizations from ethyl acetate – ether (1: 1) or from ethyl acetate – petroleum ether (b.p. 40–60°C.) (4: 1), the product melted at 141–142°C. $[\alpha]_D^{26}$ −11.4 ± 0.7° (*c*, 3.05 in methanol). Calc. for $C_{20}H_{26}ON_2$: C, 77.4; H, 8.44; N, 9.03; one act. H, 0.323%. Found: C, 77.51, 77.34; H, 8.01, 8.21; N, 9.14; act. H, 0.33%.

Electrometric Titration

A solution of 100 mgm. of tetrahydrodesoxygelsemine in 8 ml. of methanol–water (1: 1) consumed 4.48 ml. of methanolic (50%) 0.0723 *N* hydrochloric acid; this corresponds to an equivalent weight for the base of 310 (calc. 310.4) and to a basic group with pK 8.86 (obtained from the value of the pH at half-titration). Titration with aqueous 0.1 *N* hydrochloric acid revealed the presence of a second, weakly basic group with pK 3.4.

Tetrahydrodesoxygelsemine picrate

The picrate, prepared in 99% ethanol, separated immediately as a yellow precipitate which rapidly turned orange. Recrystallization from methanol–acetone (3: 1) gave rosettes of orange-red needles melting at 216–217°C. (dec.) (uncorr.). Calc. for $C_{20}H_{26}ON_2 . C_6H_3O_7N_3$: C, 57.9; H, 5.42; N, 12.98%. Found: C, 57.23, 57.40; H, 5.23, 5.19; N, 12.80%.

N-Acetyltetrahydrodesoxygelsemine

A solution of 250 mgm. of the base in 3 ml. of acetic anhydride and 0.05 ml. of pyridine was refluxed for two hours. After removal of the acetic anhydride *in vacuo*, the crystalline residue[5] was dissolved in water and the solution was made alkaline with sodium carbonate and extracted with chloroform. The chloroform solution was dried over sodium sulphate, and concentrated on the steam bath to an oil which crystallized from 2-3 ml. of acetone, whereby there was obtained 240 mgm. of hexagonal prisms with acetone of crystallization, melting at 131–133°C. after losing the acetone at 80–90°C. Recrystallization from acetone gave 170 mgm. of product melting at 132.5–133.5°C. Calc. for $C_{20}H_{25}ON_2 . C_2H_3O$: C, 75.0; H, 8.01; N, 7.95%. Found for material dried at 100°C.: C, 74.90, 75.03; H, 8.07, 8.22; N, 8.05%.

[5]*This material was investigated further. After recrystallization from a mixture of ethyl acetate and dioxane (1: 1) it melted at 182–186°C. (plates). Electrometric titration revealed that it was the acetate salt of the N-acetyl derivative. Calc. for* $C_{20}H_{25}ON_2 . C_2H_3O . C_2H_4O_2$: *C, 69.9; H, 7.82; N, 6.80%. Found: C, 69.96, 69.70; H, 7.77, 7.58; N, 6.74, 6.77%.*

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Electrometric Titration

A solution of 34.7 mgm. of the acetyl compound (dried at 100°C.) in 4 ml. of methanol–water (1: 1) consumed 1.88 ml. of 0.520*N* methanolic (50%) hydrochloric acid, which corresponded to an equivalent weight for the base of 355 (calc. 352.4) and to a basic group with pK 8.36. The presence of a second basic group was not detected.

Coupling with Diazotized Sulphanilic Acid

A solution of 31 mgm. of tetrahydrodesoxygelsemine in 0.05 ml. of glacial acetic acid was added to the ice-cold diazotization mixture of 21 mgm. of sulphanilic acid. A red color appeared immediately and the solution rapidly turned a deep blood-red on stirring. The addition of 20% sodium hydroxide solution (0.07 ml.) precipitated an orange solid which was centrifuged down, washed with water, and reprecipitated by cooling its solution in a hot mixture of 1 ml. of water and a few drops of methanol. The dried powder was copper-orange in color and weighed 26 mgm. Its solution in aqueous methanol was orange in color, became red when it was acidified, and turned orange again when it was made alkaline. These color changes are typical of a methyl orange indicator. Neither gelsemine, nor dihydrogelsemine, nor acetanilide coupled with diazotized sulphanilic acid.

Dihydrodesoxygelsemine

To a solution of 1.25 gm. of gelsemine (acetone-free) in 20 ml. of absolute dioxane was added, under nitrogen, 5 ml. of a 3.5% solution of lithium aluminum hydride in absolute ether, and the mixture was refluxed for two hours. More of the lithium aluminum hydride solution (1 ml.) was added and the refluxing was continued for one hour. To the cooled reaction mixture was added 5 ml. of methanol–water (10: 1) and the precipitate was removed by centrifugation and washed with ether. The combined supernatants were concentrated *in vacuo* to a small volume which was diluted with water and extracted with ether. The combined dried ether extracts, on concentration *in vacuo* left a crystalline residue (1.08 gm.) which was recrystallized from ethyl acetate – petroleum ether (1: 1) to give 0.9 gm. (75%) of dihydrodesoxygelsemine, melting at 136.5–137.5°C. After another recrystallization from ethyl acetate – petroleum ether the product consisted of plates melting at 137–137.5°C. $[\alpha]_D^{28} -31.8 \pm 0.5$ (*c*, 1.57; in chloroform). Calc. for $C_{20}H_{24}ON_2$: C, 77.9; H, 7.84; N, 9.08%. Found: C, 78.25, 78.13; H, 7.86, 7.69; N, 9.15, 9.19%.

Electrometric Titration

A solution of 51.2 mgm. of dihydrodesoxygelsemine in 4 ml. of methanol–water (1: 1) consumed 2.22 ml. of 0.0755 *N* methanolic (50%) hydrochloric acid, corresponding to an equivalent weight for the base of 306 (calc. 308.4), and to a basic group with pK 8.4. After the addition of an excess of acid (up to pH 2), the titration curve indicated the presence of a weakly basic group with pK 3.4.

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Dihydrodesoxygelsemine Oxalate

On addition of an ether solution of anhydrous oxalic acid (40 mgm.) to an ether solution of the base (60 mgm.), the oxalate of dihydrodesoxygelsemine immediately precipitated and was crystallized from a mixture of methanol and ether. Yield, 42 mgm. (plates); m.p. 218–220°C. (dec.) when immersed in a bath at 200°C., heated at the rate of 1–2° per min. Calc. for $C_{20}H_{24}ON_2 \cdot C_2H_2O_4$: C, 66.3; H, 6.58; N, 7.03%. Found: C, 66.41, 66.57; H, 6.63, 6.81; N, 7.14%.

N-Nitrosodihydrodesoxygelsemine

To a solution of 75 mgm. of the base in 1 ml. of methanol was added 0.8 ml. of a 10% aqueous solution of sodium nitrite. The cold (0°C.) solution was acidified with 2 *N* hydrochloric acid and after 10 min. was made alkaline with sodium carbonate and extracted with ether. The dried ether solution was evaporated and the amorphous residue was crystallized from a mixture of ether and petroleum ether (b.p. 40–60°C.), whereby 45 mgm. of yellow rods melting at 137–139°C. were obtained. Calc. for $C_{20}H_{23}O_2N_3$: C, 71.2; H, 6.87; N, 12.46%. Found: C, 70.78, 70.65; H, 6.47, 6.64; N, 12.50%.

Lieberman Test

When two drops of concentrated sulphuric acid were added to a mixture of 1 mgm. of the nitroso compound and a few milligrams of phenol, a green-blue color appeared which turned to red on the addition of water and changed to green on the addition of alkali.

Conversion of Dihydrodesoxygelsemine to Tetrahydrodesoxygelsemine

Hydrogenation of 150 mgm. of dihydrodesoxygelsemine in 5 ml. of 95% ethanol with 40 mgm. of palladium black proceeded rapidly and was complete in 30 min. (uptake of hydrogen, 15 ml. at N.T.P., 1.3 moles). The product was crystallized twice from a mixture of ethyl acetate – petroleum ether (1:1) whereby there was obtained 19 mgm. of prisms melting alone at 140–141°C. and in admixture with tetrahydrodesoxygelsemine, at 140.5–141.5°C. Calc. for $C_{20}H_{26}ON_2$: C, 77.4; H, 8.44; N, 9.03%. Found: C, 77.58, 77.44; H, 8.48, 8.30; N, 9.04%.

Reduction of 3, 3-Dimethyloxindole with Lithium Aluminum Hydride

3, 3-Dimethyloxindole was prepared according to the procedure described by Brünner (1); m.p. 152.5–153°C. (reported, 151°C.). Calc. for $C_{10}H_{11}ON$: C, 74.5; H, 6.88; N, 8.69%. Found: C, 74.46; H, 6.85; N, 8.66%.

3, 3-Dimethyldihydroindole

To a solution of 1.2 gm. of 3, 3-dimethyloxindole in 25 ml. of absolute dioxane was added, under nitrogen, 7.5 ml. of a 3.5% solution of lithium aluminum hydride in absolute ether, and the mixture was refluxed for two

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hours. More of the lithium aluminum hydride solution (3 ml.) was added and the refluxing was continued for one hour. To the cooled reaction mixture was added 5 ml. of methanol–water (10: 1) and the precipitate was centrifuged down and washed with ether. The combined supernatants were concentrated to a small volume which was diluted with water and extracted with ether. The ether extract was dried over sodium sulphate and concentrated *in vacuo* to an oil which was distilled (8 mm., air bath temp., 90–100°C.); the distillate crystallized, on cooling, in long needles. Yield, 0.89 gm. (82%); m.p. after redistillation, 34–34.5°C. Reported for 3, 3-dimethyldihydroindole, 34.5°C.(1). Calc. for $C_{10}H_{13}N$: C, 81.6; H, 8.90; N, 9.52%. Found: C, 81.56, 81.76; H, 8.71, 8.62; N, 9.63, 9.43%.

On addition of an ether solution of anhydrous oxalic acid (0.4 gm.) to an ether solution of the 3, 3-dimethyldihydroindole (0.4 gm.), the oxalate immediately precipitated and was crystallized from a mixture of absolute ethanol and ether (1: 3). Yield, 0.53 gm.; m.p., after recrystallization, 140–141°C. (plates). Reported for the oxalate of 3, 3-dimethyldihydroindole, m.p. 139°C. (1). Calc. for $C_{10}H_{13}N \cdot C_2H_2O_4$: C, 60.7; H, 6.37; N, 5.91%. Found: C, 60.81; H, 6.26; N, 6.10%.

Acknowledgment

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THE REDUCTION OF NITROGLYCERIN WITH TITANOUS SULPHATE

By P. Fainer[1]

Abstract

A study of the reduction of nitroglycerin with titanous sulphate has been carried out. The results indicate that for each mole of nitroglycerin reduced, 18 moles of titanous ion are oxidized, two moles of ammonia, one-half mole of nitrogen trioxide, and one mole of glycerol are formed. It has been shown that the reduction takes place first to 1,3-dinitro-2-nitrosoglycerin which, after hydrolysis to 1, 3-dinitroglycerin, is reduced to glycerol with the probable intermediate formation of 1, 3-dinitrosoglycerin. The determination of nitroglycerin by the Shankster and Wilde method is more accurate when 70% acetic acid is substituted for methanol as the solvent for nitroglycerin.

It was found by Oldham (5) that in the reduction of nitric esters with titanous chloride, each mole of the ester consumed 7.5 moles of titanous ion. If the reduction were to go to completion, then eight moles of the titanous chloride would be consumed as shown by Equation (1).

$$R-ONO_2 + 8Ti^{+++} + 8H^+ \longrightarrow ROH + 8Ti^{++++} + NH_3 + 2H_2O \quad (1)$$

The reduction of nitroglycerin, if carried through to completion, might therefore be expected to correspond with the following equation:

$$\begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array} + 24Ti^{+++} + 24H^+ \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + 24Ti^{++++} + 6H_2O + 3NH_3 \quad (2)$$

Shankster and Wilde (6) showed, however, that only 18 moles of titanous chloride are consumed quantitatively by one mole of nitroglycerin, and postulated, but did not investigate, the following equation:

$$\begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array} + 18Ti^{+++} + 18H^+ \longrightarrow \begin{array}{l} CH_2-ONH_2 \\ | \\ CH-ONH_2 \\ | \\ CH_2-ONH_2 \end{array} + 18Ti^{++++} + 6H_2O \quad (3)$$

In carrying out the Shankster and Wilde procedure, which consists of refluxing a methanolic solution of nitroglycerin with excess titanous sulphate followed by back-titration of the excess titanous sulphate with standard ferric alum, low and inconsistent results were obtained (Table I).

During the war it was reported that a modification of the Shankster and Wilde procedure yielded complete reduction of the nitroglycerin to ammonia,

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TABLE I

THE REDUCTION OF NITROGLYCERIN (SHANKSTER AND WILDE METHOD)

Wt. of nitroglycerin added, mgm.	Wt. of nitroglycerin found, mgm.*	% Recovery
27.77	21.94	79.0
10.73	9.37	87.3
10.73	10.07	93.9

* *Based on 1 mole nitroglycerin = 18 gm. atom* Ti^{+++}

giving an equivalence of 24 moles of titanous salt per mole of nitroglycerin in accordance with Equation (2). This modification consisted of substituting 70% acetic acid for methanol as the solvent for nitroglycerin and the use of phosphorus-free titanous chloride. Phosphorus-free titanous chloride was employed as it was found that the presence of this element interfered in the reduction.

Attempts to repeat this result were unsuccessful (Table II), it being found that 18 instead of 24 moles of titanous ion were consumed by each mole of nitroglycerin. However, as can be seen from the results, considerably better precision and accuracy are obtainable with the modified method than with the original.

TABLE II

THE REDUCTION OF NITROGLYCERIN (MODIFIED METHOD)

Wt. of nitroglycerin added, mgm.	Wt. of nitroglycerin found, mgm.*	% Recovery
21.38	21.37	99.96
21.38	21.36	99.95
20.30	20.38	100.4
20.30	20.44	100.7
20.30	20.32	100.1
20.30	20.18	99.40
20.30	20.24	99.70
20.30	20.12	99.10
20.59	20.39	99.27
Average		99.88%
Mean deviation		±0.42%

* *Based on 1 mole nitroglycerin = 18 gm. atom* Ti^{+++}

In an endeavor to account for the higher equivalence found by the original workers using the modified method, the possible catalytic effects of iron and aluminum known to be present in the titanous solutions used by them were studied. As can be seen from Table III, no significant effect was observable in these experiments.

Attention was then turned to variation of acidity as a possible cause of difference between the results of the various workers. Table IV shows that increase in acidity brings about a decrease in the amount of titanous ion con-

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TABLE III

EFFECT OF IRON AND ALUMINUM ON THE MODIFIED METHOD

Reagent added	Nitroglycerin added, mgm.	Nitroglycerin found, mgm.*	% Nitroglycerin found
10 ml. 0.25 *M* $AlCl_3$	23.18	23.16	99.92
10 ml. 0.25 *M* $AlCl_3$+ 10 ml. 0.1 *M* ferric alum	23.18	23.22	100.2
10 ml. 0.1 *M* ferric alum	23.18	23.16	99.92

* *Based on 1 mole nitroglycerin = 18 gm. atom* Ti^{+++}

TABLE IV

EFFECT OF ACIDITY ON THE MODIFIED METHOD

Ml. H_2SO_4 added	Ml. titanous sulphate used	Millimoles titanous sulphate used	Millimoles nitroglycerin present	Moles titanous sulphate consumed per mole nitroglycerin reduced
0.56	9.58	1.695	0.09414	18.01
5	6.94	1.228	"	13.04
20	5.32	0.9411	"	9.99
40	4.85	0.8572	"	9.11
80	4.80	0.8493	"	9.02

N titanus sulphate = 0.1769.

sumed. The results, moreover, tend to a minimum corresponding with an equivalence of nine moles of titanous salt per mole of nitroglycerin (Table IV).

The minimum value reached corresponds to the equation

$$3NO_3^- + 12H^+ + 9Ti^{+++} \longrightarrow 9Ti^{++++} + 6H_2O + 3NO \qquad (4)$$

which could occur if the reduction is preceded by hydrolysis of the ester.

$$\begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 + 3H_2O \\ | \\ CH_2-ONO_2 \end{array} \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH-OH + 3HNO_3 \\ | \\ CH_2-OH \end{array} \qquad (5)$$

Since the earlier experiments had shown a consumption of 18 equivalents of titanous salt per mole of nitroglycerin, it is unlikely under the reaction conditions then used that the formation of nitric acid or nitrate ion precedes the reduction. This introduces the possibility of differences in the reactions undergone respectively by the primary and secondary nitric ester groups present in nitroglycerin. To throw further light on this, a detailed study of the reaction was undertaken.

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Behavior of the Primary Nitrate Group

To verify that polyfunctional aliphatic primary nitric esters are reduced to ammonia and the corresponding alcohols, solutions of pentaerythritol tetranitrate and methyltrimethylolmethane trinitrate (containing 4 and 5 primary nitrate groups respectively) were refluxed with titanous sulphate. It was found that these compounds are reduced to the extent of about 90% to ammonia and the corresponding alcohols with no formation of nitrogen trioxide.

It was thought probable that the reduction of the primary nitric ester groups of nitroglycerin to ammonia takes place with the intermediate formation of 1,3-dinitrosoglycerin. If such is the case, then primary nitrites should be reduced by titanous sulphate to ammonia. This was verified by refluxing *n*-butyl nitrite with titanous sulphate and analyzing the reaction products.

It was found that ammonia was formed, titanous sulphate was oxidized, and no oxides of nitrogen were evolved.

Behavior of the Secondary Nitrate Group

Analysis of the gaseous products (Table V) formed in the reduction of nitroglycerin with titanous sulphate shows that for each mole of nitroglycerin reduced, two moles of ammonia and one-half mole of nitrogen trioxide are formed,

TABLE V

DETERMINATION OF GASEOUS REACTION PRODUCTS

Wt. of nitroglycerin, mgm.	Wt. of ammonia recovered, mgm.	Molar ratio ammonia/ nitroglycerin	Wt. of nitrogen trioxide recovered, gm.	Molar ratio nitrogen trioxide/ nitroglycerin
32.07	4.81	2.00	0.0163	0.455
32.07	4.72	1.96	0.0923	0.500
		Av. 1.98		Av. 0.48

suggesting that two of the nitrate groups are completely reduced and the third only partially, forming 1,3-dinitro-2-nitrosoglycerin as an intermediate. It is not unreasonable to assume then that the reduction is symmetrical in that the two moles of ammonia formed are derived from the two primary nitrate groups which are equivalent to each other, the nitrogen trioxide being formed through the partial reduction of the secondary nitrate group, followed by hydrolysis without further reduction. If such is the case, then it would be expected that the reaction is a stepwise one. Indeed, the potentiometric titration of nitroglycerin with titanous sulphate bears this out (Fig. 1).

It may be calculated from the data given in Fig. 1 that the first inflection in the curve takes place at the point where just enough titanous sulphate has been added to reduce one nitrate group to the nitroso stage. Since this reduction is only a partial one, it appears to be the secondary nitrate group which is thus affected since it has already been shown that the primary nitrate groups in nitroglycerin are completely reduced.

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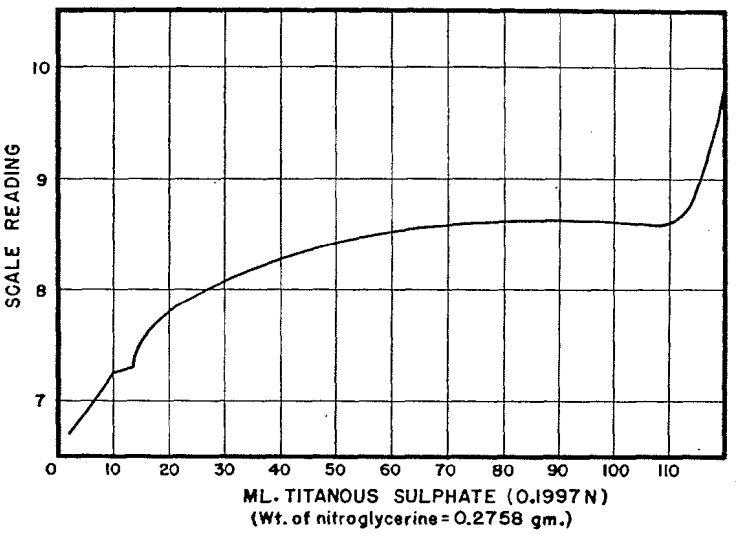

FIG. 1. *The potentiometric titration of nitroglycerin with titanous sulphate.*

To show that the intermediate compound 1, 3-dinitro-2-nitrosoglycerin may be hydrolyzed, without further reduction, in the presence of titanous sulphate, secondary butyl nitrite was prepared (4) and refluxed with titanous sulphate. There occurred an immediate evolution of a gas which, when analyzed, was shown to be nitrogen trioxide. Titration of the solution with standard ferric alum showed no oxidation of the titanous salt. Analysis of the reaction products showed no evidence of ammonia formation.

We may therefore conclude on the basis of the above evidence that the nitrogen trioxide formed during the reduction of nitroglycerin comes from the secondary nitrate group, through hydrolysis of the intermediate nitroso compound (Equation (6)).

$$2\left[\begin{array}{l}CH_2-ONO_2\\ |\\ CH-ONO\\ |\\ CH_2-ONO_2\end{array}\right] + H_2O \longrightarrow 2\left(\begin{array}{l}CH_2-ONO_2\\ |\\ CH-OH\\ |\\ CH_2-ONO_2\end{array}\right) + N_2O_3 \quad (6)$$

Isolation of 1, 3-Dinitroglycerin

1, 3-Dinitroglycerin was isolated from the reaction mixture and yielded a benzoyl derivative melting at 67–68°C. and a *p*-nitro benzoyl derivative melting at 94–95°C. These melting points correspond to those given by Will (7) for the benzoyl and *p*-nitrobenzoyl derivatives of 1, 3-dinitroglycerin.

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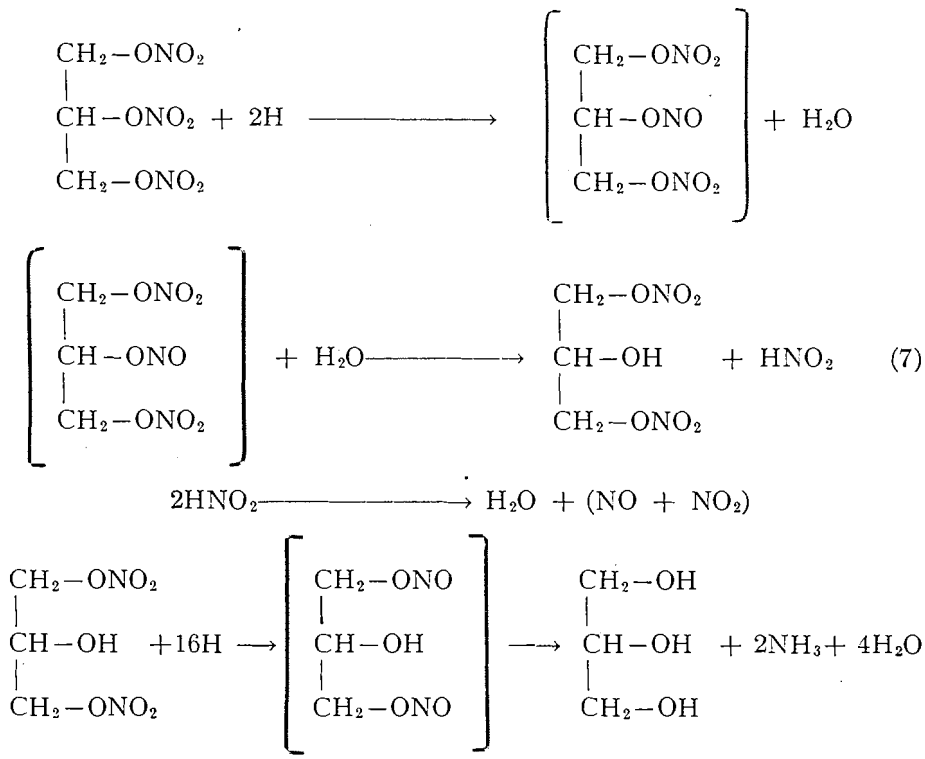
The reduction of nitroglycerin with titanous sulphate may now be formulated as follows:



Experimental

Materials

1. Pure titanous sulphate in 1*N* sulphuric acid prepared by dissolving pure titanium hydride in 145 ml. of warm 35% sulphuric acid. The resulting solution after filtration was diluted to one liter with freshly boiled distilled water and stored under an atmosphere of carbon dioxide.

2. A standard solution of nitroglycerin in 70% acetic acid (about 0.2%), prepared by weighing out a definite amount of nitroglycerin into a tared stoppered weighing bottle and transfering quantitatively into a volumetric flask.

3. Standard solutions of: ferrous ammonium sulphate; ferric ammonium sulphate; potassium permanganate; hydrochloric acid.

4. 5% Ammonium thiocyanate; 40% sodium hydroxide; 5% nitric acid in 95% sulphuric acid.

5. Milligan gas washing bottles; Beckman Model H-2 pH meter equipped with a platinum and tungsten electrode.

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Modified Method

A 10 ml. aliquot of the standard nitroglycerin solution was pipetted into an Erlenmeyer flask equipped with a side arm, and the air expelled by a stream of carbon dioxide which was maintained throughout the determination. Twenty milliliters of 0.2 *N* titanous sulphate was then added from a carbon dioxide filled burette. The contents was boiled under reflux for 10 min., cooled to room temperature, and the excess titanous sulphate titrated with standard 0.15*N* ferric ammonium sulphate, 5 ml. of 5% ammonium thiocyanate being added toward the end of the titration as indicator.

A blank determination using 10 ml. of 70% acetic acid in place of the nitroglycerin solution was carried on simultaneously. The difference between the two titrations gave the titanous sulphate consumed by the nitroglycerin.

This method differs from that of Shankster and Wilde (6), mainly in the use of 70% acetic acid instead of methanol as a solvent for nitroglycerin.

Effect of Acidity

The modified method was employed except that varying amounts of acid were added before reflux was begun. The practice was adopted of diluting to a final normality of not more than 5*N* with respect to sulphuric acid (in the case of the concentrated acid solutions) since the end point was unsatisfactory at higher concentrations.

Determination of Ammonia

After reduction of the nitroglycerin, enough 40% sodium hydroxide was added to the cold solution both to precipitate the titanium salts and to make the solution alkaline. The ammonia formed was distilled from the solution into boric acid and determined by titration with standard hydrochloric acid.

Determination of Nitrogen Trioxide

The basic method employed is that of Milligan (3). A stream of carbon dioxide (source—dry-ice) was bubbled through the boiling reaction mixture into a train of two Milligan gas washing bottles. The first bottle (*A*) contained 200 ml. of 95% sulphuric acid for the absorption of nitrogen dioxide, and the second bottle (*B*) contained 200 ml. of a 5% solution of nitric acid in 95% sulphuric acid for the absorption of nitric oxide. Carbon dioxide was swept through the apparatus for a period of two hours, after which time a 25 ml. aliquot was removed from each bottle, and added, with cooling, to 800 ml. of diluted potassium permanganate (containing 10 ml. of phosphoric acid to prevent the precipitation of oxides of manganese). An excess of standard ferrous sulphate was then added, the excess being back-titrated with the standard permanganate.

Results in Table V indicate that the gas formed from the reduction of one mole of nitroglycerin consists of one-half mole of nitrogen trioxide (or of an equimolar mixture of nitric oxide and nitrogen dioxide).

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According to Lunge and Berl (1, 2), the absorption of an equimolecular mixture of nitric oxide and nitrogen dioxide is practically complete in concentrated sulphuric acid, two moles of nitrosylsulphuric acid being formed as shown by the following equations:

$$NO_2 + NO \longrightarrow N_2O_3 \quad (8)$$

$$N_2O_3 + 2H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O \quad (9)$$

Since there was no gas absorbed in bottle (*B*), nitric oxide alone was not evolved.

When nitrogen dioxide alone is absorbed in sulphuric acid, only one mole of nitrosylsulphuric acid is formed for each two moles of nitrogen dioxide.

$$2NO_2 + H_2SO_4 \longrightarrow NOHSO_4 + HNO_3 \quad (10)$$

The results obtained from the analysis of the gases absorbed in bottle (*A*) (Table V) clearly indicate that nitrogen dioxide alone was not evolved since one mole of nitrosylsulphuric acid was formed per mole of nitroglycerin reduced, and it had already been shown that two of the three nitrogen atoms in nitroglycerin were reduced to ammonia.

Potentiometric Titration of Nitroglycerin with Titanous Sulphate

To 50 ml. of 70% acetic acid containing 0.275 gm. of nitroglycerin was added 150 ml. of 30% sodium acetate. After each addition of 1 ml. of 0.2*N* titanous sulphate, the solution was allowed to react for five minutes before measurements of the e.m.f. were taken. Throughout the titration the solution was kept at 95°C. and at constant volume in an atmosphere of carbon dioxide. The results obtained are plotted in Fig. 1.

Isolation of 1, 3-Dinitroglycerin

To a solution of nitroglycerin in acetic acid was added just enough titanous sulphate to reduce the secondary nitrate group to the nitrite. The solution was refluxed and after the reaction was complete, the mixture was cooled, filtered free from hydrated titanic oxide, and extracted with ether. A yellow oil obtained after evaporation of the ether yielded a benzoyl derivative melting at 67–68°C. and a *p*-nitrobenzoyl derivative melting at 94–95°C.

Acknowledgments

The author acknowledges his indebtedness to Dr. A. L. Lovecy and Mr. J. L. Myers for their helpful suggestions and criticisms, and to the Defence Research Board for permission to publish this paper.

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POLAROGRAPHIC DETERMINATION OF BENZOYL PEROXIDE AND CUMENE HYDROPEROXIDE[1]

By Paul A. Giguère and D. Lamontagne

Abstract

Benzoyl peroxide and cumene hydroperoxide (CHP) are reduced at the anodically polarized dropping mercury electrode, the former at about +0.3 volt vs. S.C.E., and the latter at +0.1 v. Their half-wave potentials as well as that of the two reduction steps of dissolved oxygen are gradually shifted towards more negative values with increasing concentration of organic peroxides. The polarographic method is suitable for determining these peroxides in concentrations up to 2×10^{-3} mole per liter. Dissolved oxygen does not interfere seriously with the analyses.

Previous applications of the polarographic method to analysis of organic peroxides have not led to conclusive results. Neumann and his coworkers (2, 7) investigated the electroreduction at the dropping electrode of methyl hydroperoxide and diethyl peroxide in various supporting electrolytes. Indepenpendently Stern and Polak (9) made similar measurements and arrived at quite different values for the reduction potentials. Recently the method has been applied to the detection and identification of peroxides in oxidized fats (5, 6). The widespread use of benzoyl peroxide and cumene hydroperoxide (CHP) as polymerization catalysts in the manufacture of synthetic rubber has prompted us to study the possibility of determining low concentrations of these compounds polarographically.

Experimental

All measurements were done with a Heyrovský polarograph of the photographic recording type (Sargent, Model XI). The sensitivity of the galvanometer was 0.16 μamp. per mm. with the shunt used, and the characteristics of the dropping mercury electrode were $m^{2/3} t^{1/6} = 1.42$ mgm.$^{2/3}$ sec.$^{-1/2}$ with a drop-time of 5.45 sec. in 0.1 *N* potassium chloride at −1.0 v., except for the first few runs (Fig. 1) for which they were 2.12 mgm.$^{2/3}$ sec.$^{-1/2}$ and 3.43 sec. In most cases the cell was an open 50 cc. beaker connected through agar bridges to the reference electrode which was a saturated calomel electrode in all cases. The resistance of the circuit was of the order of 1600–1800 ohms. It was not convenient to use a Heyrovský cell because of the oxidation of the mercury anode by the organic peroxides. The measurements were all done at 25.0° ± 0.2 C.

The sample of cumene hydroperoxide was Hercules Powder Company's commercial solution kindly supplied by the Polymer Corporation Ltd., Sarnia, Ont. It contained about 96% peroxide, the impurities being mainly the decomposition products: acetophenone, α, α′-dimethylbenzyl alcohol, etc. (3). As far

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Contribution from the Department of Chemistry, Laval University, Québec, Que., with financial assistance from the National Research Council through its associate Committee on Synthetic Rubber.

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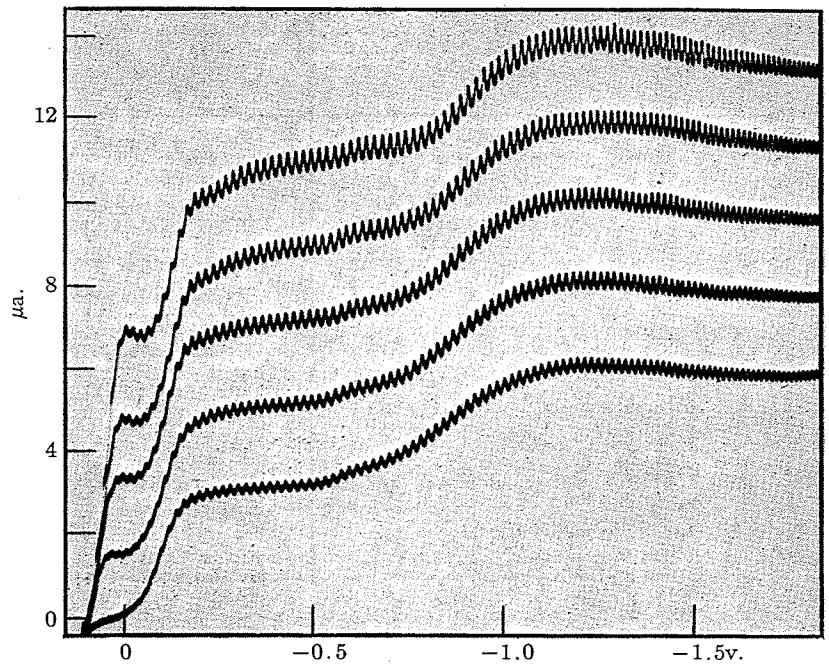

FIG. 1. *Current-voltage curves of cumene hydroperoxide in 0.1 N potassium chloride. The cumene hydroperoxide concentrations are, from bottom to top, (1) blank, (2) 2.85, (3) 5.7, (4) 8.55, and (5) 11.4 × 10^{-4} mole per liter. Methyl red as maximum suppressor.*

as could be ascertained, the impurities did not interfere with the polarographic analysis except for acetophenone, as explained below. The benzoyl peroxide was Eastman Kodak's recrystallized from alcohol.

Results

The first analyses were done in 0.1 *N* potassium chloride solutions; previous investigators of organic peroxides used lithium chloride (2, 9), but a few tests showed that the potassium salt gives essentially the same results. The most remarkable features of the current–voltage curves in Fig. 1 is the reduction of cumene hydroperoxide at the anodically polarized (vs. S.C.E.) dropping electrode. The electroreduction of quinone (8) gives the same type of curves. The beginning of the peroxide wave at about + 0.1 v. is obscured by the fact that at positive potentials the mercury of the electrode goes into solution, forming complexes with the chloride ion. Therefore the following determinations were done in 0.1 *N* potassium nitrate as supporting electrolyte. In this medium the complete reduction wave may be obtained, Fig. 2.

The exact value of the reduction potential cannot be ascertained first, because of the poorly defined shape of the wave, and second, because it is displaced towards more negative values with increasing concentration of cumene hydroperoxide. The two reduction steps of dissolved oxygen are af-

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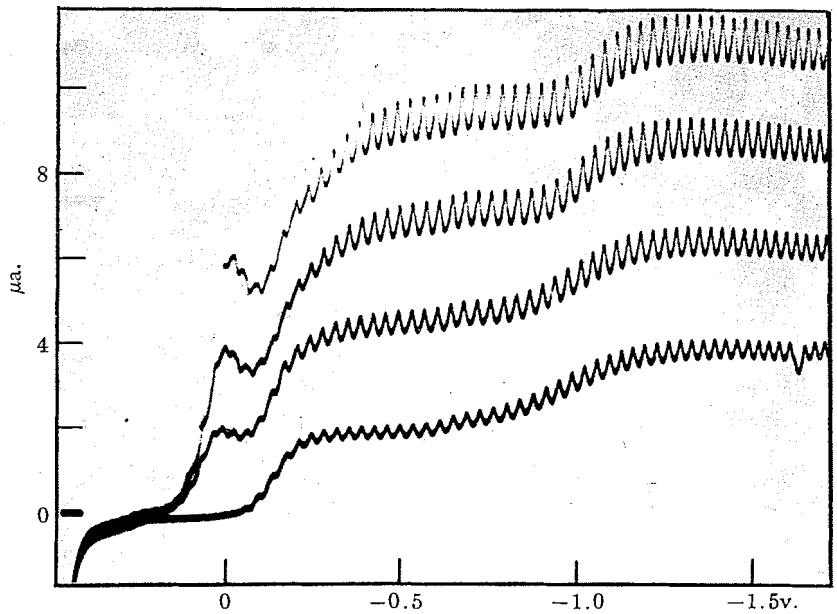

FIG. 2. *Current-voltage curves of cumene hydroperoxide in 0.1 N potassium nitrate. From bottom to top the cumene hydroperoxide concentrations are (1) blank, (2) 5.43, (3) 10.87, and (4) 16.31 × 10^{-4} mole per liter. Methyl red as maximum suppressor.*

TABLE I

POLAROGRAPHIC REDUCTION OF BENZOYL PEROXIDE AND CUMENE HYDROPEROXIDE

Peroxide conc., mole/l. × 10^4	Half-wave potentials, volts*			Diffusion current of peroxide, μ amp.	Diff. current / Peroxide conc.
	Peroxide wave	1st Oxygen wave	2nd Oxygen wave		
Cumene hydroperoxide in 0.1 N potassium chloride (Fig. 1)					
0.00	–	−0.103	−0.872	**	–
2.85	–	−0.105	−0.883	1.92	0.674
5.70	–	−0.109	−0.898	3.84	0.674
8.50	–	−0.121	−0.911	5.76	0.678
11.40	–	−0.122	−0.918	7.68	0.674
Cumene hydroperoxide in 0.1 N potassium nitrate (Fig. 2)					
0.00	–	−0.107	−0.870	**	–
5.43	+0.097	−0.112	−0.890	2.40	0.441
10.87	+0.090	−0.154	−0.930	4.80	0.441
16.31	+0.073	−0.172	−0.957	6.20	0.441
Benzoyl peroxide in 0.1 N potassium nitrate (Fig. 3)					
0.00	–	−0.223	−1.159	***	–
3.86	+0.290	−0.226	−1.157	1.19	0.308
7.73	+0.278	−0.232	−1.160	2.24	0.290
11.60	+0.279	−0.234	−1.147	3.36	0.290
15.47	+0.269	−0.240	−1.144	4.48	0.290

* *All potentials corrected for IR drop.* ** *Measured at −1.2 v.* *** *Measured at +0.07 v.*

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fected in a similar way (Table I); the waves also show a tendency to become steeper, especially the second one at −1.0 v., as may be noted in Figs. 1 and 2.

Benzoyl peroxide had to be electrolyzed in water–alcohol mixtures because its solubility in aqueous solutions of electrolyte is below the limit of sensitivity of the polarographic method. Its half-wave potential near +0.3 v. is also dependent on its concentration in the solution (Fig. 3), but those of oxygen show no regular trend. However, they are widely affected by the composition of the supporting electrolyte, owing mainly to the much greater solubility of oxygen in alcohols than in water. Since we are dealing here with irreversible reactions the significance of the various factors involved in these phenomena is not easily deciphered.

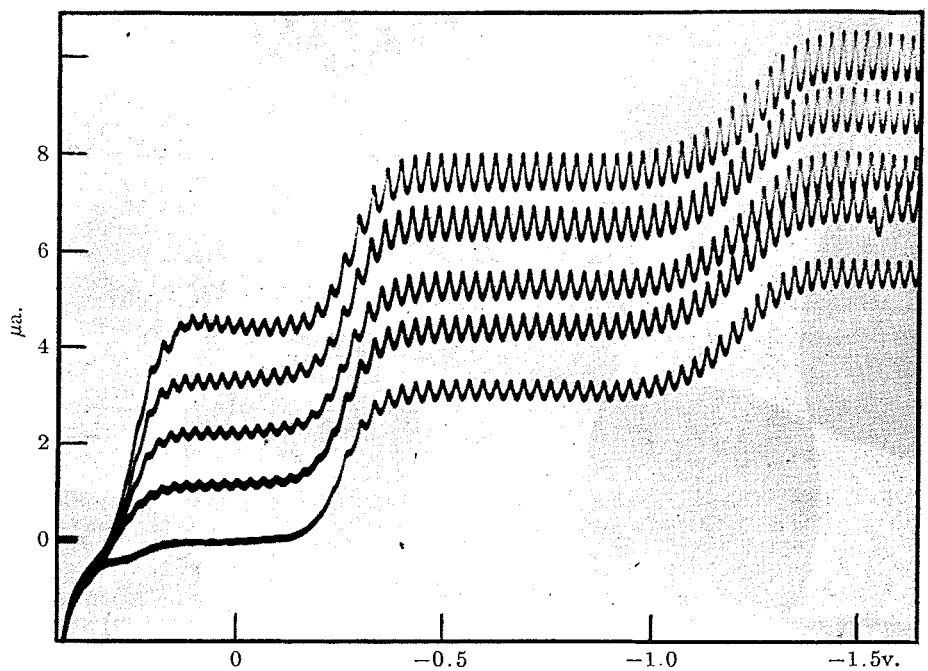

FIG. 3. *Reduction curves of benzoyl peroxide in ethanol–water mixture (50: 50 in volume) 0.1 N potassium nitrate. The concentrations of peroxide are (1) blank, (2) 3.86, (3) 7.73, (4) 11.60, and (5) 15.47 × 10^{-4} mole per liter. Methyl red as suppressor of maxima.*

Another feature of the reduction curves of these two peroxides is the appearance of maxima even in absence of oxygen. The polarograms in Fig. 4 were obtained by bubbling through the solutions a stream of nitrogen that had passed through alkaline pyrogallol and over heated copper turnings. Methyl red was an efficient maximum suppressor for benzoyl peroxide (Fig. 3) and for cumene hydroperoxide in potassium chloride solution (Fig. 1) but less so in potassium nitrate solution (Fig. 2). Strychnine sulphate was not satisfactory for this purpose, contrary to the case of hydrogen peroxide (4). Under the operating conditions reported above, the diffusion coefficient of benzoyl peroxide was calculated to be 2.8 × 10^{-6} cm.^{2} sec.$^{-1}$ and that of cumene hydroperoxide, 6.4 × 10^{-6}.

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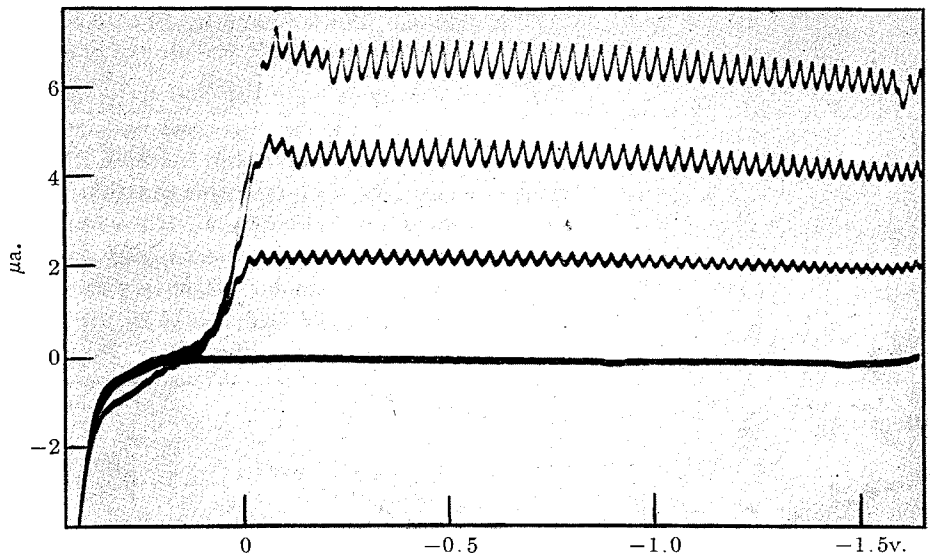

FIG. 4. *Reduction curves of cumene hydroperoxide in 0.1 N potassium nitrate, air-free solution. The concentrations of cumene hydroperoxide are: (1) blank, (2) 5.26, (3) 10.53, and (4) 15.79 × 10^{-4} mole per liter. No maximum suppressor added.*

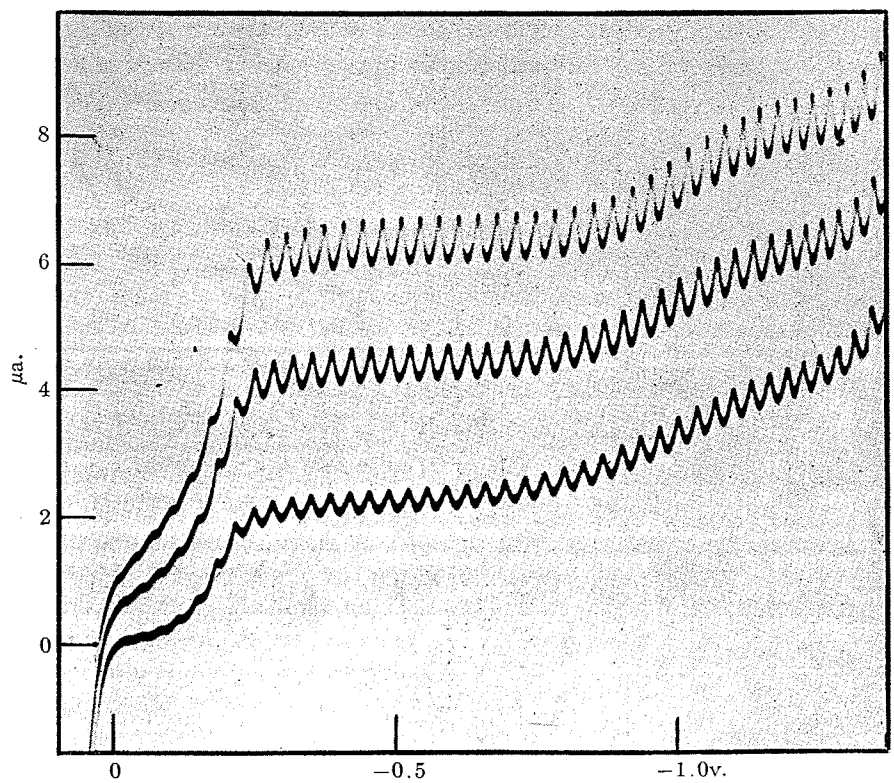

FIG. 5. *Current–voltage curves of cumene hydroperoxide in 0.1 N potassium nitrate solution buffered at pH 2. Bottom curve: no peroxide; middle, 4.53; top, 9.06 × 10^{-4} mole per liter.*

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As a practical conclusion the polarographic method appears, therefore, suitable for the analysis of these two peroxides in concentrations up to about 2×10^{-3} mole per liter. Also, because they are reduced readily at the dropping mercury electrode the presence of dissolved oxygen does not interfere seriously with their determination. Indeed their diffusion current may be measured as well from the two oxygen plateaus, provided, of course, that the blank and peroxide analyses are all done in air saturated solutions. In particular the method may be used to follow the disappearance of these catalysts in polymerization reactions. Furthermore the degree of purity of cumene hydroperoxide can be estimated easily since acetophenone, one of the decomposition products, is reduced at -1.6 v. (1). There is no need for buffering the solutions; at pH 2 the peroxide wave is considerably distorted (Fig. 5), and tends to merge into the first oxygen wave.

It would be of interest to extend this investigation further to include other organic peroxides for, aside from its practical interest, it could provide valuable data for the theory of irreversible electrode reactions.

Acknowledgment

The authors are grateful to Dr. H. Leverne Williams and his associates of the Polymer Corporation Ltd. for the preparation of the pure sample of cumene hydroperoxide and for helpful advice. The preliminary measurements on benzoyl peroxide were done by Mr. A. Weingartshofer-Olmos of this laboratory.

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Résumé

Le peroxyde de benzoyle et l'hydroperoxyde de cumène employés comme catalyseurs de polymérisation dans la fabrication du caoutchouc synthétique peuvent être déterminés à des concentrations allant jusqu'à 2×10^{-3} mole par litre au moyen de l'électrode à gouttes de mercure. Ils sont réduits à des potentials d'environ $+0.3$ et $+0.1$ volt respectivement (par rapport à l'électrode de calomel saturée). La présence d'oxygène dissous dans la solution n'affecte pas les mesures.

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THE EXCHANGE OF IODINE BETWEEN INORGANIC IODIDES AND *n*-BUTYL IODIDE[1]

By G. W. Hodgson, H. G. V. Evans, and C. A. Winkler

Abstract

Lithium, sodium, and caesium iodides are highly ionized in acetonitrile solution and have practically the same rates and activation energies (18 kcal. per mole) for their exchange reactions with *n*-butyl iodide in this solvent. There seems little doubt, therefore, that these exchange reactions occur between the organic iodide and iodide ion derived from the inorganic salt. Zinc and cadmium iodides, and iodine, are only slightly ionized in acetonitrile and exchange with *n*-butyl iodide with rates that are widely different from one another and from the rate of iodide ion exchange. The activation energies are 21.9, 20.6, and 17.5 kcal. per mole respectively. It is concluded that these exchange reactions involve predominantly complex ions.

Introduction

The halogen exchange reaction between aliphatic and alkali metal halides has generally been assumed, from indirect evidence, to be a reaction between the organic molecule and a halide ion derived from the inorganic halide (3, 7, 8, 9, 10, 13). On the other hand, aluminum halides apparently exchange by ionization of the organic halide (1, 5, 6) while exchange of elemental halogens with organic halides appears to involve an atomic mechanism (2, 12).

Direct evidence has recently been presented (4) for the ion mechanism in exchanges between lithium bromide and alkyl bromide in anhydrous acetone and between sodium iodide and alkyl iodides in methanol. Velocity coefficients were found to vary with dilution for the former, but not for the latter, reaction. The results correlate with the degree of dissociation of the inorganic halide inferred from conductance measurements.

In the present study, the mechanism of exchange between aliphatic and inorganic halides was sought by comparing the rates of halogen exchange between *n*-butyl iodide and different inorganic iodides in acetonitrile with the degree of ionization of the inorganic halides in the same solvent.

Experimental and Results

Because of the ready availability and convenient half life of I^{131}, this isotope was used in the exchange reactions of *n*-butyl iodide with iodine and with the iodides of lithium, sodium, caesium, zinc, and cadmium, in acetonitrile solutions.

Molecular Weight Determinations

Molecular weight determinations were made to demonstrate the relative degrees of ionization of the alkali iodides and zinc and cadmium iodides in

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acetonitrile solution. The ebullioscopic method, with standard Cottrel apparatus, was used. Fig. 1 shows the linear relations obtained by plotting apparent molecular weight against concentration of dissolved iodide. The results indicate that the alkali iodides are completely ionized, zinc iodide is not appreciably ionized, and cadmium iodide is associated.

Conductance Measurements

Conductance measurements were made on solutions of the various iodides in acetonitrile, using a conductivity cell designed for solutions of high resistance and an Industrial Instruments Inc., Model RC-1, conductivity bridge. All measurements were made at 25°C. and corrections were applied for the specific

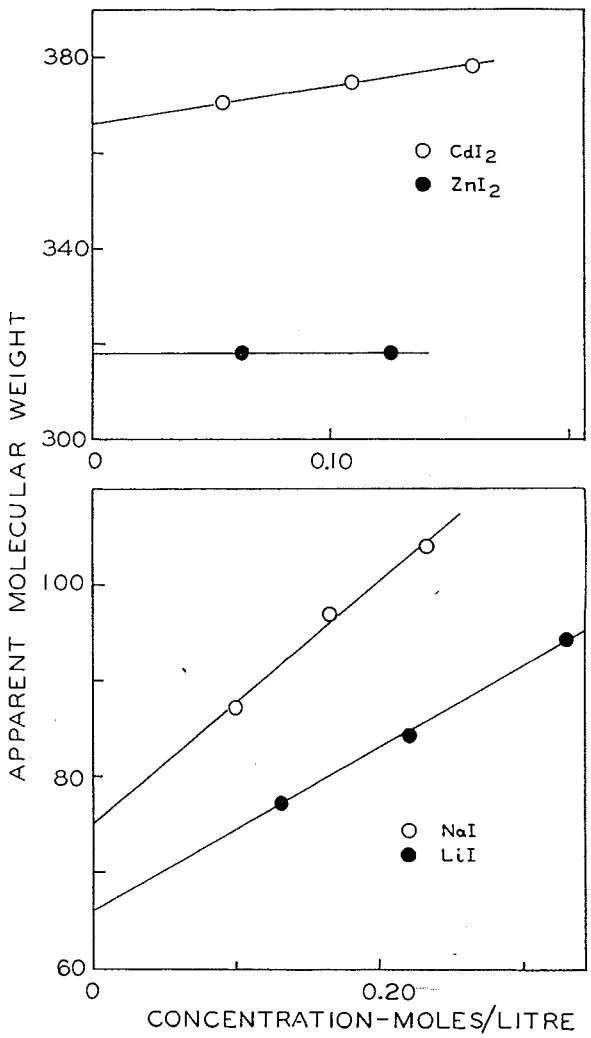

FIG. 1. *Molecular weight determinations in acetonitrile.*

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conductance of the solvent. Fig. 2 shows that the three alkali iodides behaved as strong electrolytes in acetonitrile, while zinc and cadmium iodides and iodine behave as weak electrolytes.

Exchange Experiments

Radioactive iodine, I^{131}, was obtained as carrier-free sodium iodide from the National Research Council Atomic Energy Project, Chalk River.

Technical grade acetonitrile was dried over anhydrous potassium carbonate, and a fraction distilling in the range 81.4–81.5°C. used as solvent in all the exchange reactions. Exhaustive tests showed that no reaction of the solvent with sodium iodide occurred, even at temperatures of 200°C.

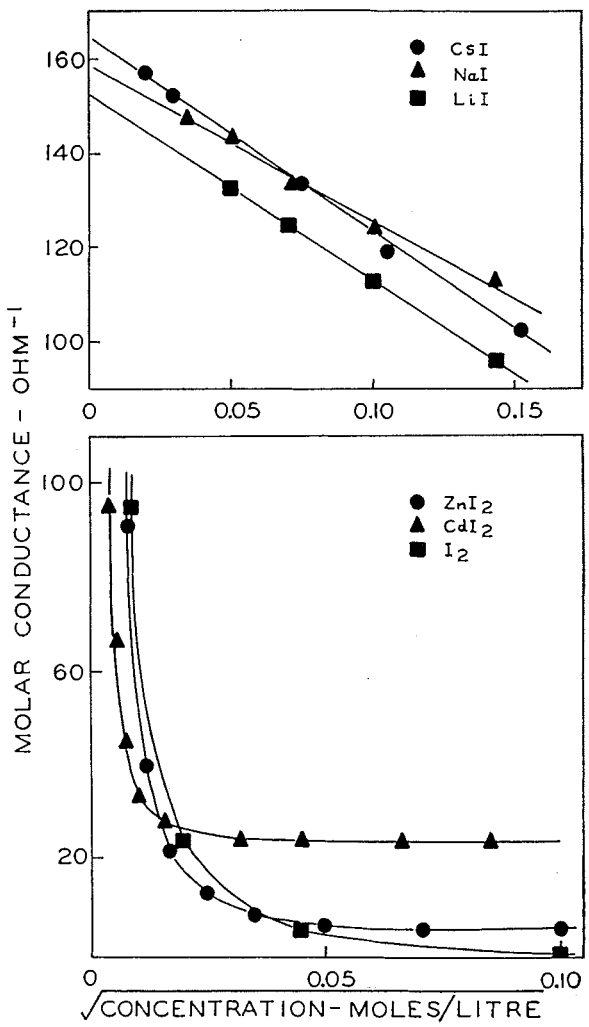

FIG. 2. *Conductance of inorganic iodides in acetonitrile.*

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n-Butyl iodide was shaken with mercury to remove traces of free iodine, and a fraction boiling at 128.4–128.5°C. taken for the kinetic studies.

Lithium iodide trihydrate was dehydrated at 130°C. and the residue, containing some free iodine, was dissolved in acetonitrile to yield a solvate which was recrystallized several times from acetonitrile. A stock solution of the solvate was prepared in acetonitrile and its concentration determined by gravimetric iodide analysis.

Sodium, caesium, and zinc iodides were reagent grade and were merely dried at 120°C. before use. Cadmium iodide ("crystals") and reagent grade iodine were used without treatment.

Prior to an exchange experiment, a solution of each reactant, of appropriate concentration, was brought to the temperature of the thermostat, which was regulated within $\pm$ 0.02°. The solutions were mixed at zero time, and at suitable intervals samples were withdrawn with a rapid-delivery pipette. Reaction in the sample was quenched by separation of the inorganic and organic iodides.

Early in the investigation, separation of the iodides was achieved by a benzene–water extraction. The water layer, containing the inorganic iodide, was washed several times with benzene, after which its iodide content was precipitated with aqueous silver nitrate. The iodine content of the butyl iodide in the benzene layer was precipitated with alcoholic silver nitrate. This reaction, which took place very slowly at room temperature, went to completion in a few minutes at 80°C.

In later experiments it was found possible to dispense with the time-consuming extraction when analysis of only the inorganic iodide was to be made. When aqueous silver nitrate was added to a faintly acid solution of butyl iodide in acetonitrile, methanol, or mixtures of these, cloudiness developed at room temperature only after about two minutes, and no silver halide could be centrifuged down even after five minutes. Hence, the inorganic iodide could be precipitated directly from the reaction mixture, since to precipitate, centrifuge, and decant from the packed precipitate required less than one minute. Experiments showed that this direct precipitation gave essentially the same results as the earlier extraction procedure.

The silver iodide precipitate was washed successively with methanol and water, and was then slurried in boiling, concentrated nitric acid to remove any silver cyanide or traces of organic material that might be present, and to obtain the silver iodide in a form that gave very fine suspensions in subsequent washings. Loss of some silver iodide by decomposition in the acid was of no concern, since total recovery of the iodide was not required for calculations based on specific activities. After the acid treatment, the precipitate was washed once with water and twice with methanol. It was then slurried in 5 cc. of anhydrous methanol, in which coarse particles settled out immediately. The remaining suspension was poured into a glass ring which was ground to give

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leak-proof contact with a weighed glass plate. On evaporation of the methanol, without boiling, under an infrared lamp, a smooth deposit of silver iodide was obtained. After determining the weight of the deposit, its activity was measured with a standard counting assembly using an end-window Geiger tube and a scale of sixty-four scaler. A preliminary five minute count was followed by a count of such duration that at least 10,000 counts were registered. The activity of the original solution was adjusted where possible so that a sample of silver iodide weighing about 35 mgm. required only two or three minutes for counting.

Extensive tests showed no evidence of self-absorption in smooth deposits of silver iodide weighing less than 60 mgm. However, if heavy particles of the iodide were not allowed to settle out before decanting the methanol suspension into the glass ring, the specific activity was significantly reduced as a result of self-absorption.

In most of the experiments, the inorganic iodide was made radioactive initially and the course of the exchange was followed by the decrease in its specific activity. This procedure was justified by following the course of an exchange reaction from the change in activity of both the organic and inorganic iodides. The two sets of results were essentially the same. Similarly, experiment showed that it was immaterial which iodide, organic or inorganic, was made radioactive initially.

The derivation of the rate constant as presented by McKay (11) may be generalized for inorganic halides of the type MI_n, where the reacting species is M_pI_q formed from MI_n by dissociation or association. Assuming that these processes are fast compared with the exchange reaction, the active iodide will be statistically distributed over all the inorganic species present at any time.

For the exchange reaction

$$RI + M_pI_{q-1}I^* \rightleftharpoons RI^* + M_pI_q.$$

Let V be the total number of exchanges per hour,

b the total concentration of organic halide, RI (moles per liter),

a the total concentration of MI_n added to the system,

α the ratio of the concentration of the reacting species to the total concentration of inorganic iodide,

c the initial concentration of active inorganic iodide

and x the concentration of active organic iodide at any time t.

Then,

$$\frac{dx}{dt} = \frac{V}{q} \cdot \frac{aq(c-x)}{n \cdot \alpha a} - V \cdot \frac{x}{b}$$

$$= \frac{V}{nab} \left\{ bc - x(b + na) \right\}.$$

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The first term on the right hand side represents the fact that, of the V moles of active species reacting, the small fraction $\frac{aq(c-x)}{naa}$ contains active iodine, and that because this fraction is small only $\frac{1}{q}$ of these exchanges will lead to a transfer of active iodine. Correspondingly, the second term gives the number of exchanges that transfer active atoms from organic to inorganic molecules.

If $x = 0$ initially, integration gives

$$V = \frac{nab}{(na+b)t} \ln \frac{1}{1 - \frac{x}{c}\left(1 + \frac{na}{b}\right)}.$$

But $V = k \cdot aab$,

where k is the second order rate constant for the reaction. Hence,

$$ak = \frac{n}{(na+b)t} \ln \frac{1}{1 - \frac{A}{A_0}\left(1 + \frac{b}{na}\right)}$$

$$= \frac{n}{(na+b)t} \ln \frac{1}{1-\sigma},$$

where $A = \frac{x}{b}$ and $A_0 = \frac{c}{na}$ are the specific activities determined experimentally and σ is the degree of exchange. If the reaction is third order involving two reactants derived from the inorganic iodide, the rate expression becomes

$$a_1a_2k = \frac{n}{a(na+b)t} \ln \frac{1}{1-\sigma}.$$

Table I summarizes the data obtained for the various exchange reactions investigated. The value of ak recorded in the table for a given temperature is the average of the individual values calculated for different reaction times. The mean deviation of the individual values of ak from the average was generally less than $\pm 3\%$.

The results for cadmium iodide have been calculated from both the second order and third order rate expressions. Unfortunately, data for only a single variation in concentration of cadmium iodide are available, but there seems little doubt that this reaction conforms better to the third order than to the second order rate equation.

The activation energies for the six exchange reactions are given in Table II, together with the value of ak (or a_1a_2k) for each exchange calculated for 25°C. The Arrhenius lines were sufficiently good that the activation energies were calculated with a probable error of approximately 1%.

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TABLE I

EXCHANGE OF INORGANIC IODIDES WITH *n*-BUTYL IODIDE

Temp. °C.	Concentration of inorganic iodide, moles/liter	Concentration of *n*-butyl iodide, moles/liter	ak 1-mole^{-1}–hr^{-1}	a_1a_2k 1-mole^{-2}–hr^{-2}
Lithium iodide				
0	0.010	0.052	0.67	
14.2	0.010	0.051	3.7	
29.2	0.010	0.050	17.4	
	0.025	0.025	15.7	
47.5	0.010	0.024	108	
Sodium iodide				
0	0.010	0.260	0.68	
	0.010	0.025	0.62	
14.2	0.010	0.051	3.93	
29.2	0.010	0.248	15.6	
	0.050	0.025	14.8	
47.5	0.010	0.012	95.5	
Caesium iodide				
0	0.0076	0.052	0.75	
12.2	0.0095	0.051	2.98	
29.2	0.0075	0.050	18.8	
	0.0050	0.050	21.0	
39.9	0.00454	0.005	71.2	
Zinc iodide				
47.5	0.048	0.483	6.0×10^{-3}	
60.0	0.047	0.474	2.2×10^{-2}	
81.0	0.046	0.458	0.141	
100.0	0.0089	0.224	1.08	
	0.0089	0.446	1.06	
	0.022	0.224	1.07	
122.0	0.043	0.043	4.49	
Cadmium iodide				
30.0	0.050	0.496	3.85×10^{-3}	7.76×10^{-2}
48.0	0.049	0.491	2.85×10^{-2}	0.58
60.0	0.047	0.238	8.93×10^{-2}	1.88
82.0	0.046	0.230	0.598	13.0
	0.023	0.230	0.333	14.5
	0.023	0.115	0.328	14.2
Iodine				
69.7	0.023	0.093	0.205	
81.0	0.023	0.092	0.449	
100.0	0.022	0.089	1.85	
122.0	0.022	0.087	6.99	
	0.035	0.035	6.99	

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TABLE II

ARRHENIUS PARAMETERS FOR THE EXCHANGE REACTIONS

	αk calculated at 25°C. 1-mole^{-1}–hr.$^{-1}$	E, kcal./mole
Lithium iodide	11.4	18.2
Sodium iodide	10.2	18.0
Caesium iodide	11.1	18.2
Zinc iodide	4×10^{-4}	21.9
Cadmium iodide	(4×10^{-2} 1-mole^2–hr.$^{-2}$)*	20.6
Iodine	4×10^{-3}	17.5

* *Since the exchange of cadmium iodide is considered to be a third order reaction, the value* ($\alpha_1\alpha_2 k$) *calculated for it is not directly comparable with the other values.*

Discussion

Since lithium, sodium, and caesium iodides are highly ionized in acetonitrile solution, and have virtually identical rates and activation energies for their exchange reactions with *n*-butyl iodide in this solvent, it seems reasonable to conclude that these exchange reactions occur between the organic iodide and iodide ion. Values of αk at one temperature decrease slightly with increase of inorganic iodide concentration, which may be attributed to a decrease in α corresponding to ion association. An average of the values in Table II gives the second order rate constant ($\alpha = 1$) at 25°C. for the reaction between iodide ion and *n*-butyl iodide in acetonitrile solution, as 10.8 1–mole^{-1}–hr.$^{-1}$.

It should be noted that if α, the degree of dissociation, varies with the temperature exponentially, the calculated activation energies will include a corresponding factor. The close agreement between the values for the alkali metal iodides indicates, as might be expected, that this factor is relatively small.

The values of αk are much less for cadmium and zinc iodides, and iodine, than for the alkali iodides. The conductivity curves for cadmium and zinc iodides, characterized by a rapid decrease in molar conductance with concentration at very low concentrations, followed by a plateau at about 25 ohm^{-1} and 18 ohm^{-1} respectively, indicate that simple ions are present at very low concentrations but that complex formation predominates at higher concentrations. The linear plots of apparent molecular weight against concentration (Fig. 2), which extrapolate to the true molecular weight at zero concentration, further indicate that, over the range of concentrations in which the measurements were made, the concentration of simple ions was negligible.

Comparison of the observed αk values for different inorganic iodide concentrations at the same temperature shows that α is approximately constant for zinc iodide and iodine. If the reacting species were iodide ion formed by dissociation of molecules or complex ions, increasing the concentration should lead

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to a decrease in α. Again it would seem that the simple iodide ion is not the main reacting species in these two reactions. This conclusion assumes that some step in the attainment of inorganic equilibrium is not rate controlling, but it seems reasonable that such a step could not have an activation energy of the order of 20 kcal.

There remains to consider the possibilities that the exchange reactions with zinc iodide and iodine involve either complex ions or undissociated molecules (ion pairs). With zinc iodide, which shows no association (Fig. 1) and no third order behavior, the reacting species might well be undissociated iodide or a complex anion (e.g., ZnI_3^-) formed bimolecularly from zinc iodide, e.g.,

$$2\,ZnI_2 \rightleftharpoons ZnI^+ + ZnI_3^-.$$

In either case, α would be nearly constant with change in concentration. Similarly, with iodine the reacting species might be I_2 or I_3^-. If two reacting species are simultaneously involved in exchange, the form of the rate equation is altered only to the extent that αk is replaced by the sum of two such terms.

With cadmium iodide, the exchange reaction appears to be third order. This could be explained by assuming exchange with undissociated CdI_2 molecules, or with a complex anion such as $CdI_4^=$, in which exchange is made possible by polarization of covalent bonds by Cd^{++} ions. As the ionic species are formed bimolecularly from CdI_2, values of α_1 and α_2 in the third order expression $\alpha_1\alpha_2 k$ should be nearly independent of concentration.

Indistinguishable kinetically, however, would be a second order exchange that occurred through an associated complex formed, for example, by

$$2\,CdI_2 \rightleftharpoons Cd^{++} + CdI_4^= \rightleftharpoons CdCdI_4$$

leading to an increase of α, and hence αk, with increased concentration. The boiling point results show that association does occur in solutions of cadmium iodide, and this might well be due to formation of complex ion pairs such as $CdCdI_4$. In such a complex, the associated Cd^{++} ion may be regarded as promoting exchange by polarization of the covalent bonds in the $CdI_4^=$ anion. If the sphere of influence within which the Cd^{++} ion may polarize $CdI_4^=$ ions is the same as that within which Cd^{++} and $CdI_4^=$ ions may be regarded as associated to form $CdCdI_4$, as reflected by the colligative properties of the solution, then it is probably justified to consider the associated complex as the main reacting species. It seems difficult to offer any explanation of the apparent third order behavior in the cadmium iodide exchange without involving polarization in some way.

Uncertainty about the nature of the reacting species in the exchange reactions with zinc and cadmium iodides, and iodine, makes it impossible to obtain true activation energies for these reactions, since any exponential temperature dependence of α is included in the calculated activation energies. However, the differences in the values recorded (Table II) are of the order of magnitude to be expected for variation of α with temperature, from which it

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seems reasonable to infer that the activation energy for exchange with undissociated molecules or complexes (iodide ion carriers) is essentially the same as for simple iodide ion exchange. If this is true, an activation energy of about 18 kcal. is to be associated with activation of the organic iodide.

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SYNTHESIS OF AMINO ACIDS FROM SUBSTITUTED CYANOACETIC ESTERS[1]

By Paul E. Gagnon, Paul A. Boivin[2], and Hugh M. Craig[3]

Abstract

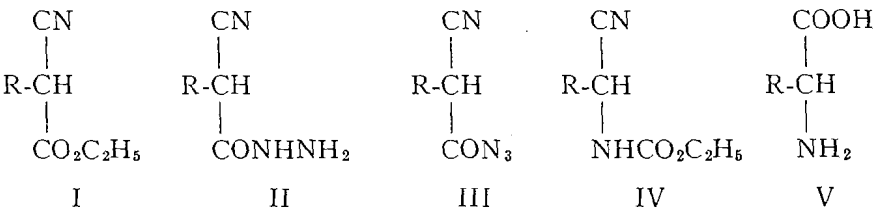
The Darapsky degradation, by which a carbethoxy group is replaced by an amino group, has been applied successfully to substituted cyanoacetic esters for the preparation of 10 amino acids. The esters were formed by condensation of ethyl cyanoacetate with alkyl or arylalkyl halides. The hydrazides were obtained by treatment of the esters with hydrazine hydrate and identified by their anisal derivatives. Diazotization of the hydrazides gave rise to azides. These were transformed into carbethoxyaminonitriles by refluxing with absolute ethanol. The urethanes, on acid hydrolysis, yielded the amino acids. The following amino acids were synthesized: DL-β-methylleucine, DL-α-amino-β-methylisoheptanoic acid, DL-α-amino-β-cyclohexylpropionic acid, DL-C-*o*-methylcyclohexylglycine, DL-C-*m*-methylcyclohexylglycine, DL-C-*p*-methylcyclohexylglycine, DL-C-*o*-xylylglycine, DL-C-*m*-xylylglycine, DL-C-*p*-xylylglycine, DL-*p*-ethylalanine.

Introduction

The Curtius reaction, whereby acid azides break down on heating into isocyanates and nitrogen, was applied in 1915 to the preparation of an amino acid from cyanoacetic ester by Darapsky and Hillers (4), who obtained glycine. Since that time a considerable number of amino acids (3, 6, 7, 8, 9, 10, 11) have been synthesized from substituted cyanoacetic esters by application of the Darapsky degradation. The aim of the present work was to extend the limits of this synthesis to 10 other amino acids and to observe the effect of the various substituents on the properties of the new compounds.

The starting materials, the alkyl or arylalkyl halides, were prepared in three different ways. By chloromethylation (2) of toluene and ethylbenzene, *p*-xylyl chloride and ethylbenzyl chloride respectively were obtained. The bromides were prepared by the action of phosphorus tribromide on the carbinols (17). The iodide was obtained by the reaction of iodine on a mixture of cyclohexylcarbinol and red phosphorus (5). The yields varied from 26 to 90%.

By refluxing the halides with ethyl cyanoacetate in sodium ethylate solution, the esters (I) were obtained in yields varying from 18 to 60%.



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R = 2-methyl-3-butyl, C_5H_{11}-; 2-methyl-4-pentyl, C_6H_{13}-; cyclohexylmethyl, C_6H_{11}-CH_2-; *o*-methylcyclohexyl, CH_3-C_6H_{10}-; *m*-methylcyclohexyl, CH_3-C_6H_{10}-; *p*-methylcyclohexyl, CH_3-C_6H_{10}-; *o*-xylyl, CH_3-C_6H_4-CH_2-; *m*-xylyl, CH_3-C_6H_4-CH_2-; *p*-xylyl, CH_3-C_6H_4-CH_2-; *p*-ethylbenzyl, C_2H_5-C_6H_4-CH_2-.

Hydrazine hydrate mixed with the esters (I) at room temperature gave rise to the hydrazides (II). These were identified by their condensation products with anisaldehyde.

The conversion of the hydrazides into the corresponding azides (III) took place by treatment with nitrous acid, the azides being extracted with ether. On boiling the alcoholic solutions of the azides under reflux, the ethyl urethanes (IV) were formed.

The hydrolysis of the urethanes to amino acids (V) was effected by refluxing in hydrochloric acid (20%). A mixture of equal volumes of concentrated hydrochloric acid, formic acid (85%), and water did not increase the yield whenever it was used.

The following α-amino acids were synthesized: DL-β-methylleucine, DL-α-amino-β-methylisoheptanoic acid, DL-α-amino-β-cyclohexylpropionic acid, DL-C-*o*-methylcyclohexylglycine, DL-C-*m*-methylcyclohexylglycine, DL-C-*p*-methylcyclohexylglycine, DL-C-*o*-xylylglycine, DL-C-*m*-xylylglycine, DL-C-*p*-xylylglycine, and DL-*p*-ethylalanine.

Experimental*

Starting Materials

The halides, R-X, were prepared by three different methods.

(*a*) *Chloromethylation of Aromatic Hydrocarbons*

A mixture of aromatic hydrocarbon (2.5 moles), trioxymethylene (1.0 mole), and pulverized zinc chloride (20 gm.) was treated with a rapid current of moist hydrochloric acid while stirring. The reaction was exothermic. The mixture was cooled to 60°C. and maintained at this temperature until the reaction was complete. The mixture was placed in a separatory funnel, the aqueous portion discarded, and the upper layer washed repeatedly with water and dilute sodium carbonate, dried over anhydrous sodium sulphate, and filtered. By fractional distillation of the filtrate at reduced pressure the aromatic chloride was obtained.

(*b*) *Alkyl Bromides*

Phosphorus tribromide (1.0 mole) was placed in a round bottomed flask with a condenser attached, and the alcohol (1.0 mole) was slowly added. The reaction proceeded with evolution of heat. The reaction mixture was allowed to stand overnight at room temperature, after which it was refluxed gently for two hours, cooled, and poured into cold water (500 ml.), and placed in a

**All melting points are uncorrected.*

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separatory funnel. The aqueous layer was discarded. The upper layer was dried over anhydrous sodium sulphate and, by fractional distillation at reduced pressures, the bromide obtained.

(*c*) *Cyclohexylmethyl Iodide*

Iodine (20 gm.) was added to a mixture of cyclohexylcarbinol (161 gm., 1.5 moles) and dry red phosphorus (20 gm.). The mixture was heated on a water bath until the iodine had dissolved. After cooling, another portion of iodine (20 gm.) was added. The same procedure was repeated until sufficient iodine (170 gm.) had been added. The reaction mixture was heated for five minutes at 120°C., cooled, poured into ice-water and diluted sodium hydroxide, and extracted with ether. The ether was evaporated and the iodide obtained by fractional distillation at reduced pressure.

The properties and yields of the organic halides are given in Table I.

TABLE I

SUBSTITUTED HALIDES, R–X

Compound	B.p., °C.	Yield, %	Formula	Halogen, %	
				Calc.	Found
2-Methyl-3-butyl bromide*	60 (25 mm.)	80	$C_5H_{11}Br$	53.0	52.5
2-Methyl-4-pentyl bromide**	68 (25 mm.)	60	$C_6H_{13}Br$	48.5	48.0
Cyclohexylmethyl iodide†	99 (17 mm.)	55	$C_6H_{11}CH_2I$	56.7	56.4
o-Methylcyclohexyl bromide††	86 (30 mm.)	75	$C_7H_{13}Br$	45.2	45.0
m-Methylcyclohexyl bromide†††	78 (20 mm.)	80	$C_7H_{13}Br$	45.2	44.7
p-Methylcyclohexyl bromide‡	92 (30 mm.)	90	$C_7H_{13}Br$	45.2	44.6
p-Xylyl chloride‡‡	96–97 (25 mm.)	75	C_8H_9Cl	25.3	24.8
p-Ethylbenzyl chkoride‡‡‡	92 (12 mm.)	26	$C_9H_{11}Cl$	23.0	22.6

*Ref. (19) **Ref. (18) †Ref. (13) ††Ref. (15) †††Ref. (14)
‡Ref. (12) ‡‡Ref. (16) ‡‡‡Ref. (2)

Substituted Cyanoacetic Esters (I)

Ethyl cyanoacetate (113 gm., 1.0 mole) was added to a clear solution of sodium ethoxide (11.5 gm., 0.5 mole; 250 ml. of absolute ethanol) and the suspension heated to the boiling point. After cooling, the substituted halides (0.5 mole) were slowly added, and the reaction mixture refluxed until neutral to wet litmus paper. The alcohol was distilled off under reduced pressure and the remainder poured into cold water (500 ml.) and acidified with hydrochloric acid. The aqueous solutions were extracted three times with ether and the combined extracts dried over anhydrous sodium sulphate. The ether was evaporated and the esters obtained by fractional distillation under reduced pressure.

The properties and yields are summarized in Table II.

Substituted Cyanoacethydrazides (II)

The monosubstituted cyanoacetic esters (0.05 mole) were vigorously stirred with 100% hydrazine hydrate (2.5 gm., 0.05 mole). There was evolution of heat and the two layers passed into solution from which the white hydrazide pre-

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TABLE II

ETHYL α-SUBSTITUTED CYANOACETATES, RCH(CN)COOC$_2$H$_5$

R	Starting material	Yield, %	B.p., °C.	Formula	Nitrogen, %		n_D^{25}
					Calc.	Found	
2-Methyl-3-butyl	$C_5H_{11}Br$	45	123 (17 mm.)	$C_{10}H_{17}O_2N$	7.65	7.52	1.4280
2-Methyl-4-pentyl	$C_6H_{11}Br$	60	181 (19 mm.)	$C_{11}H_{19}O_2N$	7.11	7.34	1.4303
Cyclohexylmethyl	$C_6H_{11}CH_2I$	51	166 (19 mm.)	$C_{12}H_{19}O_2N$	6.69	6.32	1.4570
o-Methylcyclohexyl	$CH_3C_6H_{10}Br$	18	149 (15 mm.)	$C_{12}H_{19}O_2N$	6.69	6.44	1.4488
m-Methylcyclohexyl	$CH_3C_6H_{10}Br$	32	180 (20 mm.)	$C_{12}H_{19}O_2N$	6.69	6.47	1.4501
p-Methylcyclohexyl	$CH_3C_6H_{10}Br$	32	154 (2 mm.)	$C_{12}H_{19}O_2N$	6.69	6.63	1.4485
o-Xylyl	$CH_3C_6H_4CH_2Br$	55	175 (19 mm.)	$C_{13}H_{15}O_2N$	6.45	6.38	1.5052
m-Xylyl	$CH_3C_6H_4CH_2Br$	55	180 (19 mm.)	$C_{13}H_{15}O_2N$	6.45	6.38	1.5101
p-Xylyl	$CH_3C_6H_4CH_2Cl$	48	178 (19 mm.)	$C_{13}H_{15}O_2N$	6.45	6.32	1.5023
p-Ethylbenzyl	$C_2H_5C_6H_4CH_2Cl$	50	116 (17 mm.)	$C_{14}H_{17}O_2N$	6.06	6.03	1.5001

cipitate appeared after a few minutes. The products were recrystallized from ethanol. On occasion it was found necessary to place the solution in a desiccator, where on standing the precipitate formed.

The properties are listed in Table III.

TABLE III

α-SUBSTITUTED CYANOACETHYDRAZIDES, RCH(CN)CONHNH$_2$

R	M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found
2-Methyl-3-butyl	101	$C_8H_{15}ON_3$	24.9	24.8
2-Methyl-4-pentyl	144	$C_9H_{17}ON_3$	23.0	23.2
Cyclohexylmethyl	246	$C_{10}H_{17}ON_3$	21.5	21.5
o-Methylcyclohexyl	174	$C_{10}H_{17}ON_3$	21.5	21.5
m-Methylcyclohexyl	207	$C_{10}H_{17}ON_3$	21.5	21.8
p-Methylcyclohexyl	148	$C_{10}H_{17}ON_3$	21.5	21.4
o-Xylyl	116	$C_{11}H_{13}ON_3$	20.7	20.5
m-Xylyl	107	$C_{11}H_{13}ON_3$	20.7	20.6
p-Xylyl	128	$C_{11}H_{13}ON_3$	20.7	20.6
p-Ethylbenzyl	88	$C_{12}H_{15}ON_3$	19.4	19.5

Anisal Derivatives of Substituted Cyanoacethydrazides

The hydrazides were dissolved in ethanol and anisaldehyde added to the hot solutions. If precipitation did not take place immediately, one drop of concentrated hydrochloric acid was added and the solutions let stand until precipitation occurred. The products were purified by recrystallization from ethanol.

The properties are listed in Table IV.

Amino Acids (V)

The hydrazides (0.05 mole) were dissolved in aqueous hydrochloric acid (15%, 100 ml.), cooled to 0°C., and covered with a layer of ether (75 ml.). Sodium nitrite (10 gm.) dissolved in water (30 ml.) was added dropwise to the

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TABLE IV

ANISAL DERIVATIVES

Compound	M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found
2-Methyl-3-butyl	219	$C_{16}H_{21}O_2N_3$	14.6	14.7
2-Methyl-4-pentyl	196	$C_{17}H_{23}O_2N_3$	14.0	13.9
Cyclohexylmethyl	109	$C_{18}H_{23}O_2N_3$	13.4	13.3
o-Methylcyclohexyl	213	$C_{18}H_{23}O_2N_3$	13.4	13.3
m-Methylcyclohexyl	183	$C_{18}H_{23}O_2N_3$	13.4	13.6
p-Methylcyclohexyl	139	$C_{18}H_{23}O_2N_3$	13.4	13.4
o-Xylyl	147	$C_{19}H_{19}O_2N_3$	13.1	13.4
m-Xylyl	172	$C_{19}H_{19}O_2N_3$	13.1	12.7
p-Xylyl	162	$C_{19}H_{19}O_2N_3$	13.1	12.8
p-Ethylbenzyl	152	$C_{20}H_{21}O_2N_3$	12.5	12.7

mechanically stirred mixtures. The azides, on formation, passed into the ether layer. On completion of the reaction, the ether was decanted and the aqueous layers rapidly extracted with two fresh portions of ether. The extracts were combined, dried over anhydrous sodium sulphate, and filtered into absolute ethanol (75 ml.). The ether was evaporated and the azides (III) refluxed on a water bath for one hour to complete the transformation to the urethanes (IV). The alcohol was removed by distillation at reduced pressure. The urethanes were hydrolyzed to the amino acids by refluxing in aqueous hydrochloric acid (20%, 200 ml.) for 48 hr. at 140°C. The mixtures were evaporated to dryness, dissolved in water, boiled with charcoal, and filtered several times. The filtrates were neutralized, concentrated to a small volume, and cooled. On the addition of acetone (2.5 liters) the amino acids precipitated. These were purified by reprecipitation in the same manner and dried in the oven at 100°C.

Table V summarized the physical constants as well as the derivatives formed.

TABLE V

AMINO ACIDS AND DERIVATIVES

Compound	Yield, %	Derivative	M.p., °C.	Formula	Nitrogen, %	
					Calc.	Found
DL-β-Methylleucine	50	Ureido	168	$C_{14}H_{20}O_3N_2$	10.6	10.3
DL-α-Amino-β-methyliso-heptanoic acid	58	Hydantoin	145	$C_9H_{16}O_2N_2$	15.2	14.8
DL-α-Amino-β-cyclohexyl-propionic acid*	39	Copper salt	—	$(C_9H_{16}O_2N)_2Cu$	6.94	6.68
DL-C-*o*-Methylcyclohexyl glycine	39	Copper salt	—	$(C_9H_{16}O_2N)_2Cu$	6.94	6.84
DL-C-*m*-Methylcyclo-hexylglycine	35	Hydantoin	180	$C_{10}H_{16}O_2N_2$	14.2	14.2
DL-C-*p*-Methylcyclo-hexyglycine	78	Hydantoin	210	$C_{10}H_{16}O_2N_2$	14.2	14.7
DL-C-*o*-Xylylglycine	54	Hydantoin	215	$C_{11}H_{12}O_2N_2$	13.7	14.0
DL-C-*m*-Xylylglycine	80	Ureido	172	$C_{17}H_{18}O_3N_2$	9.40	9.71
DL-C-*p*-Xylylglycine	75	Hydantoin	190	$C_{11}H_{12}O_2N_2$	13.7	13.9
DL-*p*-Ethylalanine	17	Hydantoin	182	$C_{12}H_{14}O_2N_2$	12.8	13.0

*Ref. (1).

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SUR LA FLAMME FROIDE DE L'ETHER[1]

LUDOVIC OUELLET[2] ET CYRIAS OUELLET

Résumé

Un appareil permettant de mesurer la lumière émise par une flamme froide est décrit. L'influence de la concentration des réactifs, du diamètre de la chambre à réaction et de la température est étudiée. L'émission intégrale croît avec la concentration de chacun des réactifs (éther ou oxygène). La durée de la flamme froide croît avec le diamètre des récipients et la pression totale des réactifs. Une élévation de température influence surtout la forme des courbes représentant l'intensité lumineuse en fonction du temps.

Introduction

Quelques propriétés des flammes froides, observées par une méthode photoélectrique, ont été décrites récemment (4). Des enregistrements oscillographiques ont permis de suivre les pulsations de l'intensité lumineuse et ont révélé qu'elles coincident avec celles de la pression. Les lueurs obtenues avec des mélanges d'éther éthylique et d'oxygène en système statique ont des intensités et des émissions intégrales sensiblement indépendantes de la température entre 200° et 250°C., mais croissant avec la pression. L'émission intégrale passe par un maximum très net à la composition de 50% d'éther en volume. Ce fait suggère l'intervention d'un intermédiaire, probablement un peroxyde, dans la constitution duquel l'éther et l'oxygène entrent en proportion équimoléculaire.

Comme l'exploration de ce phénomène exige un examen détaillé des effets de plusieurs variables, les résultats précédents sont complétés et précisés dans le présent travail par des données supplémentaires, portant surtout sur l'influence des concentrations et celle du diamètre du récipient, ainsi que sur la question de la limite inférieure. Les effets de l'addition de gaz étrangers et l'interprétation des pulsations seront l'objet de publications subséquentes.

Méthode expérimentale

La description du mode de production et d'enregistrement oscillographique de lueurs uniformes en système statique a déjà été esquissée (4). L'appareil complet est représenté sur la Fig. 1. L'un des petits ballons A et E contenait à l'abri de l'air l'éther débarrassé des peroxydes (7) par distillation en présence de permanganate de potassium en solution acide et séché par contact avec du sodium métallique. L'autre ballon renfermait, le cas échéant, une autre substance que l'on désirait incorporer au mélange combustible. On transférait par évaporation une certaine quantité d'éther dans un ballon B de deux litres, préalablement évacué, et on introduisait par la voie i la quantité voulue d'oxygène. Avant chaque expérience, on introduisait dans un ballon auxiliaire C de 1000 cc. la quantité de mélange apte à produire une pression déterminée

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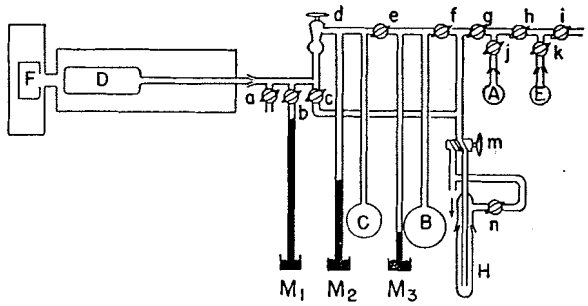

FIG. 1. *Appareil avec la cellule photomultiplicatrice F et la chambre à réaction D.*

dans la chambre à réaction D, où on faisait ensuite pénétrer les gaz en ouvrant aussi brusquement que possible le robinet creux d dont l'ouverture latérale avait été agrandie à dessein. On évacuait le système au moyen soit d'une pompe à diffusion VMF 5 par la voie a, soit d'une pompe Hyvac par la voie $c\ m\ n\ H$. Le piège H permettait de recueillir les produits de la réaction condensables à la température de la glace sèche ou à celle de l'air liquide. On laissait de robinet b fermé durant une expérience et on ne mesurait que la pression finale en ouvrant ce robinet immédiatement après l'extinction de la flamme froide. La chambre à réaction D était, pour la plupart de nos expériences, un tube de Pyrex de 46 × 130 mm., placé dans un four électrique à l'intérieur duquel la température était constante et uniforme à ± 1°C. près.

La lumière émise en D tombait en F sur une cellule photomultiplicatrice de type IP28, enfermée dans un manchon en laiton percé d'une fenêtre et refroidi par une circulation d'eau. Pour amplifier et enregistrer les courants photoélectriques sur un oscillographe à rayons cathodiques à balayage lent, on se servait d'un montage dont les particularités ont été décrites dans la publication précédente (4).

Les raisons de croire que les lueurs observées par cette méthode étaient statiques et homogènes ont été exposées au même endroit. Dans certains cas, la lueur principale était suivie, à une ou deux secondes d'intervalle, d'un dard lumineux qui sortait du tube d'entrée des gaz et traversait une partie du cylindre D. Ce phénomène se produisait généralement trop tard pour apparaître sur l'oscillogramme et était précédé d'une période d'obscurité complète, de sorte qu'on ne pouvait le confondre avec l'une des crêtes de l'oscillogramme principal. Nous nous contentons de signaler l'existence occasionnelle de cette seconde flamme que nous n'avons pas étudiée en détail.

Résultats

Description des oscillogrammes

Les oscillogrammes de la Fig. 2 montrent l'allure générale de la variation de l'émission lumineuse en fonction du temps. Ils indiquent en même temps le degré moyen de reproductibilité du phénomène. Bien que ces exemples de

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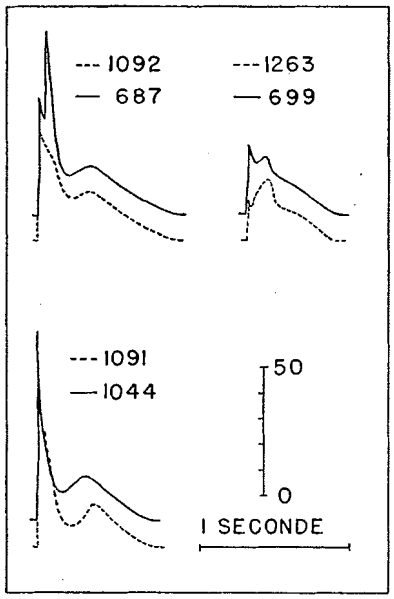

FIG. 2. *Couples d'oscillogrammes enregistrés dans des conditions identiques, illustrant le degré de reproductibilité du phénomène (voir Tableau I.).*

concordance n'aient pas été choisis parmi les meilleurs, il a fallu décaler verticalement les courbes de chaque paire afin d'éviter une superposition partielle qui rendrait le graphique illisible.

Tous les oscillogrammes présentés dans ce travail portent une échelle de temps et une échelle d'intensité lumineuse arbitraire mais uniforme, exprimée en millimètres de déplacement sur l'écran de l'oscillographe. Pour décrire ces oscillogrammes, il a fallu choisir un ensemble de paramètres commodes sans trop présumer de leur signification éventuelle. A quelques détails près, la plupart des oscillogrammes présentent deux crêtes principales, la première généralement aiguë, la seconde plus arrondie. Autant que possible, les oscillogrammes seront caractérisés par les hauteurs h_1 et h_2 de la première et de la seconde crête, la position t_2 sur l'axe des temps de la seconde crête et la durée totale t de la lueur dans les cas où cette grandeur peut être appréciée avec une précision suffisante. On désignera par A, exprimée en millimètres carrés, l'aire comprise sous la courbe; cette aire représente l'émission intégrale. Cette division arbitraire du phénomène en deux étapes principales ne s'applique pas aux cas où l'on observe plus de deux crêtes et ne tient pas compte des crénelures de faible amplitude.

Malgré les observations visuelles et autres précautions qui ont été prises (4), il reste possible, bien que peu probable à notre avis, que la crête initiale, généralement aiguë, soit attribuable à un éclair prématuré et fugitif, localisé à l'orée du tube d'entrée des gaz, tel que celui qui a été signalé récemment par Chamberlain et Walsh (1). Cependant, la comparaison des photogrammes et des manogrammes a montré que le début simultané de l'émission lumineuse et de l'élé-

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vation de pression est postérieur à l'établissement de l'équilibre thermique, du moins aux températures inférieures à 230°C. Le décalage des limites publiées par Chamberlain et Walsh augmente brusquement au-dessus de 230°C.; ceci pourrait être la raison des aberrations qui nous ont empêchés de vérifier dans cette région les régularités constatées aux températures moins élevées. Certains oscillogrammes indiquent un éclair initial très bref et très brillant que notre dispositif actuel est incapable d'enregistrer convenablement et que nous représentons en pointillé sur les graphiques. Ce phénomène semble se produire surtout lorsque la pression d'oxygène est grande ou la température élevée.

TABLEAU I

CONDITIONS DANS LESQUELLES ONT ÉTÉ OBTENUS OSCILLOGRAMMES DES FIGS. 2 ET 3

Exp. No.	Température, °C.	Pression, mm. Hg	Composition, Ether, %	Diamètre, mm.
687	215	66	50	46
1092	215	66	50	46
1091	215	58	50	46
1044	215	58	50	46
1263	215	57	50	34
699	215	57	50	34
1312	215	71	65	46
1164	215	48	50	46
1241	215	35	33	46
1213	215	29	20	46
277	215	97	80	46
1139	215	53	65	46
1167	215	36	50	46
1243	215	27	33	46

Influence des concentrations

Certains aspects de l'influence des concentrations des réactifs ont déjà été exposés (4). Comme complément à la famille d'oscillogrammes montrant l'influence de la pression partielle de l'oxygène, nous présentons la famille de la Fig. 3, qui illustre l'influence de la pression d'éther à pression d'oxygène constante.

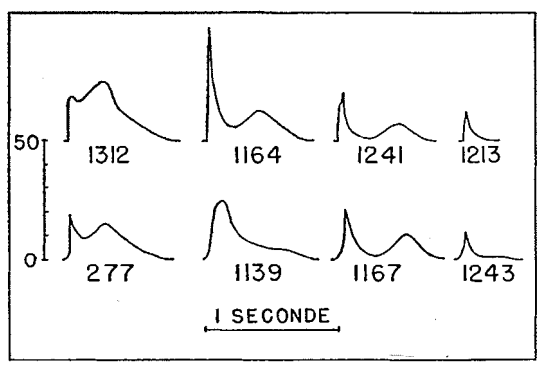

FIG. 3. *Oscillogrammes montrant l'influence de la pression d'éther à pression d'oxygène constante, à 215°C.*
1ère rangée : P_{O_2}= 24 mm. Hg.
2ième rangée: P_{O_2}= 18 mm. Hg.

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Comme nous l'avons déjà mentionné, l'ensemble des émissions intégrales mesurées à 215°C. peut être représenté approximativement par la relation empirique

$$A = K.\left(\frac{P_{E_t} \cdot P_{O_2}}{P}\right) P_m ,$$

où P est la pression totale, P_{E_t} et P_{O_2} celles de l'éther et de l'oxygène, tandis que P_m est la pression partielle de celui des deux constituants qui entre pour moins de 50% dans la composition du mélange. La Fig. 4 illustre cette relation. Les écarts constatés ne semblent pas être entièrement statistiques; aux pressions supérieures à 100 mm., le maximum de la cloche de la Fig. 5 se déplace vers les compositions inférieures à 50% d'éther. Nos données actuelles ne sont pas suffisamment abondantes pour permettre une étude détaillée de cette tendance.

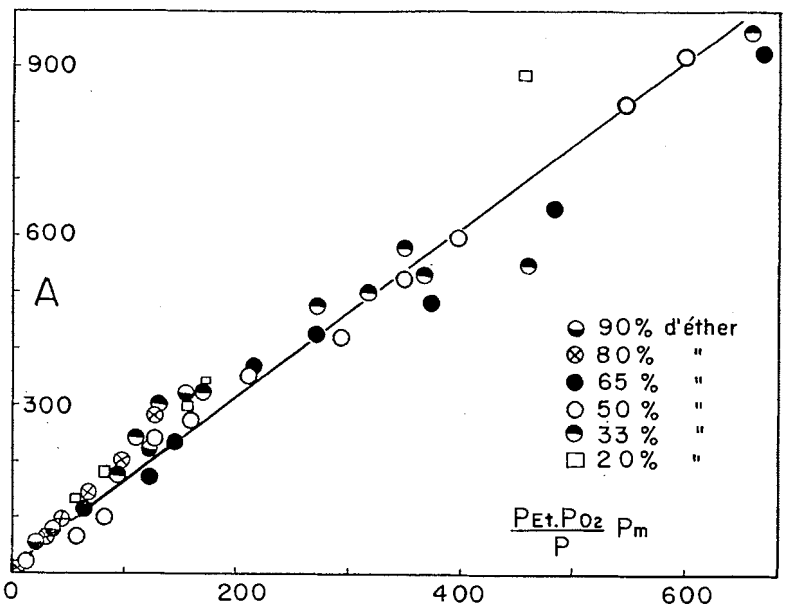

FIG. 4. *Emission intégrale (A) d'une flamme froide en fonction des pressions partielles des réactifs.*
Pm = pression partielle de la substance minoritaire.

Contrairement à l'observation visuelle, qui ne donne qu'une perception globale du phénomène, l'examen des oscillogrammes permet d'étudier séparément les variations de plusieurs grandeurs et d'obtenir une représentation analytique de ce qu'on appelle communément la limite inférieure. On a déjà vu (4) que l'émission intégrale ne présente pas de discontinuité quand on abaisse la pression. Les variations des hauteurs des crêtes sont représentées sur les Figs. 6, 7 et 8. Celle de la première crête ne présente aucune discontinuité; celle de la seconde devient nulle en-dessous d'un seuil de pression comprise

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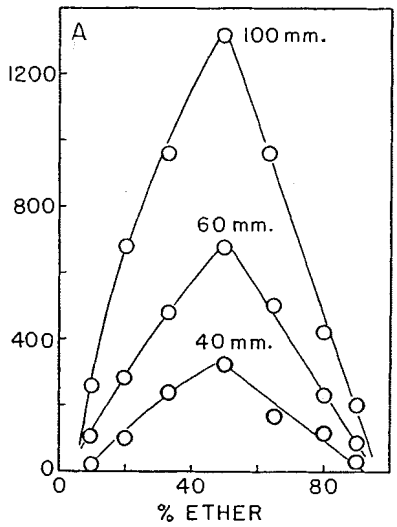

FIG. 5. *Emission intégrale (A) d'une flamme froide en fonction de la composition du mélange à des pressions totales de 40, 60 et 100 mm. T = 215°C.*

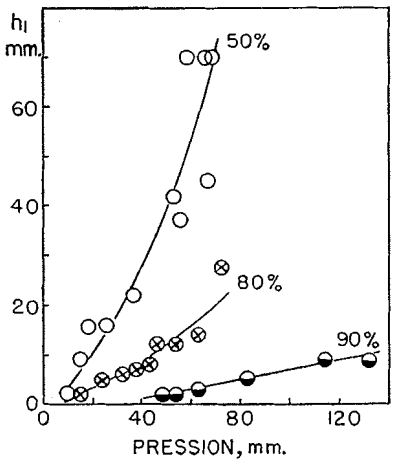

FIG. 6. *Hauteur de la première crête* h_1, *en fonction de la pression des réactifs à différentes compositions.*

entre 20 et 45 millimètres, suivant la composition du mélange, mais ne manifeste généralement pas un effondrement assez rapide pour donner l'illusion d'une limite nette. Si l'on porte en graphique (Fig. 9) les valeurs de ce seuil de pression en fonction de la composition du mélange, on trouve qu'il passe par un minimum pour une composition voisine de 50% d'éther, que nos résultats ne permettent cependant pas de définir avec exactitude.

En fonction de la composition du mélange, la hauteur de la seconde crête varie suivant les cloches arrondies et sensiblement symétriques de la Fig. 10,

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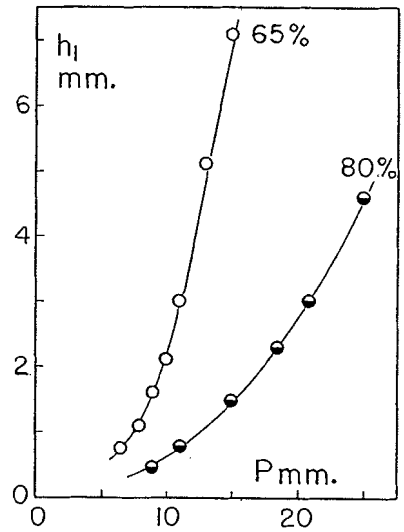

FIG. 7. *Aux faibles pressions, la hauteur de la première crête* h_1, *tend asymptotiquement vers zéro lorsque la pression s'abaisse.*

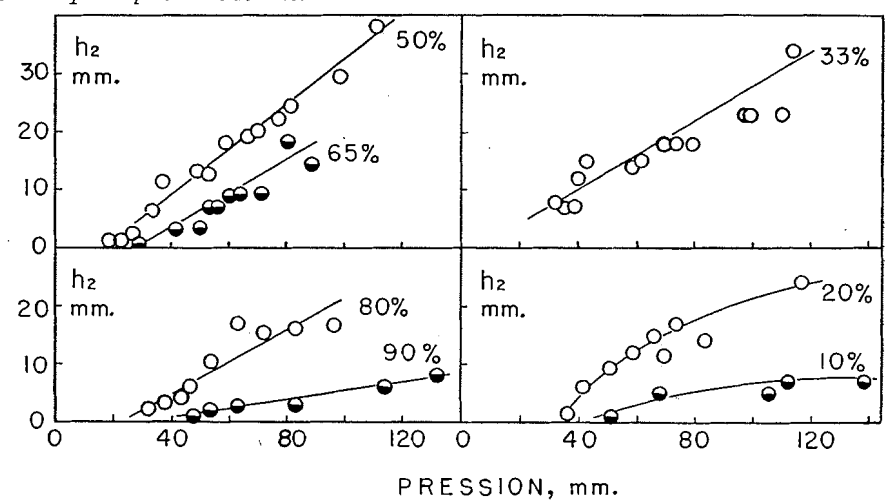

FIG. 8. *Hauteur de la seconde crête* h_2, *en fonction de la pression à 215°C. à diverses compositions exprimées en pourcentage d'éther.*

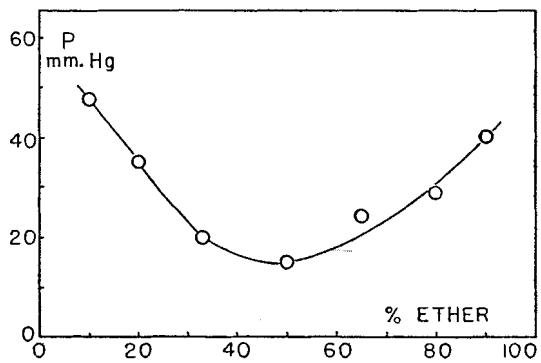

FIG. 9. *Pression limite pour l'existence d'une seconde crête à 215°C. en fonction du pourcentage d'éther.*

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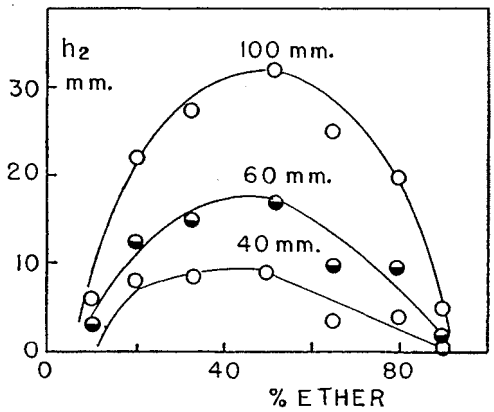

FIG. 10. *Variation de la hauteur de la seconde crête* h_2 *en fonction de la composition à pression constante, montrant le maximum à 50%.*

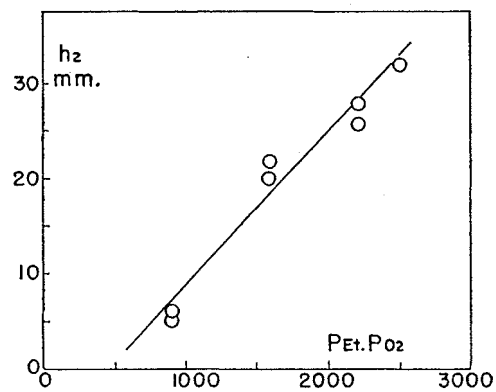

FIG. 11. *Hauteur de la seconde crête* h_2 *en fonction du produit* P_{Et}. P_{O_2} *à pression totale constante (100 mm. Hg).*

qui passent par un maximum lorsque les concentrations des deux constituants sont égales. En supposant que l'intensité h_2 est proportionnelle à la vitesse maximum d'un processus bi-moléculaire, on doit s'attendre à des courbes de cette allure. La Fig. 11 et le Tableau II montrent que l'on obtient, du moins avec les résultats à 100 mm. approximativement, une relation de la forme

$$h_2 = k\,(P_{Et}\,P_{O_2} - a),$$

où k est une constante et a une valeur limite du produit $P_{Et}P_{O_2}$, pour laquelle on a $h_2 = 0$ et qui représente le seuil décrit plus haut (Figs. 8 et 9).

TABLEAU II

VALEURS DE h_2 EN FONCTION DU PRODUIT P_{Et}. P_{O_2}

% d'éther	10	20	33	50	65	80	90
P_{Et}. P_{O_2}	900	1600	2200	2500	2200	1600	900
h_2	6	22	28	32	27	20	5

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Influence du diamètre du récipient

On a utilisé quatre récipients en Pyrex: une sphère de 70 mm. de diamètre et trois cylindres de 130 mm. de longueur et de 46, 34, et 21 mm. de diamètre. Seuls des mélanges contenant 50% d'éther en volume ont été étudiés jusqu'ici. A cause des modifications de la géométrie de l'appareil, les intensités enregistrées ne sont pas comparables; seules les variations dans la durée et dans le rapport des hauteurs sont significatifs. La Fig. 12 contient des exemples d'oscillogrammes obtenus à 201, 215, et 236°C. en employant ces divers récipients. On trouvera dans le Tableau III les données essentielles concernant ces expériences et quelques autres.

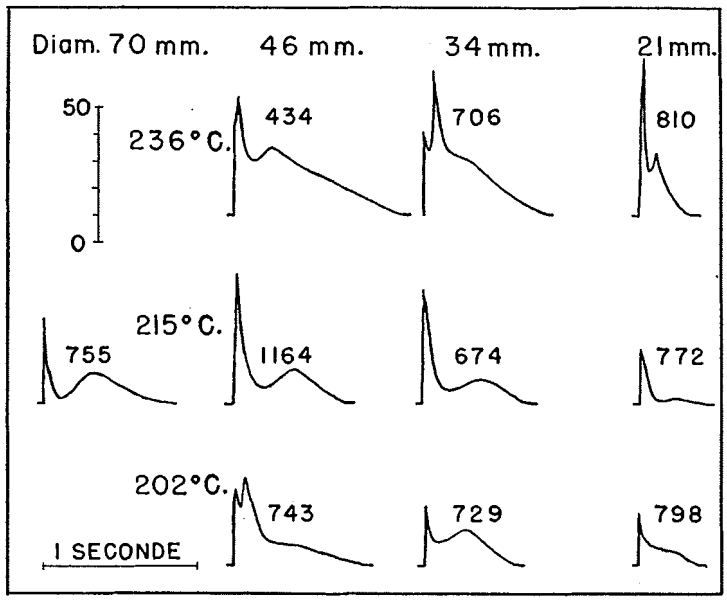

FIG. 12. *Oscillogrammes montrant l'influence du diamètre du récipient à pression constante: 80 mm. à 236°C., 49 mm. à 215°C. et 50 mm. à 201°C. Voir Tableau III.*

La durée totale de la lueur et l'importance relative de la seconde crête croissent avec le diamètre du récipient. Les courbes de la Fig. 13 montrent que, lorsque le diamètre décroît, les durées à différentes pressions totales semblent converger de plus en plus rapidement vers une valeur nulle qu'elles atteindraient pour un diamètre voisin de 10–15 mm. Il semble donc y avoir un diamètre inférieur en-dessous duquel la réaction n'aurait pas lieu. Prettre (5) a trouvé que la vitesse d'oxydation du pentane à 270°C. décroît elle aussi rapidement lorsque le diamètre du récipient s'approche de 10 mm. En fonction de la pression, les durées varient comme l'indique la Fig. 14. L'effondrement de la courbe 4 vers 40 mm. est attribuable à la disparition de la seconde crête et correspond aux brusques changements d'allure, aux basses pressions, des courbes de la Fig. 13.

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TABLEAU III

INFLUENCE DU DIAMÈTRE DU RÉCIPIENT SUR LA FLAMME FROIDE D'UN MÉLANGE ÉQUIMOLÉCULAIRE D'ÉTHER ET D'OXYGÈNE

Exp. No	Diam., mm.	Température, °C.	Pression, mm. Hg	t, sec.	h_2 mm.
432	46	236	124	1.26	11
434	46	236	79	1.05	7
437	46	236	57	0.73	4
706	34	236	83	0.75	21
713	34	236	58	0.66	11
719	34	236	40	0.70	2
808	21	236	87	0.35	20
810	21	236	81	0.35	23
818	21	236	57	0.30	–
750	70	215	95	1.22	9
755	70	215	48	0.87	11
1164	46	215	48	0.71	13
670	34	215	91	0.89	23
674	34	215	49	0.69	9
763	21	215	78	0.47	14
772	21	215	49	0.43	2
462	46	201	95	1.08	19
743	46	201	50	0.87	–
723	34	201	95	0.95	37
729	34	201	51	0.62	13
877	21	201	93	0.47	21
798	21	201	51	0.40	6

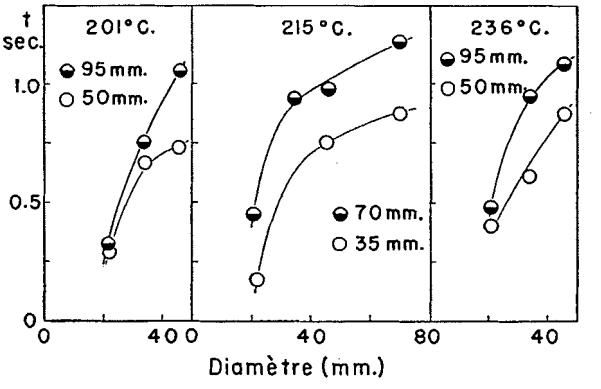

FIG. 13. *Durée* t *de la flamme froide de l'éther en fonction du diamètre du récipient aux pressions indiquées à 201, 215 et 236°C. Composition: Éther: oxygène 1: 1.*

Influence de la température

On sait (4) que les paramètres des oscillogrammes varient peu avec la température entre 200 et 250°C., bien que trois crêtes soient visibles entre 185° et 210°C. et deux seulement entre 210° et 250°C. Quelques observations éparses ayant indiqué des modifications dans l'allure du phénomène aux températures élevées, nous avons effectué quelques expériences entre 250° et 305°C., à des pressions suffisamment basses pour éviter les explosions. Comme le fait voir la

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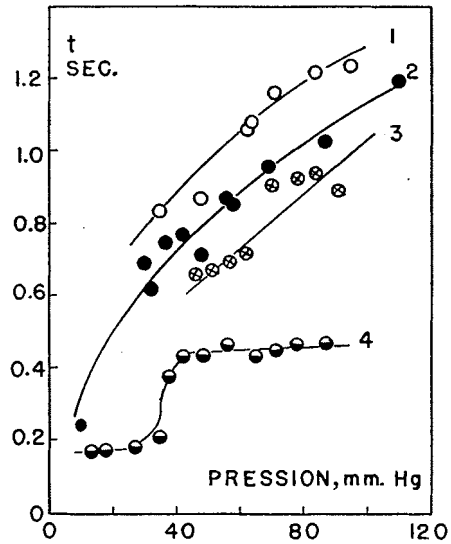

FIG. 14. *Durée* t *de la flamme froide de l'éther en fonction de la pression à 215°C. Diamètre: 1. 70 mm. 2. 46 mm. 3. 34 mm. 4. 21 mm.*

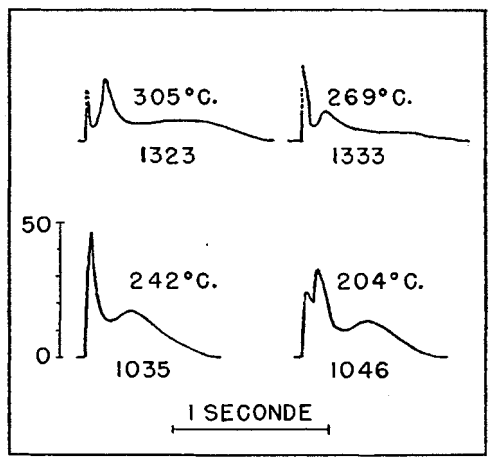

FIG. 15. *Variation de la forme des oscillogrammes en fonction de la température, à une pression d'environ 25 mm. Hg, pour un mélange équimoléculaire d'oxygène et d'éther.*

Fig. 15, à 305°C., la première crête, très élevée et très aiguë, n'est enregistrée qu'à sa base et est suivie de deux autres, la dernière peu accentuée et déclinant très lentement. La durée du phénomène s'en trouve accrue considérablement. Il en est ainsi de l'émission intégrale. Après la flamme à 280°C., la pression continue à croître lentement, vraisemblablement par suite d'une dégradation des intermédiaires, phénomène qui n'est pas décelable en-dessous de 250°C. Malgré cet effet, on n'observe pas de seconde flamme.

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Discussion

Certains aspects des résultats seront discutés plus tard après l'exposé des effets des gaz étrangers et l'analyse des pulsations. Nous nous contenterons ici de quelques remarques portant sur des points particuliers.

Provisoirement, nous nous entenons à l'hypothèse simple que les variations de la luminescence suivent celles de la réaction et, en particulier, que l'intensité lumineuse est à tout instant proportionnelle à la vitesse de la réaction chimique. Cette hypothèse semble justifiée par la simplicité relative des résultats et la coincidence des fluctuations de l'émission lumineuse avec celles de la pression (4). Cependant, one ne peut écarter entièrement la possibilité d'une extinction partielle de la fluorescence de la formaldéhyde par certains intermédiares ou produits de la réaction. Les données connues sur ce sujet ne permettent pas d'apprécier l'importance relative d'un tel effet.

On trouve sur la Fig. 4 une nouvelle illustration de la symétrie qui gouverne la variation de l'émission intégrale en fonction de la composition du mélange. Il est intéressant de noter que Prettre (5) a observé un maximum à la même composition, dans la vitesse d'oxydation lente du mélange pentane-oxygène. Cette observation révèle un nouvel exemple de la similitude que présentent les flammes froides de diverses substances et apporte un argument de plus en faveur de la formation initiale d'un peroxyde ou hydroperoxide de composition ROO ou ROOH.

Une symétrie analogue se retrouve dans la variation de la hauteur de la seconde crête (Fig. 10), et suggère un processus bimoléculaire (Fig. 11). En effet, a pression totale constante, la vitesse d'un processus bi-moléculaire est maximum lorsque les pressions des deux réactifs sont égales. Il se peut que l'intensité h_2 soit proportionnelle à la concentration maximum d'un hydroperoxide. Dans certaines conditions, la formation de cet hydroperoxyde suivrait, d'après Mulcahy (3), une loi bi-moléculaire:

$$\frac{d(\mathrm{ROOH})}{dt} = k\ [\mathrm{RH}]\ [\mathrm{O_2}].$$

La limite inférieure de la flamme froide n'est évidemment pas simple. L'émission intégrale et la hauteur de la première crête décroissent asymptotiquement jusqu'à des pressions de l'ordre de 5 mm. (Figs. 6 et 7). La hauteur de la seconde crête (Fig. 8) atteint un seuil entre 20 et 45 mm., mais sans variation brusque d'allure. La position de ce seuil, qui dépend à la fois de la composition (Fig. 9) et du diamètre, correspond assez bien aux limites observées par Chamberlain et Walsh (1) et par Spence et Townend (6). Ces limites indiquent aussi les pressions nécessaires pour qu'il y ait propagation de la flamme froide. Il semble que les conditions d'existence de notre seconde crête soient les mêmes que les conditions de propagation.

On est aussi tenté d'assimiler cette seconde crête à la seconde flamme de Townend (2). L'intervalle qui sépare les deux crêtes, comme celui qui sépare

les deux flammes, décroît à mesure que la pression s'élève (Fig. 3) et les deux étapes finissent par empiéter l'une sur l'autre aux pressions de l'ordre de celles auxquelles le mélange est susceptible de détonner. Cet intervalle, qui semble correspondre à l'intervalle obscur des flammes doubles de Townend, s'accroît avec le diamètre du récipient (Fig. 12); on verra plus tard que l'addition d'un gaz neutre produit le même effet. L'ensemble des effets de diamètre indique que la paroi accélère cette étape obscure, hâtant ainsi l'avènement de la seconde crête, tout en inhibant cette dernière par l'imposition d'un seuil plus élevé. Il est vraisemblable que ces deux facteurs entrent en jeu dans l'action d'un grillage sur la propagation d'une flamme froide.

Remerciements

Nous remercions le Conseil National des Recherches qui a subventionné ce travail et accordé deux bourses à l'un de nous (L.O.).

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Summary

An apparatus used to study the light emission of a cool flame of ether is described. The influence of the concentration of the reactants, the diameter of the reaction vessel, and the temperature has been studied. The total emission of light increases with the concentration of both reactants (ether or oxygen). The duration of the cool flame increases with the diameter of the vessel and the pressure of the reactants. Raising the temperature modifies the shape of the oscillograms representing the light intensity as a function of time.

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THE ISOTOPIC CONSTITUTION OF GERMANIUM[1]

By R. P. Graham, J. Macnamara,[2] I. H. Crocker,[3] and R. B. MacFarlane[3]

Abstract

A mass spectrometric study of the abundances of the isotopes of germanium has been made using germanium tetrachloride and tetrafluoride prepared from germanium compounds of different geological and geographical origins. Germanium has five isotopes: Ge^{70}, Ge^{72}, Ge^{73}, Ge^{74}, and Ge^{76}. Variations in the natural abundance ratios were found, to the extent of 0.7% for the $\frac{Ge^{76}}{Ge^{70}}$ ratio. Calculations of the chemical atomic weight of germanium from the isotope abundance of this and of other recent mass spectrometric studies yield values 0.03 to 0.05 units higher than the accepted one.

Introduction

The isotopes of germanium were first investigated by Aston in 1923 (1, 2). Using a product obtained by the action of hydrofluoric acid on germanium dioxide, he identified Ge^{70}, Ge^{72}, and Ge^{74} and roughly estimated their proportions. In 1928, Aston carried out a further investigation (3) using germanium tetraethyl and germanium tetrafluoride in an improved mass spectrograph, and reported eight isotopes in the following order of increasing abundance: Ge^{77}, Ge^{71}, Ge^{76}, Ge^{75}, Ge^{73}, Ge^{70}, Ge^{72}, Ge^{74}. In 1931 he published quantitative data (4) for these isotopes based on mass spectra obtained using germanium tetramethyl. Shapiro, Gibbs, and Laubengayer studied the absorption band spectra of germanous sulphide in 1932 (19), and reported Ge^{70}, Ge^{72}, Ge^{74}, and Ge^{76} in abundances comparable to those found by Aston (4). They considered that the bands due to Ge^{71} and Ge^{73}, if present, would have been masked by the very strong bands of the more abundant isotopes Ge^{70}, Ge^{72}, and Ge^{74}; no evidence for the existence of Ge^{75} or Ge^{77} was obtained. Bainbridge examined germanium (6, 7) using the bromide and iodide and concluded in 1933 that the isotopes Ge^{71}, Ge^{75}, and Ge^{77} that had been reported by Aston were "mainly if not entirely hydrides of Ge^{70}, Ge^{74}, and Ge^{76}" (7). Aston then applied a correction for 7.3% monohydride to the results he had obtained in 1931 (4) and agreed that it was "quite clear and that most, if not all, the effect given by the alkyl compounds at 71, 75, 77 are due to hydrides, and that the existence of these isotopes must be regarded as doubtful" (5, p. 131). In fact, when Aston reported his first results with a germanium alkyl compound in 1928 he stated that the possibility of hydride formation "cannot be entirely ruled out" (3). Aston's corrected figures of 1933 (5, p. 131) are given in Table I and, until very recently, have been the accepted values for the abundances of the isotopes of germanium.

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TABLE I

EARLIER WORK ON ISOTOPES OF GERMANIUM

Reference and year	Aston (5); 1933	Inghram *et al.* (13, 14); 1947	Hibbs *et al.* (12); 1949	Hibbs *et al.* (12); 1949
Source of ions	$Ge(CH_3)_4$	$Ge(Ge^+, Ge^{++})$	$GeF_4(GeF_3^+)$	$GeI_4(GeI^+)$
Mass number	Percentage abundance			
70	21.2	20.55	20.60	20.65
72	27.3	27.37	27.38	27.43
73	7.9	7.67*	7.83	7.86
74	37.1	36.74	36.40	36.34
76	6.5	7.67	7.78	7.72

* *The value 7.61% given for* Ge^{73} *in (14) is a misprint (13).*

The present mass spectrometric study of the isotopes of germanium was begun in 1948, and during the course of it two papers concerned with the same subject appeared. The results of these studies by Inghram, Hayden, and Hess (13, 14), and by Hibbs, Redmond, Gwinn, and Harman (12), are summarized in Table I. In comparison with Aston's data, this recent work shows lower abundances for Ge^{70}, Ge^{73}, and Ge^{74}, and higher abundances for Ge^{72} and Ge^{76}. Particular attention is drawn to the fact that Hibbs, *et al.*, like Aston, found Ge^{76} to be less abundant than Ge^{73}, whereas Inghram *et al.* found Ge^{76} and Ge^{73} to have the same abundance. Both the recent studies agree, however, in assessing the abundances of these two isotopes to be much less dissimilar than did Aston.

The present paper reports the results of a careful mass spectrometric study of the relative abundances of the germanium isotopes based on measurements of ion currents due to $GeCl^+$ and GeF_3^+ from samples of germanium tetrachloride and tetrafluoride that were prepared from germanium-bearing material of widely differing geographical and geological origins.

Materials and Methods

Samples

Germanium is widely disseminated in nature, but there are few minerals that contain a substantial percentage of it. Our efforts to obtain samples of argyrodite (the silver–germanium sulphide in which germanium was discovered by Winkler in 1886) and of the related and even rarer mineral canfieldite were unsuccessful. We did, however, secure germanium dioxide that had been prepared from germanite, a copper–germanium sulphide that occurs in South-West Africa. Germanium has been found in the coal of several countries, and one of the samples originated from English coals. It is believed that such germanium as is used in commerce on this continent is recovered as a by-product of the smelting of zinc sulphide ores from the Tri-State area (Missouri, Kansas, and Oklahoma); three of the samples are of this origin. Additional details regarding the samples are given in Table II.

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TABLE II

SOURCES OF GERMANIUM SAMPLES

Sample No.	Form supplied	Origin of sample
1	GeO_2*	Germanite from Tsumeb, South-West Africa.
2	GeO_2*	Germanite from Tsumeb, South-West Africa.
3	GeO_2	Flue dusts of coals occurring mainly in the county of Durham, England.
4	GeO_2	Zinc ores of the Joplin, Missouri, district (Tri-State area).
5	GeO_2**	Zinc concentrates of the Picher field at Picher, Oklahoma (Tri-State area).
6	$GeCl_4$	Zinc ores of Oklahoma.

* *Samples #1 and #2 were obtained in response to two separate orders for the same material from the same supplier; they are presumably identical. Supplier stated that samples may contain spectrographic trace quantities of Cu, Fe, Si, Mg, and Al.*

** *Supplier stated that sample may contain traces of As. When tetrachloride prepared from the oxide was examined in the mass spectrometer, no arsenic could be found in this or any of the samples.*

Preparation of Germanium Tetrachloride

Germanium dioxide was converted to the tetrachloride by treatment with hydrochloric acid and distillation in a stream of hydrogen chloride using a procedure similar to that recommended by Foster, Drenan, and Williston (10, p. 109). After being condensed in a cold trap, the germanium tetrachloride was redistilled in a stream of purified dry nitrogen, passed successively through anhydrous sodium carbonate and anhydrous calcium chloride, and then condensed to a solid in another cold trap. Each lot of tetrachloride so prepared from Samples #1–5, and also Sample #6 which came to us as the tetrachloride, was divided by distillation into three fractions the middle one of which was collected in a sample tube (Fig. 1(*a*)) for analysis in the mass spectrometer.

In the preparation, purification, and fractionation of the germanium tetrachloride, all collectors were flamed carefully before use while being swept with purified dry nitrogen. One and one-half gram samples of germanium dioxide were used, with the tetrachloride being obtained in excellent yield.

Preparation of Germanium Tetrafluoride

Germanium tetrafluoride was prepared by thermally decomposing barium fluorogermanate ($BaGeF_6$) *in vacuo*. Dennis and Laubengayer (8) found this method of preparing germanium tetrafluoride to be the best of several they studied.

A white salt, presumably $BaGeF_6$, was prepared by treating the samples of germanium dioxide with hydrofluoric acid and then with a solution of barium chloride. The salt, after filtering, washing, and drying, was decomposed in an evacuated Vycor tube at 700°C. The apparatus was modified from that of Dennis and Laubengayer (8) in order to permit the formation and purification of

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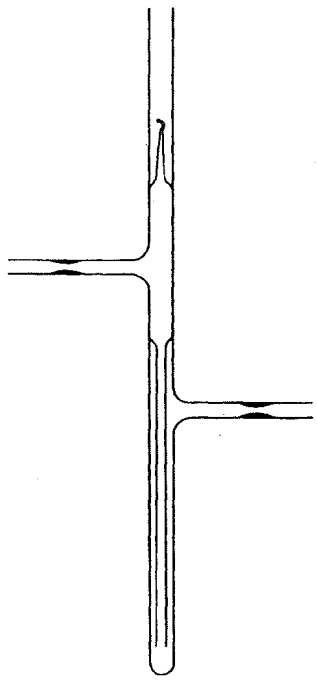

FIG. 1a

germanium tetrafluoride in a series of connected units. The product, as first prepared, was contaminated with hydrogen fluoride and silicon tetrafluoride. These were removed by distillation techniques using appropriate freezing baths. Germanium tetrafluoride has an unusual avidity for water, and careful high vacuum and other techniques were necessary for the preparation of thoroughly dry samples. The details of the method that was used for the preparation and purification of germanium tetrafluoride will be given in a separate paper. One-quarter of a gram of the samples of germanium dioxide was taken initially, with about 1.3 ml., at N.T.P., of tetrafluoride being finally collected in a sample tube (Fig. 1(*b*)) for analysis in the mass spectrometer.

Mass Spectrometry

A 180-degree direction focusing mass spectrometer was used (18). The relative ion currents were measured with a linear inverse feedback amplifier coupled to a Leeds and Northrup Speedomax recorder (15). The bombarding electrons were accelerated through a constant potential, the value of which was approximately 85 v. The accelerating potential for the ions so formed was maintained constant at 1500 v. and the spectrograms were recorded using magnetic scanning. The appropriate shunt was selected manually; the shunt factors are indicated on Figs. 2 and 3.

Although absolute mass spectrometric abundance ratios cannot consistently be determined with a reproducibility better than 0.5%, relative abundance

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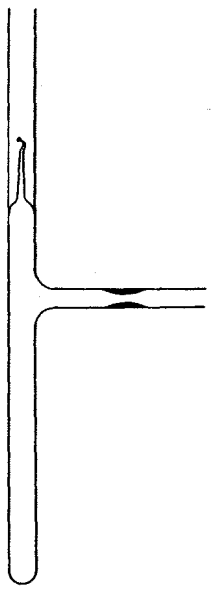

FIG. 1b

measurements can be made with a reproducibility of 0.1%. Relative abundance measurements with this order of precision are made by comparing each sample to a "standard". The procedure was to analyze the "standard", then another sample, and then the "standard" again—all as quickly as possible. The use of automatic recording equipment made it possible to compare two samples of germanium tetrafluoride or of germanium tetrachloride in this way in approximately one hour. Sample #1 was arbitrarily chosen as the "standard" in all experiments. With germanium tetrachloride, five to seven consecutively recorded spectrograms in the mass range 105–113 (corresponding to $GeCl^+$ ions) constituted a set of spectrograms, and, with germanium tetrafluoride, eight consecutively recorded spectrograms in the mass range 127–133 (corresponding to GeF_3^+ ions) constituted a set of spectrograms. Each spectrogram consisted of two peaks for a given mass number, obtained by reversing the scanning after covering the mass range under study. The heights of these two peaks were averaged to give a measure of the ion current for the given mass for the particular spectrogram.

With samples of germanium tetrachloride, attempts were first made to carry out the study in the mass range 70–76, corresponding to Ge^+ ions. A small peak was found at mass number 71 which was not due to an isotope of germanium with mass number 71, for no peak for $(Ge^{71}Cl^{35})^+$ ions could be found at mass number 106 whereas peaks due to other $GeCl^+$ ions were abundant in the mass range 105–113. The peak was probably due to $(Ge^{70}Cl^{35}Cl^{37})^{++}$ ions and, even more so, to $(Ge^{72}Cl^{35}Cl^{35})^{++}$ ions. This raised the possibility that contributions from other $GeCl_2^{++}$ ions were present in the ion currents recorded for mass

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numbers 70, 72, 73, and 74, and for this reason and also because of the possibility of contributions due to Cl_2^+ ions at mass numbers 70, 72, and 74, the mass range 70–76 was abandoned. Good spectrograms for $GeCl^+$ ions were obtained in the mass range 105–113; the absence of a peak corresponding to mass number 106, with even the most sensitive shunt, is evidence that no ion currents due to $GeCl_4^{++}$ ions were being recorded in this mass range.

Complete spectrograms of the various singly charged dissociation products of germanium tetrafluoride (mass range 70–152) showed that GeF_3^+ ions were produced in by far the greatest abundance (Table III) and, accordingly, the mass range 127–133 was chosen for study.

Investigation of the mass regions adjacent to those for $GeCl^+$ and GeF_3^+ ions showed them to be free from interfering ions of foreign substances.

TABLE III

SINGLY CHARGED GERMANIUM IONS PRODUCED IN MASS SPECTROMETER FROM GeF_4

Ion	% Abundance*
Ge^+	7.0
GeF^+	2.6
GeF_2^+	1.8
GeF_3^+	86.8
GeF_4^+	1.8

* *Values probably good to within 1%.*

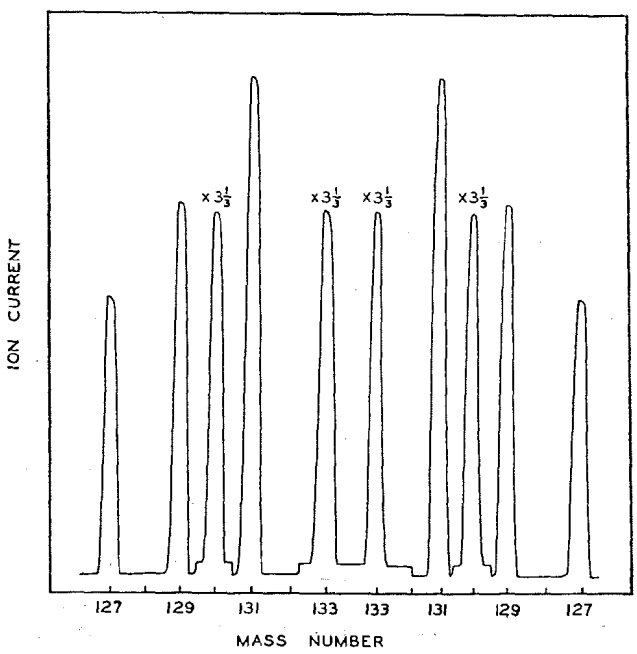

FIG. 2

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Experimental Results with Germanium Tetrafluoride

Fig. 2 shows a typical spectrogram for GeF_3^+. The relative abundances of the germanium isotopes are directly related to the recorded peak heights (after multiplying the latter by the appropriate shunt factor) since fluorine is monoisotopic.

Some of the abundance ratios are shown in Table IV, with the samples listed vertically in the order in which they were admitted to the mass spectrometer. Eight spectrograms were recorded with each sample listed and the average value for a ratio and the standard deviation were calculated for each set of spectrograms. Chauvenet's criterion (21, p. 170) was used as a basis for the rejection of a possible erratic ratio in a given set. The averages and standard deviations given in Table IV are those of the "refined" data. The use of Chauvenet's criterion led to the rejection of only 8 out of the 288 ratios with which Table IV is concerned; in no case was more than one ratio rejected in a given set, and thus each value in Table IV is the average of the data from at least seven spectrograms, and in most cases from eight.

TABLE IV

ABUNDANCE RATIOS FOR INDIVIDUAL SAMPLES FROM GeF_3^+ SPECTROGRAMS
(Standard deviation × 10^3 shown in brackets)

Sample No.	$\frac{Ge^{76}}{Ge^{70}}$	$\frac{Ge^{76}}{Ge^{73}}$	$\frac{Ge^{74}}{Ge^{70}}$	$\frac{Ge^{74}}{Ge^{72}}$
1	0.3837 (0.7)	1.005 (1)	1.799 (2)	1.340 (1)
5	0.3835 (0.5)	1.005 (1)	1.797 (2)	1.338 (1)
1	0.3838 (0.5)	1.005 (1)	1.800 (2)	1.339 (1)
2	0.3833 (0.9)	1.004 (1)	1.798 (3)	1.339 (2)
1	0.3839 (0.8)	1.005 (3)	1.799 (3)	1.339 (2)
3	0.3844 (0.5)	1.007 (1)	1.799 (1)	1.340 (1)
1	0.3836 (0.7)	1.006 (2)	1.797 (2)	1.339 (2)
4	0.3808 (0.4)	1.003 (1)	1.789 (2)	1.335 (2)
1	0.3834 (0.3)	1.007 (2)	1.798 (2)	1.339 (2)

The data from all GeF_3^+ spectrograms, except those of Sample #4, were combined and averaged, and Chauvenet's criterion applied to the combined data. The results are shown in Table V in comparison with the corresponding data for Sample #4, and in Table VI as percentage abundances.

Experimental Results with Germanium Tetrachloride

The ions believed to be responsible for the currents recorded in the mass range 105–113 (Fig. 3) are shown in Table VII. If h_x is the height of the peak (with the appropriate shunt factor applied) due to mass x, then $\frac{h_{105}}{h_{108}} = \frac{Ge^{70}}{Ge^{73}}$, and $\frac{h_{110}}{h_{113}} = \frac{Ge^{73}}{Ge^{76}}$, and hence $\frac{h_{105}}{h_{108}} \times \frac{h_{110}}{h_{113}} = \frac{Ge^{70}}{Ge^{76}}$. The values for the $\frac{Ge^{70}}{Ge^{76}}$ ratios of the various samples are given in Table VIII. Each figure in

TABLE V

COMBINED ABUNDANCE RATIOS FROM GeF_3^+ SPECTROGRAMS
(Standard deviation × 10^3 shown in brackets)

Ratio	From all spectrograms except those of sample #4*	From spectrograms of sample #4**
$\frac{Ge^{76}}{Ge^{70}}$	0.3837 (0.7)	0.3808 (0.4)
$\frac{Ge^{76}}{Ge^{72}}$	0.2856 (0.5)	0.2843 (0.1)
$\frac{Ge^{76}}{Ge^{73}}$	1.005 (2)	1.003 (1)
$\frac{Ge^{76}}{Ge^{74}}$	0.2133 (0.3)	0.2129 (0.2)
$\frac{Ge^{74}}{Ge^{70}}$	1.798 (3)	1.789 (2)
$\frac{Ge^{74}}{Ge^{72}}$	1.339 (2)	1.335 (2)
$\frac{Ge^{74}}{Ge^{73}}$	4.712 (7)	4.709 (7)
$\frac{Ge^{73}}{Ge^{70}}$	0.3816 (0.6)	0.3798 (0.6)
$\frac{Ge^{73}}{Ge^{72}}$	0.2842 (0.4)	0.2834 (0.2)
$\frac{Ge^{72}}{Ge^{70}}$	1.343 (2)	1.340 (2)

* *Each figure in this column is the average of data from 62–64 spectrograms.*
** *Each figure in this column is the average of data from 7–8 spectrograms.*

TABLE VI

PERCENTAGE ABUNDANCES OF GERMANIUM ISOTOPES
(Standard deviation × 10^2 shown in brackets)

Mass Number	From GeF_3^+ spectrograms*		From $GeCl^+$ spectrograms	
	Sample #4	All others	Sample #4	All others
70	20.45 (2)	20.38 (2)	20.27	20.23
72	27.41 (2)	27.37 (2)	27.37	27.30
73	7.77 (1)	7.78 (1)	7.70	7.70
74	36.58 (2)	36.65 (2)	36.80	36.87
76	7.79 (1)	7.82 (1)	7.86	7.90

* *Averages given are from eight spectrograms of Sample #4, and from 61–64 spectrograms of "All others". Chauvenet's criterion was applied to refine the data.*

the second column of this table is an average value obtained after Chauvenet's criterion has been applied to the data. Each figure in the third column is an average value obtained after Chauvenet's criterion has been applied to the combined data for the two sets of spectrograms for the "standard" sample—one set being recorded before the sample under test was admitted to the mass spectrometer and the other set afterwards. The agreement between the two sets of spectrograms for the "standard" sample was such as to allow the comparison with the sample under test to be a fair one.

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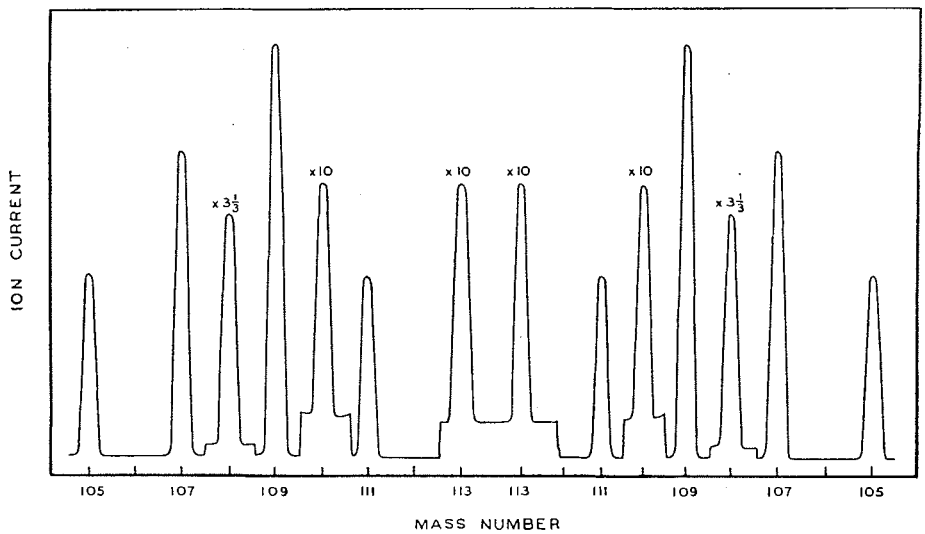

FIG. 3

TABLE VII

GeCl+ SPECTRUM

Mass number	Ions
105	$(Ge^{70}Cl^{35})+$
107	$(Ge^{70}Cl^{37})+$, $(Ge^{72}Cl^{35})+$
108	$(Ge^{73}Cl^{35})+$
109	$(Ge^{72}Cl^{37})+$, $(Ge^{74}Cl^{35})+$
110	$(Ge^{73}Cl^{37})+$
111	$(Ge^{74}Cl^{37})+$, $(Ge^{76}Cl^{35})+$
113	$(Ge^{76}Cl^{37})+$

TABLE VIII

$\frac{Ge^{70}}{Ge^{76}}$ RATIOS FROM GeCl+ SPECTROGRAMS

(Standard deviation × 10^3 shown in brackets)

Sample No.	Ge^{70}/Ge^{76} ratio for sample under test	Ge^{70}/Ge^{76} ratio for "Standard" (Sample #1)
1	2.561* (2)	2.564* (10)
2	2.557 (4)	2.555 (7)
3	2.561 (5)	2.559 (4)
4	2.581 (8)	2.571 (6)
5	2.562 (5)	2.557 (6)
6	2.563 (9)	2.560 (3)

** These figures appear to represent a comparison of Sample #1 (the "Standard") with itself; actually it is a comparison of two fractions of Sample #1, a "light" and a "heavy" one to investigate a possible fractionation effect during preparation of the tetrachloride. The application of Chauvenet's criterion resulted in the rejection of 6 of the 104 ratios that are summarized in this table.*

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From Table VII it will be seen that the ratio $\frac{h_{108}}{h_{110}} = \frac{Cl^{35}}{Cl^{37}}$. Compilation of this ratio from 118 spectrograms (120 less 2 rejected) gave the value 3.000 with a standard deviation of 0.008 which corresponds to an abundance for Cl^{35} of 75.00% with a standard deviation of 0.05%. (The divergence of this value from the commonly accepted abundance for Cl^{35} will be discussed later.)

The data from all $GeCl^+$ spectrograms, except those for Sample #4, were then grouped together and treated as follows (the data for Sample #4 were treated similarly, but separately). The ratios $\frac{h_{107}}{h_{105}}$, $\frac{h_{109}}{h_{105}}$, $\frac{h_{111}}{h_{105}}$, $\frac{h_{105}}{h_{108}}$, and $\frac{h_{110}}{h_{113}}$ were calculated, averaged, and refined (this caused the rejection of 5 ratios out of 600). From the average values of these ratios, and the relative abundance of the chlorine isotopes that was established for the conditions of experimentation from the $\frac{h_{108}}{h_{110}}$ ratios, and the data of Table VII, it was possible to calculate abundance ratios for the isotopes of germanium, and hence percentage abundances. The percentage abundances so calculated from the $GeCl^+$ spectrograms are shown in Table VI.

Discussion

Variation in Abundances of the Germanium Isotopes

The calculation of isotope abundances from the spectrograms of GeF_3^+ is straightforward, whereas the calculation from those of $GeCl^+$ is rather involved because of the two isotopes of chlorine. Accordingly, the isotope abundances calculated from the GeF_3^+ analyses are considered the more reliable; nevertheless the correlation between the two experimental approaches is very good. Thus, from the analyses of both GeF_3^+ and $GeCl^+$ ions there was obtained very strong evidence that the isotopic constitution of the germanium in Sample #4 is different from that in the other samples. When the test of significance of the difference of two means known as the "*t* test" (11, p. 14) was applied to the pairs of means given in Table VIII (involving $\frac{Ge^{70}}{Ge^{76}}$ ratios obtained from $GeCl^+$ spectrograms), it was found that in all comparisons, except that involving Sample #4, the probability of the differences of the means (of the "sample under test" and of the "standard") being due to chance was greater than 0.1, whereas for the differences to be regarded as real or significant the probability should be 0.05 or less. For Sample #4 in comparison with the "standard", the probability was only 0.01, indicating that Sample #4 was different in kind. Again, the application of the "*t* test" to the data of Table V involving isotope abundance ratios obtained from GeF_3^+ spectrograms, showed that in every case, except one (see below), there was a probability of less than 0.01 of the differences between the average ratios for Sample #4 and those for the other samples being due to chance, i.e., the probability of the differences being

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significant was greater than 0.99 (out of unity). Reference to Table VII will show that relative to the other samples the lighter isotopes of Sample #4 are favored at the expense of the heavier ones; this was found in the analyses of both GeF_3^+ and $GeCl^+$ ions. If Sample #4 had been subjected in nature to some fractionation process, it might be expected that two isotopes of intermediate mass numbers such as Ge^{73} and Ge^{74} would remain in approximately constant ratio—and it was in the comparison of the $\frac{Ge^{74}}{Ge^{73}}$ ratios that the one case occurred, as noted above, in which the "t test" did not clearly indicate a difference that should be regarded as significant. A more stringent test than the comparison of the ratios given in Table V is the comparison of the average abundance ratios for Sample #4 with those obtained for the "standard" sample admitted to the mass spectrometer just before and just after Sample #4. When this comparison was made using the "t test" it was found that all the 10 possible abundance ratios, except $\frac{Ge^{74}}{Ge^{73}}$, had a probability of less than 0.01 of being different from those of the "standard" sample as a result only of chance. On the other hand, similar comparisons of the abundance ratios of the other samples with the ratios of the bracketing "standard" samples showed high probabilities that the differences in the average values of the ratios were due to chance only. The difference between the average $\frac{Ge^{76}}{Ge^{70}}$ ratio for Sample #4 and that for all other samples (or that for the "standard") is 0.7% (Tables IV and V).

Thus in our opinion the isotopic constitution of the germanium in all the samples except Sample #4 was the same, within the precision of the measurements. The abundances of the germanium isotopes in Sample #4 are considered to be significantly different from those of the other samples, and it is for this reason that the data for Sample #4 are separately recorded in Tables V and VI. Thus, for the first time, evidence has been found for the occurrence of variations in the natural abundances of the germanium isotopes. It was not expected that Sample #4 would differ from Samples #5 and #6 nor can we explain the difference, because all three of these samples (according to the information given us by the suppliers) originated from the Tri-State ore field. It should be recorded, however, that the supplier of Sample #4 stated at the time the sample was purchased that he could not be sure of the origin of the raw material from which it was made; then, some months later in answer to a further enquiry we were informed that the germanium had its origin in the Tri-State area. There is, accordingly, perhaps some doubt regarding the origin of Sample #4.

The possibility that the variation in isotope abundances observed was due to a fractionation effect during the preparation of samples was ruled out by the results of experiments in which a sample of germanium tetrachloride was submitted to a more severe fractionation process than those involved in the pre-

paration of the samples, and then the "light" and "heavy" fractions were compared in the mass spectrometer. There was no detectable difference in the abundances of the germanium isotopes due to this fractionation procedure.

Relative Proportions of Ge^{76} and Ge^{73}

Reference was made earlier to the disagreement among those who have studied the isotopic constitution of germanium on the question of the relative abundances of Ge^{76} and Ge^{73}. Aston and, very recently, Hibbs *et al.*, found Ge^{76} to be the less abundant of these two isotopes, whereas Inghram *et al.* found the abundances to be the same (Table I).

In our study, involving 252 spectrograms recorded in the mass ranges corresponding to GeF_3^+, $GeCl^+$, and Ge^+ ions, we have found the ion current for Ge^{76} to be greater than that for Ge^{73}. Not only are all the average values for the $\frac{Ge^{76}}{Ge^{73}}$ ratios for sets of GeF_3^+ spectrograms greater than unity (Table IV), but every individual $\frac{Ge^{76}}{Ge^{73}}$ ratio entering into these averages is greater than unity. The data from the $GeCl^+$ spectrograms yield a similar result. The ratio $\frac{h_{113}}{h_{110}}$ from these spectrograms gives the ratio $\frac{Ge^{76}}{Ge^{73}}$ directly; every such ratio is greater than unity. It was mentioned earlier that attempts were made to study the mass range 70–76 (corresponding to Ge^+ ions) after admitting germanium tetrachloride into the mass spectrometer, but that this range was abandoned; nevertheless 53 spectrograms were recorded for this mass range. Examination of these shows, and again in every case, the ion current at mass 76 to be greater than that at mass 73. And this is so in spite of the possibility that $GeCl_2^{++}$ ions may have been contributing to the ion currents recorded at mass 73 (although not to those at mass 76).

The consistency of the data from the three mass ranges and with samples of different origins leads us to believe that Ge^{76} is more abundant than Ge^{73}. There can be no significant peak-height discrimination in our determinations of the relative proportions of Ge^{76} and Ge^{73} because the peak heights are substantially the same. There remains, however, the possibility of mass discrimination; if our mass spectrometer was discriminating in favor of the heavier of these two isotopes to the extent of 0.5%, then our finding of a higher proportion of Ge^{76} than of Ge^{73} would not be significant.

Chemical Atomic Weight from Isotope Abundances

The values for packing fractions are not yet as clearly defined as one would wish. Mattauch (16, p. 113) gives the value 6.7×10^{-4} for germanium, whereas interpolation from the very recent packing fraction curve of Duckworth (9) gives the value 7.7×10^{-4}. Using the latter value, and 1.000278 as the factor

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relating the physical and chemical mass scales (17), the chemical atomic weights given in Table IX were calculated from the abundance data of the present and of other recent mass spectrometric studies. In all cases the atomic weights derived from isotope abundance studies are significantly higher than the currently accepted atomic weight for germanium; the use of 6.7×10^{-4} instead of 7.7×10^{-4} for the packing fraction yields even slightly higher atomic weights.

TABLE IX

ATOMIC WEIGHT OF GERMANIUM FROM ISOTOPE ABUNDANCE DATA

Reference	Ions measured	Calculated atomic weight
Inghram, *et al.* (13, 14)	Ge^+, Ge^{++}	72.63
Hibbs, *et al.* (12)	GeF_3^+, GeI^+	72.63
Present work	GeF_3^+ $GeCl^+$	72.64 72.65
International atomic weight:		72.60

From both the GeF_3^+ and $GeCl^+$ spectrograms, we find the atomic weight of the germanium in Sample #4 to be slightly lower than that of the germanium in the other samples studied, but the difference (0.004) is not sufficient to affect the second decimal place.

The Abundance of the Chlorine Isotopes

In this work the ratio $\frac{Cl^{35}}{Cl^{37}}$ was calculated from the $GeCl^+$ spectrograms to be 3.000, whereas the commonly accepted value is 3.07 as found by Nier (18). We are not able to say whether the difference is due to the different source of chlorine, or to an isotope effect in the dissociation of molecules by electron impact, or to some other cause. We hope, however, to resolve the matter in the course of a mass spectrometric study of chlorine now in progress.

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NOTES

The Photolysis of Mercury Dipropyl[1]

The mercury dialkyls are attractive sources of free radicals because of the low bond dissociation energy of the mercury–carbon bonds. The lower alkyls have been widely used as sensitizers and there is no question that free radicals are produced in their thermal and photodecomposition. A satisfactory source of propyl radicals is much to be desired, and an investigation of the photolysis of mercury di-*n*-propyl was therefore undertaken. The reaction has proved to be rather too complex to be useful as a radical source, and the investigation has been discontinued. The results obtained, however, seemed to be of sufficient interest to record.

The apparatus was of the usual type, but mercury cutoffs were used throughout since the mercury alkyl is very soluble in stopcock grease. The products of the reaction consisted of hydrogen, methane, ethane, ethylene, propane, propylene, *n*-butane, and *n*-hexane. They were divided into C_1, C_2, C_3, C_4, and C_6 fractions by low-temperature distillation. The fractions were then analyzed with a Blacet–Leighton apparatus and in one case a mass spectrometer.

The Thermal Decomposition

Some preliminary experiments on the thermal decomposition were made by sealing off a small amount of liquid mercury dipropyl in a quartz tube and then heating the vessel in a furnace for a definite length of time. The results were very erratic and suggested that the decomposition occurred much more rapidly in the liquid phase than in the gas.

Later experiments were made in a 5-liter Pyrex flask at a pressure of the order of the vapor pressure at room temperature (*ca.* 0.5 mm.). These were still quite erratic, but not as much so as the first series. The rate was very much influenced by the previous history of the reaction vessel, and the reaction was undoubtedly catalyzed by the walls. The decomposition was negligible below 100°C. At temperatures in the neighborhood of 170°C. the products were almost entirely C_3 hydrocarbons.

In view of the erratic nature of the results, the only conclusion which can be drawn is that the reaction is a surface one. Below 100°C. the thermal reaction should not be a complication in photochemical experiments, but above this temperature it will cause serious difficulties.

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The Photodecomposition

Photochemical experiments were carried out in a quartz cell 5 cm. in diameter and 10 cm. long. The light source was a Hanovia S-500 mercury arc. The light was filtered by 5 cm. of chlorine at 250 mm. pressure, and a Corning 9863 filter. The system transmitted a region from about 2500 Å to 3000 Å, with most of the intensity in the region 2500–2700 Å. The percentage conversion was in all cases kept small. At low pressures (0.5 mm.) a circulating system was used with or without nitrogen as a carrier.

The results of a number of typical runs at 5 mm. pressure are given in Table I.

TABLE I

RUNS AT 5 MM. PRESSURE AND 108°C.

Time, min.	N_2 added, mm.	Products, cc. per min. × 10^4					C_2/C_3
		C_1	C_2	C_3	C_4	C_6	
30	0	2.0	7.3	21	2.6	41.3	0.35
30	80	–	3.2	18	1.5	41.3	0.18
60	80	–	3.5	23	2.4	42.6	0.15
65	0	1.5	5.8	17	3.4	31.9	0.34
90	80	–	2.8	20	2.3	35.4	0.14
90	0	1.9	5.6	17	3.2	31.4	0.33

The C_6 hydrocarbons were almost exclusively *n*-hexane, the C_3 fraction contained C_3H_6 and C_3H_8, the propylene being somewhat in excess of C_3H_8. These products are obviously to be accounted for by

$$Hg(C_3H_7)_2 + h\nu \rightarrow Hg + 2C_3H_7$$
$$2\ C_3H_7 \rightarrow C_6H_{14}$$
$$2\ C_3H_7 \rightarrow C_3H_6 + C_3H_8$$

All evidence points to the propyl radical being stable at 100°C., and the considerable amount of C_2 and C_4 hydrocarbons is therefore surprising. They presumably arise either by a direct molecular change, such as

$$Hg(C_3H_7)_2 + h\nu \rightarrow Hg(C_3H_7)_2^*$$
$$Hg(C_3H_7)_2^* \rightarrow C_2 \text{ and } C_4 \text{ hydrocarbons}$$

or else the propyl radicals formed as indicated above carry over energy from the primary step and decompose

$$C_3H_7^* \rightarrow C_2H_4 + CH_3, \text{ etc.}$$

The decrease in C_2 and C_4 hydrocarbons in the presence of nitrogen could be accounted for by deactivation of either excited $Hg(C_3H_7)_2$ or of $C_3H_7^*$. The latter mechanism seems the more likely.

Decrease in the pressure of $Hg(C_3H_7)_2$ would be expected on this basis to lead to increased products of radical breakdown. This was found to be the case, a C_2/C_3 ratio as high as 1.5 being obtained in experiments at 100°C. with

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0.5 mm. of $Hg(C_3H_7)_2$. The presence of nitrogen again decreased C_2 formation. In these experiments C_6 and C_3 were definitely increased by the presence of nitrogen at the expense of the C_2 and C_4 hydrocarbons. This indicates that the mechanisms are not independent and therefore strongly favors hot radical breakdown as the cause of C_2 and C_4 formation, rather than an excited molecule mechanism.

Temperature had practically no effect on the rate or products from 30° to 108°C.

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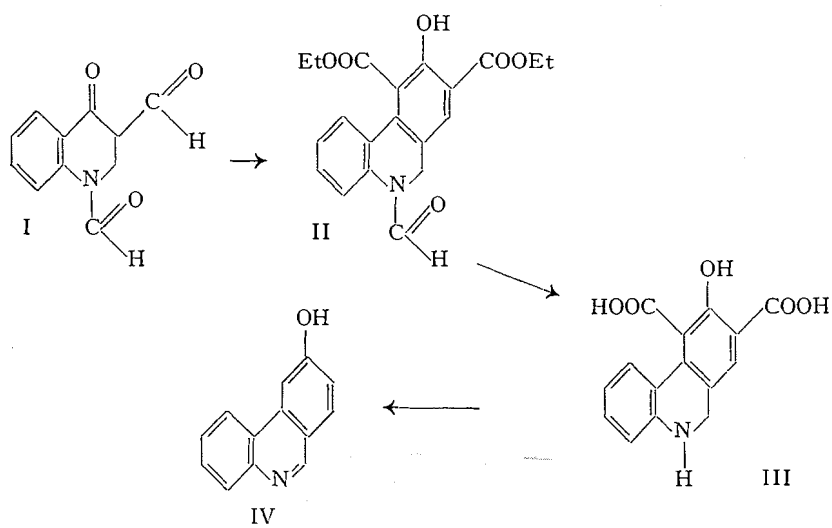
Synthesis of Some Phenanthridine Derivatives

In connection with a project which we have discontinued we have applied the reaction between alpha-hydroxymethylene ketones and ethyl acetonedicarboxylate (2) to 4 ketotetrahydroquinoline (1). This compound gave with ethyl formate in the usual way 1-formyl-3-hydroxymethylene-4-keto-1, 2, 3, 4-tetrahydroquinoline, *I*, which was condensed with ethyl acetonedicarboxylate to ethyl 5-formyl-9-hydroxy-5, 6-dihydrophenanthridine-8, 10-dicarboxylate, *II*. By saponification of the ester groups and simultaneous deformylation the acid *III* was obtained. This acid by decarboxylation in quinoline gave only polymeric material, but it could be dehydrogenated with simultaneous decarboxylation by palladium–charcoal to 9-hydroxyphenanthridine, *IV*.



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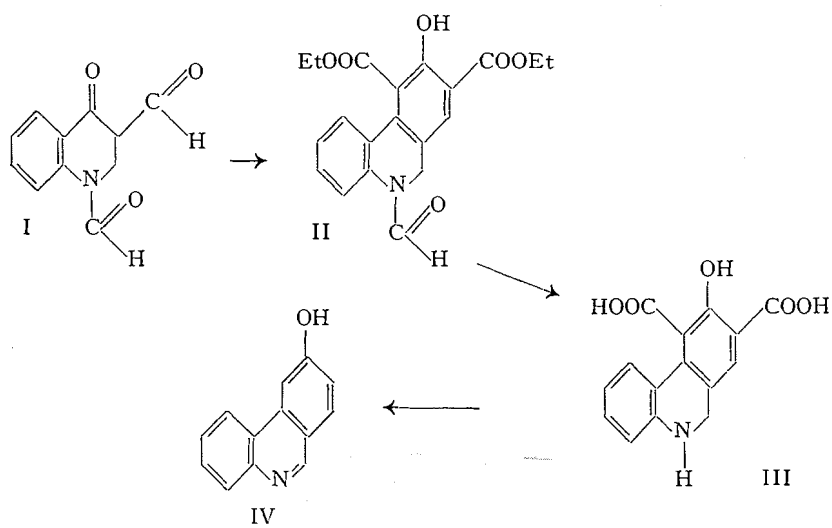

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Experimental Part

1-Formyl-3-hydroxymethylene-4-keto-1, 2, 3, 4-tetrahydroquinoline.—4-Keto-tetrahydroquinoline (4.00 gm.), ethylformate (2.223 gm.), and sodium (0.692 gm.) were dissolved in absolute alcohol (25 cc.). After several days the sodium salt of the hydroxymethylene compound precipitated and a further crop was obtained by the addition of ether. The compound was characterized as the 3-phenylaminomethylene compound which formed crystals from ethanol, m.p. 116°–117°C. Calc. for $C_{17}H_{13}O_2N_2$: C, 73.36; H, 5.07; N, 10.07%. Found: C, 73.46; H, 5.25; N, 9.79%.

Ethyl 5-formyl-9-hydroxy-5, 6-dihydrophenanthridine-8, 10-dicarboxylate.—The sodium salt of the hydroxymethylene compound (23.8 gm.) was dissolved with 15.7 gm. of ethyl acetonedicarboxylate in 100 cc. of alcohol and the solution was shaken for 24 hr. After this period the alcohol was evaporated to dryness *in vacuo*, water added and extracted with ether. The oily residue of the extract crystallized from an alcohol–ether mixture. After repeated crystallization and sublimation *in vacuo* 4.166 gm. of a white crystalline compound, m.p. 140°–141°C. was obtained. Calc. for $C_{20}H_{19}O_6N$: C, 65.03; H, 5.19; N, 3.79%. Found: C, 64.87; H, 5.07; N, 3.55%.

9-Hydroxy-5, 6-dihydrophenanthridine-8, 10-dicarboxylic Acid.—The diester was saponified by boiling with 15% methanolic potassium hydroxide for 12 hr. After evaporation of the methanol the acid salt was dissolved in water and the acid obtained as a precipitate by making the solution slightly acidic with hydrochloric acid. It was reprecipitated in this way several times and finally boiled with water to remove inorganic salts. It was dried in a high vacuum at 100°C. Calc. for $C_{15}H_{11}O_5N$: N, 4.91%. Found: N, 5.08%.

9-Hydroxyphenanthridine.—The diacid (1 gm.) and 1 gm. of 30% palladium–charcoal were heated in a test tube for 20 min. at 300°C. The mixture was then extracted with ether, giving 0.119 gm. of a crystalline compound. It was recrystallized several times from ether and sublimed for analysis in a high vacuum. It melted with vigorous decomposition between 230° and 240°C. Calc. for $C_{13}H_9ON$: C, 80.00; H, 4.62%. Found: C, 79.74; H, 4.63%.

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Estimation of Ribonucleic Acid with Orcinol

The orcinol color test for pentoses and uronides was adapted by Mejbaum (5) to estimate ribose in purine nucleotides and nucleosides (ribose linked to pyrimidine bases did not react with the orcinol). Since pentoses, uronides, and some desoxypentoses (4) developed the same color and since other carbohydrates, lead, and nitrates developed extraneous colors, Mejbaum analyzed only purified preparations. Schlenk (7) extended the heating time for color development from 20 min. to 30 min.

Schmidt and Thannhauser (8) encountered serious difficulties in adapting color tests normally used on carbohydrates to the measurement of nucleic acids; they favored a procedure that involved estimating phosphorus. Cori and Cori (2) found that, on the basis of phosphorus content, yeast nucleic acid gave only 40% of the pentose color developed by muscle adenylic acid. Davidson and Waymouth (3) prepared calibration curves in terms of nucleic acid phosphorus and found no theoretical relation between ribose present and intensity of color developed.

A possible explanation of the discrepancies in various investigations was found in the results of Albaum and Umbreit (1) who showed that different pentoses and pentose-containing compounds developed color with orcinol at widely differing rates. This suggests that procedures suitable for estimation of nucleosides and nucleotides might be unsuitable for nucleic acid unless the procedures were modified.

Preliminary tests showed that the yellow color of ferric chloride in the reagent did not interfere, because the color complex had a maximum absorption at 660 mμ, at which wave length ferric chloride had little absorption. Consequently extracting the color complex with *n*-butanol, suggested by Militzer (6), is unnecessary. Mejbaum's reagent, 1% orcinol and 0.1% ferric chloride in concentrated hydrochloric acid, was satisfactory. This reagent must be prepared immediately before use. The color complex was stable overnight.

One sample of orcinol (Schuchardt) that had been in the laboratory for several years gave slightly lower light absorption readings than a new sample (Eastman). Each sample changed slightly over a period of two years.

To determine the effect of heating time, 2 ml. of test solution and 2 ml. of orcinol reagent were heated in 10-ml. cylinders immersed in a vigorously boiling water bath. Ribose, arabinose, and wheat germ ribonucleic acid and nucleoprotein were compared. The results (Table I) show that with ribose 20 min. was sufficient for maximum color development, but with the others, 60 min. was required. With this longer heating time the color density was the same regardless of the source of the pentose. (Obviously the protein did not interfere.) Two pure samples of ribonucleic acid, one from yeast (9.40% phosphorus) and the other from wheat germ (9.49% phosphorus), were found to contain the theoretical amount of reacting pentose, assuming that half the

TABLE I

EFFECT OF TIME OF HEATING ON COLOR DEVELOPED WITH ORCINOL
(Each 2 ml. aliquot tested contained 15 μgm. of reacting pentose.)

Time, min.	Light transmission at 660 mμ, %			
	Ribose	Arabinose	Wheat germ ribonucleic acid*	Wheat germ ribonucleo-protein*
20	41.0	48.0	46.75	46.75
30	40.75	42.5	43.0	44.0
40	—	41.0	42.25	42.75
50	—	41.25	41.75	42.0
60	41.0	40.5	41.25	41.0
100	—	40.5	41.0	41.25
120	40.5	40.75	41.0	40.75

* *Assuming that half the phosphorus was in purine nucleotides.*

phosphorus was bound to purine bases and using a calibration curve prepared with arabinose. Additional tests with ribonucleic acid showed the importance of vigorous boiling: when a bath at 99°C. was used, heating for 60 min. was insufficient.

When the described heating precautions were used, the color reaction between orcinol (Schuchardt) and the pentose of ribonucleic acid obeyed Beer's law over a range of concentrations of 0.5 to 2.5 μgm. per ml., which corresponds to a range of 20–65% transmittance. Beer's constant varied from 0.0263 to 0.0281 over a period of two years but each constant had an average variation of ± 0.0004 for the range indicated. It is concluded therefore that previously reported discrepancies were due to insufficient heating of the reaction mixture.

The procedure adopted is as follows:—A 2 ml. aliquot of a solution containing 5 to 25 μgm. of reacting pentose is placed in a 10 ml. graduated glass-stoppered Pyrex cylinder with 2 ml. of orcinol reagent (1.0% orcinol and 0.1% chloride in concentrated hydrochloric acid prepared immediately before use). A blank test is made without orcinol in the hydrochloric acid. The cylinders are shaken and then placed in vigorously boiling water for 60 min. After cooling, the solutions are made to volume, mixed, and their light transmittance measured at 660 mμ.

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HEMICELLULOSES OF WHEAT STRAW[1]

BY G. A. ADAMS AND A. E. CASTAGNE

Abstract

Various hemicellulose fractions were extracted from wheat straw holocellulose (extractive and pectin free) by successive treatments with cold and hot water, 0.5%, 1.0%, and 2.0% potassium hydroxide and were recovered by precipitation with alcohol. Approximately 25% of the holocellulose material was removed, one half being in the hot water soluble fraction. The original holocellulose, the extracted residue, and the recovered fractions were analyzed for pentosan, uronic acid anhydride, acetyl, methoxyl, and ash content. In general, the more soluble fractions had a higher uronic acid and methoxyl content; the less soluble had a higher pentosan content and a more negative rotation $[\alpha]_D^{20}$. Intrinsic viscosity measurements indicated that all fractions had a degree of polymerization of 25–30. Hydrolysis of the main fraction yielded D-xylose, L-arabinose, D-glucose; in addition D-galactose was found in the water soluble fractions. Quantitative determinations of the sugars in the hydrolyzates showed that D-xylose predominated, with L-arabinose, D-glucose, and D-galactose (when present) in progressively smaller amounts. On hydrolysis all fractions yielded an acid-resistant uronic acid complex that contained D-xylose and a uronic acid tentatively identified as monomethoxyl galacturonic acid.

Introduction

Hemicelluloses may be extracted from plant materials by two general methods. The older and simpler of these employs direct extraction of the extractive-free plant tissue with dilute alkali. Precipitation of the hemicelluloses from the alkali by acids, alcohols, and other precipitants accomplishes a certain amount of fractionation. Various subfractionations and purification steps have been developed, and detailed summaries of these are reported in comprehensive reviews (19, 20). While much valuable information has been obtained with this approach, certain shortcomings have become apparent; a considerable proportion of the hemicelluloses are not extractable by dilute alkali except after removal of the lignin. In addition, a portion of the lignin that is simultaneously removed with the hemicellulose causes difficulties in the recovery and purification of the hemicellulose fractions.

The other general method, which is a recent development, makes use of holocellulose instead of the whole plant tissue as the starting material. Several satisfactory methods have been developed for the complete removal of lignin from plant material leaving a residue (holocellulose) that contains all the polysaccharide materials (27, 28, 29). Absence of the lignin permits ready

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extraction of hemicelluloses from the holocellulose. While it is believed that hemicelluloses are unchanged by the delignification processes, some are more readily soluble in water and mild alkali solutions after delignification, and a wider range of extraction conditions becomes possible (25). A study of the hemicelluloses from maple wood holocellulose by Mitchell and Ritter showed that approximately 20% of the holocellulose was extracted by water and dilute alkali (18). Chemical analyses of the fractions and molecular weight determination by end group assay indicated that a broad separation into different polysaccharides had occurred. Using a number of physical methods, Millet and Stamm found that hemicelluloses isolated with water and mild alkali treatments from aspen holocellulose showed only minor molecular weight differences (17). A similar extraction procedure applied to aspen holocellulose by Thomas indicated that chemical differences existed between the various fractions (25).

While this new approach to the study of hemicelluloses by the holocellulose route has been applied to a number of woods, no corresponding information appears to be available for annual plants and straws. The purpose of the present investigation was to extract the hemicelluloses of wheat straw holocellulose by means of mild solvents, and to determine the composition of the isolated fractions. Estimation of the approximate degree of polymerization of each fraction by viscosity measurements was also included. No attempt was made to obtain quantitative extraction of all the hemicellulose material; only the readily soluble material was sought by a combination of successive extractions and fractional precipitation.

Materials and Methods

Wheat straw holocellulose that had been prepared from mature straw by an acid chlorite method previously described (1) was used as starting material. Lignin determinations were made by the 72% sulphuric acid method (23). Pentosans were determined by distillation with 12% hydrochloric acid and the evolved furfural was measured by the bromine oxidation procedure described by Hughes and Acree (13). Corrections for furfural arising from uronic acid groups were applied, and pentosan values were calculated as xylan. Acetyl groups were determined by Clark's semimicro method (6). Uronic acid anhydride was estimated by a modification of the method of Dickson *et al.* (7) in which the carbon dioxide produced by decarboxylation was removed in a stream of carbon-dioxide-free nitrogen in an all glass apparatus. When only small amounts of material were available the micro method of Tracy was more convenient and equally satisfactory (26). The micro method of Somogyi was used for determination of reducing sugars (24). Detection and quantitative estimation of individual sugars in acid hydrolyzates of the various hemicelluloses were made by a combination of chromatographic techniques (11, 16, 21) which will be described in detail in the section dealing with separation and identification of sugar components. Moisture was determined by

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drying to a constant weight at 100°C. in a vacuum oven unless otherwise stated; ash by incinerating at 550°C. Optical rotations of the hemicellulose fractions were measured at 1.0% concentration in 2.5% potassium hydroxide solution.

Experimental Procedures and Results

The investigation was developed in three steps: preparation of the hemicellulose fractions; chemical analyses of the isolated fractions and determination of their intrinsic viscosities; and hydrolysis of the hemicelluloses, followed by identification and quantitative determination of the component sugars.

Preparation of Hemicellulose Fractions

Preliminary Trials on Small Batch

Preliminary experiments were carried out on a 50 gm. lot of air-dried holocellulose to determine the amount of material extracted by successive treatments with water at 100°C., and 0.5%, 2.0%, 5.0%, 8.0% and 10.0% potassium hydroxide respectively, at 25°C. It was found desirable not to dry the residue after each extraction as the subsequent extraction period was prolonged owing to slow swelling of the cellulose. The alkaline extracts were neutralized with acetic acid, concentrated to a small volume, and precipitated by pouring into three volumes of 95% alcohol. The recovered hemicelluloses were washed repeatedly with warm alcohol, and then ether and finally dried to constant weight *in vacuo*. Table I records the conditions for extraction

TABLE I

Preliminary Extraction of Wheat Straw Holocellulose
(49.2 gm. of holocellulose (ash free))

Extracting agent	Vol. extracting agent, ml.	No. of extractions	Duration of each extraction, hr.	Weight of fraction (ash-free), gm.	Yield, % (ash-free)
Water at 100°C.	1000	3	4	5.28	10.7
Potassium hydroxide, 0.5%	800	2	3	4.27	8.7
Potassium hydroxide, 2.0%	600	2	3	2.23	4.5
Potassium hydroxide, 5.0%	600	2	3	2.12	4.3
Potassium hydroxide, 8.0%	600	2	2	1.10	2.2
Potassium hydroxide, 10.0%	500	2	2	1.21	2.4
			Residue:	31.00	63.0
				Accounted for:	95.8%

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and the yield of each fraction. The most interesting result obtained was the unexpected solubility of about 11% of the holocellulose in hot water. Extraction with 0.5% potassium hydroxide, which is regarded as a mild treatment, removed a further 8.7%. The total amount of material removed by the extracting agents up to and including 5% potassium hydroxide totalled 28.2% of the holocellulose. This yield is in good agreement with a yield of approximately 29% when 5% potassium hydroxide was used as the sole extracting agent, reported earlier (2). These results indicated the feasibility of extracting wheat straw holocellulose with a succession of relatively mild solvents to yield appreciable amounts of hemicellulose materials.

On the basis of the foregoing preliminary experiments a further study was planned in which a 10-fold amount of holocellulose was used and a succession of even milder extracting agents employed. It was hoped that by using cold and hot water, 0.5%, 1.5%, and 2.0% potassium hydroxide successively, such extractions might preferentially separate polyuronide material from cellulosan fractions.

Extraction of a Large Batch of Holocellulose

The quantity of holocellulose used was 600 gm. (air dry weight). The extraction apparatus consisted of a 5 gal. glass jar fitted with a monel rake agitator travelling at 30 r.p.m. The jar was covered by a tight fitting lid containing ports for passage of nitrogen through the vessel. The jar was placed in a water bath and the temperature thermostatically controlled at 25°C. ± 0.5°. For hot water extractions a steam coil was installed in the bath.

Cold Water Extract

A cold water soluble fraction was prepared by extracting the holocellulose with 15 liters of distilled water at 25°C. for 120 hr. Microbial growth was prevented by the addition of 0.075 gm. of Dowcide 6 dissolved in 2 ml. of 0.1 *N* sodium hydroxide. The aqueous extract was removed by suction through a sintered glass filter stick (porosity C) immersed in the suspension and the residue was thoroughly washed with water. The extract and washings were slightly opalescent but contained no fine fibrous material. The solution was concentrated to about 2000 ml. in a laboratory flash evaporator at a temperature not exceeding 50°C. The pH of the concentrated extract was 6.82. Centrifuging the concentrated solution removed 0.19 gm. of material (Fraction 1) which was discarded and four volumes of alcohol were added slowly with stirring to the clarified solution. A white flocculent precipitate that came down was centrifuged off and dried by solvent exchange through alcohol and ether (Fraction 2). The supernatant solution from the recovery of Fraction 2 was concentrated to a small volume. On the further addition of alcohol another fraction was recovered (Fraction 3). Reconcentration of the supernatant solution and adjustment to pH 4.0 with hydrochloric acid followed by addition of four volumes of alcohol brought down another small precipitate

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(Fraction 4). No further removal of hemicellulose being possible with alcohol, the solution was brought to pH 7.0 and evaporated to dryness at 45–50°C. (Fraction 5).

Hot Water Extract

A sufficient quantity of water was added to the wet residue from the previous extraction to bring the total volume to 15 liters. The water surrounding the extraction vessel was kept boiling vigorously. Four extraction periods of six hours each were made. The first extracts were brownish in color and had a pH of approximately 5.5. Efforts to control the pH at neutrality by the addition of alkali were only partially successful; relatively large amounts were required and contributed greatly to the difficulties of reducing the ash in the recovered fractions. The pH of the solution increased in successive extractions and color decreased until the final extract was only slightly colored. After thorough washing of the insoluble residue all the extracts were combined, adjusted to pH 6.0, and concentrated at 50°C. to a small volume. This solution was then dialyzed against running tap water for 48 hr. Total solids and ash in the solids were determined on an aliquot after dialysis was complete. Three volumes of alcohol were then added to the dialyzed solution and the white flocculent precipitate was removed and dried by solvent exchange through alcohol and ether (Fraction 6). The alcoholic supernatant solution was reconcentrated, five volumes of alcohol were added, and the precipitate was removed and dried (Fraction 7). A further small fraction was recovered by alcoholic precipitation after adjustment of the pH of the solution to 7.0 (Fraction 8). Since no further fractions could be obtained with alcohol the solution was taken to dryness under reduced pressure (Fraction 9).

Alkali Extract, 0.5% Potassium Hydroxide

The residue from the hot water extraction was made up to a total volume of 15 liters containing 0.5% potassium hydroxide. The extraction mixture was held at 25°C. and nitrogen was continuously passed over its surface. The pH of the solution was approximately 12.0. Three extraction periods of three hours each were employed. The combined extracts and washings were neutralized with hydrochloric acid and concentrated at 50°C. to 1/10 their volume. The concentrated solution was dialyzed successively in Visking casings against tap and distilled water until chloride-free (36 hr.). The solution was again concentrated and three volumes of alcohol were added with stirring. The heavy white precipitate was washed with alcohol and ether and dried (Fraction 10). Neither further addition of alcohol nor adjustment of pH caused further precipitations and the solution was taken to dryness under reduced pressure (Fraction 11).

Alkali Extraction, 1.0% Potassium Hydroxide

The extraction procedure was similar to that described above. Two extraction periods were used; one for six hours and another for 16 hr. The

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extracted solutions were neutralized, concentrated, and dialyzed until salt-free. By addition of alcohol a flocculent precipitate was recovered (Fraction 12). A further small precipitate was obtained by a further addition of alcohol (Fraction 13). Evaporation of the alcoholic solution yielded a brown solid (Fraction 14).

Alkali Extract, 2.0% Potassium Hydroxide

The residue from the previous extraction treatment was subjected successively to a six- and a sixteen-hour extraction period with 2.0% potassium hydroxide. The residue was thoroughly washed with water and the extract and washings after neutralization reduced to about 1/10 their volume. Dialysis against tap water was carried out for 42 hr. After reconcentration of the dialyzed solution a small amount of brownish solid settled out and was centrifuged off (Fraction 15). By alcoholic precipitations a major fraction (Fraction 16) and a minor fraction (Fraction 17) were recovered and dried. The alcohol soluble portion was recovered as a brown powder (Fraction 18).

The cellulosic residue was washed with dilute acetic acid solution and then with water until free of acid. After three successive washes with alcohol the material was dried in warm air.

All major isolated hemicellulose fractions were purified by resolution in water or alkali and precipitation with alcohol. Some fractions on reprecipitation with alcohol tended to form gels which were difficult to recover and dry. Dehydration was finally achieved by adding the gels to large volumes of hot alcohol. Final drying after treatment with absolute alcohol and ether was carried out by desiccation under high vacuum. Fractions recovered by alcohol were all greyish powders; those taken to dryness were amorphous brown powders which were hygroscopic in air.

The yields of the various fractions are given in Table II. The total weight of the fractions recovered accounted for 94% of the original holocellulose; this recovery was satisfactory considering the number of operations involved. The fraction that was soluble in cold water amounted to approximately 2.4% of the holocellulose. The total amount of water-soluble material was about 14.7% and was considerably in excess of that found for hot water extraction in the preliminary experiment; this result was attributed to the exhaustive extraction employed. A total of 25.3% of the holocellulose was extracted by all treatments and of this approximately half was recovered from the hot water extract.

Analyses of Hemicellulose Fractions

The major fractions were analyzed for pentosan, uronic acid anhydride, methoxyl, and acetyl content and, in addition, their reducing power was determined. Optical rotations in alkali solution were also measured.

Many of the minor fractions were insufficient for complete analyses. However their composition was not regarded as a significant contribution to the

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TABLE II

YIELD OF HEMICELLUOSE FRACTIONS FROM WHEAT STRAW HOLOCELLULOSE
(536.06 gm., moisture- and ash-free)

Fraction	Description of fraction	Weight (ash-free), gm.	% of original holocellulose	
	Cold water extract			
1	Material centrifuged from extract	0.1930	0.036	
2	First alcoholic precipitate	5.3317	0.995	
3	Second alcoholic precipitate	3.3576	0.626	
4	Alcoholic precipitate at pH 4.0	0.4694	0.083	
2*a*	Insoluble material from purification of 2	0.0852	0.016	
5	Alcohol soluble residue	3.3134	0.618	
				2.37
	Hot water extract			
6	First alcoholic precipitate	55.6728	10.38	
6*a*	Insoluble material from purification of 7	0.8276	0.154	
7	Second alcoholic precipitate	3.7712	0.704	
8	Alcoholic precipitate at pH 4.0	1.2874	0.240	
9	Alcohol soluble residue	4.4361	0.826	
				12.30
	0.5% KOH extract			
10	First alcoholic precipitate	28.0000	5.220	
11	Alcohol soluble residue	1.6434	0.306	
				5.53
	1.0% KOH extract			
12	First alcoholic precipitate	8.8218	1.645	
13	Second alcoholic precipitate	0.0538	0.010	
14	Alcohol soluble residue	0.8225	0.153	
				1.81
	2% KOH extract			
15*	Insoluble material appearing on dialysis	.....	.....	
16	First alcoholic precipitate	16.2130	3.03	
17	Second alcoholic precipitate	0.3233	0.062	
18	Alcohol soluble material	0.9653	0.179	
				3.261
	Residue	368.59	68.70	
		Total yield recovered:	94.0%	

**Sample lost.*

over-all interpretation of the hemicellulose components of holocellulose. The results of the analyses are given in Table III.

The main fractions Nos. 12 and 16 had optical rotations similar to those generally reported for plant and wood hemicelluloses high in xylan content (14, 18). The high negative rotation is indicative of β configuration in the molecule. The other fractions had rotations somewhat lower owing to a lower pentosan content. The low rotations of the alcohol soluble fractions indicated a low hemicellulose content—an observation confirmed by the small

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TABLE III

COMPOSITION OF HEMICELLULOSE FRACTIONS
(All values calculated on a moisture-free basis)

	Fraction No.	Description of fraction	$[\alpha]_D^{20}$	Reducing power*	Pentosan, %	Uronic acid anhydride, %	Methoxyl, %	Acetyl, %
Water at 25°C.	2	First alcoholic precipitate	−72.0	6.34	64.6	8.84	1.30	2.92
	3	Second alcoholic precipitate	−58.6	11.4	57.4	8.36	2.05	2.64
	5	Alcohol soluble	−11.0	25.9	13.4	8.16	10.30	1.73
Water at 100°C.	6	First alcoholic precipitate	−67.0	6.3	64.7	8.44	3.50	3.17
	7	Second alcoholic precipitate	−44.0	18.8	48.4	7.84	5.21	4.25
	9	Alcohol soluble	−29.6	42.1	15.0	5.84	7.70	2.01
Potassium hydroxide, 0.5%	10	Alcoholic precipitate	−69.1	1.4	79.9	10.40	3.48	.00
	11	Alcohol soluble	+2.2	12.9	2.43	3.00	15.00	.00
Potassium hydroxide, 1.0%	12	Alcoholic precipitate	−90.0	1.3	82.0	5.00	0.95	.00
	14	Alcohol soluble	−12.5	11.2	8.0	4.88	10.46	.00
Potassium hydroxide, 2.0%	16	Alcoholic precipitate	−92.0	2.0	85.0	4.72	1.08	.00
	18	Alcohol soluble	+28.0	11.7	—	—	12.28	.00
		Holocellulose residue			17.5	2.04	0.14	

**Expressed as milliliters of 0.05N thiosulphate per gram of hemicellulose.*

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pentosan content found in all these materials. The uronic acid anhydride content of the more easily soluble fractions was considerably higher than those removed by the 1 and 2% alkali. This result is in agreement with the general behavior of polyuronide hemicelluloses whose polar carboxyl groups render them more readily soluble in aqueous solution. In general, alkali of increasing strength extracted material successively higher in pentosan and lower in uronic acid anhydride. Apparently the fractionation procedure effected partial separation of the polyuronide and cellulosan components. The molar ratio, methoxyl : uronic acid anhydride was approximately unity for Fractions 2, 12, and 16, and indicated the presence of monomethoxyhexuronic acids in the hemicellulose molecules. In the other fractions, the methoxyl contents were high and excessively so in the alcohol soluble material. The source of the excess methoxyl may have been lignin residues in the holocellulose since the lignin content of the holocellulose decreased from 1.56% to 0.60% after the various extractions. No acetyl groups were found in the fractions prepared by alkali extraction because of the saponifying action of the alkali.

Intrinsic Viscosity Determinations

For viscosity measurements the five main hemicellulose fractions were fully acetylated by the method of Carson and MacLay (5). Solutions containing 0.5% of the acetylated material were made up in chloroform from which 0.25%, 0.125%, and 0.0625% solutions were also prepared by dilution of the original solution. Flow times were measured on freshly prepared solutions in an Ostwald–Cannon–Fenske type viscometer (ASTM 50) in a water bath maintained at 25°C. ± 0.02°C. All solutions were drawn into the viscometer through a thin cotton filter to remove stray dust particles. Flow time measurements were made in triplicate or until agreement to ± 0.1 sec. was obtained. Reduced viscosity values were calculated by substitution in the expression

$$\frac{T - T_0}{T_0 C}$$

where T = flow time of solution in seconds,
T_0 = flow time of solvent in seconds,
C = concentration of solute in grams per 1000 ml. of solution.

A plot of reduced viscosity against concentration of solution permitted extrapolation of the curve to zero concentration. The plots of $\eta\ sp/c$ against C were found to be straight lines for all fractions at the concentrations used, and the intercept of the curve on the ordinate gave the intrinsic viscosity $[\eta]$.

The intrinsic viscosities of the various acetylated fractions in chloroform were as follows:

	$[\eta]$
Fraction No. 2—Hemicellulose soluble in cold water	0.030
Fraction No. 6—Hemicellulose soluble in hot water	0.028
Fraction No. 10—Hemicellulose soluble in 0.5% alkali	0.027
Fraction No. 12—Hemicellulose soluble in 1.0% alkali	0.033
Fraction No. 16—Hemicellulose soluble in 2.0% alkali	0.026

The similarity of the [η] values suggested that the degree of polymerization (P) of the various fractions was of the same general order. Such a conclusion was based on values obtained by substitution in Staudinger's equation,

$$\eta\ sp/c = Km\ P.$$

When Km was assigned the value of 11×10^{-4}, the degree of polymerization of the various fractions was in the range of 25–30. The Km value of 11×10^{-4} has been used by Millet and Stamm for calculating molecular weights of acetylated hemicellulose fractions previously extracted from aspen holocellulose (17). Until the Km factor has been determined by suitable methods for acetylated hemicellulosic materials in chloroform, the value 11×10^{-4} must be used with considerable reservation. The low solubility of acetylated hemicelluloses in organic solvents—an observation made by other investigators (5) leads to difficulties in obtaining a molecularly dispersed solution for viscosity determinations. A number of organic solvents including chloroform, pyridine, formamide, methylene chloride, tetrachloroethane (alone and mixed with ethanol) were investigated; of these, chloroform proved the most satisfactory. All acetylated fractions appeared to give molecularly dispersed solutions in chloroform except No. 16, which was slightly opalescent; the rather low viscosity of the latter may be attributed to lack of complete molecular dispersion. Some viscosity determinations of the original fractions in 2% sodium hydroxide yielded [η] values of the same general order as for the acetylated material. However, the value for Fraction No. 16 was found to have the highest viscosity of all in alkali. Only limited studies were made using 2% alkali since concentration of the fractions above 0.25% in this solvent deviated from a straight line when $\eta\ sp/c$ was plotted against C.

Hydrolysis of Hemicellulose Fractions

Each of the main hemicellulose fractions was hydrolyzed by the following general procedure: approximately 0.5 gm. of the material was added to 50 ml. of 3% sulphuric acid (v/v) and the mixture heated in a boiling water bath under reflux. Most of the fractions were readily dispersed after a short period of heating except for a small residue which persisted throughout the hydrolysis period. The course of the hydrolysis was followed by change in optical rotation and total reducing power of the solution. The rotations changed from strongly negative to slightly positive readings after three to six hours' heating. The reducing power for most fractions reached their maximum in the six to nine hour period. After 12 hr. heating the reducing power began to decrease and the appearance of a brownish color indicated some sugar destruction. All insoluble residues were removed, washed with water, alcohol and ether, then dried and weighed. The amounts of the unhydrolyzed residues constituted about 4–5% of the original material. The acid hydrolyzates were neutralized by the addition of a calculated amount of barium carbonate. Vigorous stirring and heating to 40°C. precluded the addition of an excess of the carbonate. The supernatant solution was recovered by centrifuging and

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the barium sulphate precipitate was repeatedly washed with warm water. The solution and washings were decolorized and clarified by heating with 0.5-gm. quantities of Norite and Supercel respectively. After evaporation under reduced pressure the solution was poured into five volumes of alcohol. The solution was centrifuged and the precipitate of barium uronate dried with alcohol and ether and set aside for examination later. The alcoholic supernatant solution was concentrated to a thick syrup, taken up in water, and treated again with alcohol to remove further traces of barium uronate. After freeing from alcohol the syrup was taken up in 50 ml. of water for chromatographic examination for sugars.

Paper Chromatography of Sugars

The component sugars of each hydrolyzate were detected by a descending paper chromatography technique described by Partridge (21). The solvent system was ethyl acetate–water–pyridine (2:2:1) and the developing indicator was aniline phthalate. All chromatograms were run for 16–22 hr. in a sealed glass jar. In qualitative tests the reference sugars were D-xylose, L-arabinose, D-glucose, D-galactose, D-rhamnose, and D-mannose. After detection of the sugars in the hydrolyzates, the amounts of each were determined quantitatively by a procedure similar to that described by Hawthorne (11). The various individual sugar components were separated by filter paper chromatography from known volumes of the acid hydrolyzates. Known sugars on the same paper strip served to locate the exact region of the hydrolyzate spots. The spots were cut out, extracted with water and the reducing power of the extracts determined. These values were then readily calculated in terms of milligrams of the appropriate sugar. Xylose, arabinose, and glucose were found in all fractions and in addition galactose occurred in the water soluble fractions. The amounts of each sugar in the various hemicellulose fractions are shown in Table IV.

TABLE IV

SUGAR CONSTITUENTS OF HEMICELLULOSES, %

Fraction No.	Xylose	Arabinose	Glucose	Galactose
2	59.2	8.6	9.8	4.8
3	56.6	9.8	4.5	1.6
5	10.3	4.0	3.1	Nil
6	62.4	12.15	5.3	1.1
7	49.4	9.55	3.1	Nil
9	28.6	7.8	2.6	Nil
10	72.2	8.5	4.3	Nil
11	trace	trace	Nil	Nil
12	85.0	9.0	3.8	Nil
16	86.2	9.6	4.2	Nil

Identification of Sugars

The individual sugars detected by chromatography were identified by isolation and measurement of physical constants of either the sugar or derivatives. The sugar solutions from the foregoing experiments were pooled for the following tests. The aqueous sugar solution was evaporated to a thick syrup at 45°C. and the water removed by repeated distillation with absolute ethanol. The syrup was taken up in hot glacial acetic acid and on standing deposited a crop of D-xylose, which on recrystallization had an m.p. of 145–146°C., unchanged on admixture with an authentic sample, and $[\alpha]_D^{20} = +19.8$. After removal of most of the xylose by crystallization, L-arabinose was recovered as its benzoyl hydrazone, m.p. 185°C., unchanged on admixture with an authentic sample, and $[\alpha]_D^{20} = +23.8$. After removal of the excess benzoyl hydrazine by treatment with formaldehyde and extraction with ethyl ether, the addition of phenylmethylhydrazine yielded the crystalline phenylmethylhydrazone of D-galactose, m.p. and mixed m.p. 182–183°C. (12). On treatment of the remaining solution with phenylhydrazine an osazone was isolated that was converted to glucose phenylosatriazole (10), m.p. and mixed m.p. 195–196°C. Further proof of the presence of glucose was obtained by selective fermentation. A species of *Torula utilis* known to ferment only glucose was used to ferment a sample of the acid hydrolyzate. The fermented solution was chromatographed on the same paper strip as the unfermented solution and showed clearly that glucose was completely absent in the fermented solution. Arabinose, xylose, and galactose were unaffected.

Barium Uronate Salt

The barium salt precipitated by alcohol from the hemicellulose hydrolyzates was purified by repeated solution in water and reprecipitation with alcohol. The final product was recovered as a fine white powder with the following analysis: barium, 24.6%; methoxyl, 4.3%; uronic acid anhydride, 23.4. A molar ratio of methoxyl to uronic acid groups of 1.04 was evidence of a monomethoxyl hexuronic acid. The barium salt gave a strong napthoresorcinol test for uronic acid. Specific color tests for glucuronic and galacturonic acid (8, 9), were interfered with by a pentose sugar in the uronic acid complex. The presence of a pentose sugar was shown by a strongly positive Tollens orcinol test.

The barium uronate salt was hydrolyzed by sealing 123 mgm. in a glass tube with 2 ml. of 4% sulphuric acid (v/v) and heating at 120°C. for 8½ hr. The hydrolyzate was neutralized with barium carbonate, filtered, and clarified with charcoal. The solution was then chromatographed using as references substances free glucuronic acid, glucuronic acid lactone, and galacturonic acid as well as xylose, arabinose, glucose, and galactose. Xylose was clearly demonstrated as the only sugar present and must have been freed on hydrolysis, as the original barium uronate salt contained no free xylose. The spots of the reference free glucuronic and galacturonic acids showed slow migration and were approximately equidistant from the starting line; glucuronic acid lactone

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formed a fast moving spot near the bottom of the paper after 16 hr. The unknown barium uronate solution produced a spot in the same position as the free uronic acids but there was no trace of glucuronic acid lactone. Positive identification of the unknown from its position was not possible but the shape of this spot resembled very closely that of the known free galacturinic acid. Insufficient material was available to give a trustworthy mucic acid test. It was possible to conclude that the hemicelluloses contained a uronic acid complex in which the sugar unit was D-xylose and the uronic acid possibly galacturonic.

Discussion

Hemicelluloses as usually prepared by alkali extraction of plant tissue are composed of both polyuronides and cellulosans (19). The cellulosans, being an integral part of the plant cellulose, are more difficult to extract than the polyuronides. The ready preparation of holocellulose provides a source of both materials free from the interfering action of lignin, and several investigators have attempted recently to fractionate the holocellulose with solvents considerably milder than those previously used (17, 18, 25). The general conclusion drawn from these studies has been that the isolated fractions show systematic trends in chemical composition that are related to solubility. In the present investigation on the fractionation of wheat holocellulose, five main fractions were isolated by relatively mild treatments. The main water soluble fractions were characterized, in general, by a higher uronic acid anhydride and methoxyl content than the alkali soluble materials; the latter, however, contained a considerably higher pentosan content. This result was indicative of a partial fractionation into polyuronides and cellulosan although the inclusion of approximately 5% uronic acid anhydride in the alkali soluble fractions showed that the separation was by no means sharp. The heterogeneity of hemicellulose material made the usual methods of fractionation empirical and it is doubtful if separate entities can be prepared by these techniques.

From considerations of solubility, the most soluble fractions would be expected to contain the short chain material. However, as Ritter has pointed out, a long chain hemicellulose containing uronic acid groups may have the same solubility as a short chain hemicellulose with no acid groups (22). It is possible then to have long and short chain material precipitated together from the extract. The intrinsic viscosity values were approximately of the same order for all fractions. The apparent chain lengths did not appear to show the variations expected on the basis of solubility although as pointed out earlier the calculation of the *DP* is restricted by inadequate data on the *Km* factor.

Millet and Stamm found that successive hemicellulose fractions isolated from aspen holocellulose had approximately the same molecular weights (*ca.* 8000) as determined by the viscosity method (17). End group methods (iodine number) by the same authors gave quite different results. Relatively wide variations in minimum molecular weights of maple wood hemicelluloses

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extracted by water and dilute alkali were found by Mitchell and Ritter (18). However, chemical methods for molecular weight estimation involving reducing groups are known to be unreliable, especially if the material has been treated with alkali in air.

All hemicellulose fractions isolated were shown to contain xylose, arabinose, and glucose, with xylose predominating. Galactose was found only in the water soluble fractions. It is not known whether or not the hexosans are chemically combined with the pentosan material. Evidence put forward by Carson and MacLay (5) and Anderson *et al.* (3) supports the view that the hexosan and pentosan materials are chemically linked. In another method of separation studied in this laboratory for fractionating wheat straw hemicelluloses, a small constant amount of glucose and galactose was found associated with the pentosans in all fractions (4). The recent work of Isherwood (15) on pear cell wall polysaccharides using electrophoretic methods has indicated that polysaccharides generally regarded as complex may be a mixture of simple polymers containing only a single sugar each. At present, attempts are being made to resolve the hot water soluble hemicellulose (fraction No. 6) into single units by fractional precipitation of the acetylated material from chloroform solution.

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HYDROGEN PEROXIDE AND ITS ANALOGUES

II. PHASE EQUILIBRIUM IN THE SYSTEM HYDROGEN PEROXIDE - WATER[1]

By William T. Foley[2] and Paul A. Giguère

Abstract

A precision freezing point apparatus with platinum resistance thermometer was used to investigate the system hydrogen peroxide – water over the whole concentration range. The freezing point of the purest sample of hydrogen peroxide obtained by repeated fractional crystallizations of a large quantity of 99.6% pure solution was found to be −0.461°C.; that of the dihydrate was −52.10°C. The two eutectics occur at concentrations of 45.2% and 61.2% H_2O_2 and at temperatures of −52.4° and −56.5°C. respectively. Contrary to what has been reported previously, water and hydrogen peroxide do not form solid solutions together. This was proved conclusively by applying the technique of radioactive tracers to the 'wet residue' method of Schreinemakers.

The purpose of this investigation was threefold. First, to redetermine the freezing point of pure hydrogen peroxide, with greater accuracy than heretofore (3). Second, to settle the question of solid solutions in the system hydrogen peroxide – water (6). Third, to use freezing point measurements for evaluating the degree of purity of very concentrated hydrogen peroxide. Indeed, the usual chemical methods of analysis are of little use for that purpose since the remaining traces of water cannot be determined directly (4). Other physical methods investigated so far are either not sensitive enough or subject to errors due to spontaneous decomposition. These three objectives are closely interconnected; for instance, the existence of solid solutions would render determinations of freezing point rather problematic. At the same time it could rule out the possibility of using this method for accurate analysis.

Experimental Methods and Results

Freezing Points

An apparatus similar to that originated by Mair (12) and perfected subsequently by Rossini and his collaborators (7, 13, 20) at the National Bureau of Standards was constructed for this purpose. The double-walled, silvered freezing tube had an internal diameter of 3 cm. and the rate of heat transfer was controlled by adjusting the pressure inside the annular space. The cold head was provided by a large Dewar flask filled with dry ice and acetone. The problem of stirring the sample presented some experimental difficulties since most materials catalyze the decomposition of hydrogen peroxide. Stirrers made of glass rods were too fragile. Aluminum or highly polished stainless steel has been recommended as suitable for this purpose (18); the latter was selected because of its greater strength. The stirrer was in the form of a double helix fashioned

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by winding a 1/16 in. rod first downwards on a wooden mandrel 9/16 in. diameter and then upwards on a cylinder 11/16 in. diameter over a 3 in. length. The stirrer was polished electrolytically (19) by making it the anode in a bath of 47% glycerol, 42% sirupy phosphoric acid, and 11% water. Electrolysis was carried out with a cathode of the same material in a bath at 125°C. with a current density of 0.2 amp. per sq. in. After a few trials, surfaces could be obtained that were completely inactive towards hydrogen peroxide. The stirrer was actuated by a windshield wiper type of motor with a reciprocating stroke of $2\frac{1}{2}$ in. at the rate of two strokes per second. The apparatus was completed by a cork stopper covered with aluminum foil and through which the thermometer and stirrer were inserted, the latter guided by a length of glass tubing; two other inlets were provided, one for introducing crystals for seeding the sample and the other for blowing a stream of well dried air. This last precaution was necessary because concentrated hydrogen peroxide is very hygroscopic at low temperature.

The first few runs were made with a Beckmann thermometer, but it was soon realized that the time–temperature curves could not be followed long enough to give significant results, especially with the less concentrated solutions. A platinum resistance thermometer (Leeds and Northrup, type 8163) certified by the National Bureau of Standards was therefore used in conjunction with a Mueller bridge. The bridge was calibrated according to regular practice (15) against a 10 ohm Standard kept at 20.0°C. The ice point of the thermometer was determined after the method of Busse (2). Its resistance at 0°C. was 25.5188 international ohms. This value was again checked when the investigation was completed and perfect agreement obtained. The degree of reproducibility obtainable with this method and apparatus may be judged from the results in Table I.

TABLE I

TYPICAL RESULTS OF FREEZING POINT DETERMINATIONS

Run No.	Weight % H_2O_2	Freezing point, °C.
16	99.5_8	−0.869
17	99.5_8	−0.873
18	99.5_8	−0.876
33	99.7_4	−0.655
34	99.7_4	−0.655

Runs No. 33 and 34 were carried out on the same day, Nos. 16, 17, and 18 on successive days, the solution being kept at room temperature in the meantime. Although there was no evidence of streamers in the liquid it is likely that the slight drift in the freezing point is due to actual decomposition. Calculations show that the variation corresponds to a concentration change of 0.003% per day, which is far beyond the limit of accuracy of volumetric analysis in that concentration range. These observations confirm, therefore, the

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superiority of freezing point measurement over chemical analysis for determining the purity of concentrated hydrogen peroxide.

The hydrogen peroxide used for these measurements was Becco's 90% solution. By fractional distillation through a 60 cm. glass column packed with Pyrex helices the concentration could easily be brought up to around 99.6%. Then it was subjected to fractional crystallization, the progress of concentration being followed by means of freezing point determinations. To be effective this last operation had to be carried out with great care. The solution to be concentrated was cooled in a stoppered flask and crystallization induced by seeding. It was then kept at −2°C. for several hours with occasional shaking. Then the two phases were separated by means of the device shown in Fig. 1. Flask *A* containing the partly frozen solution was inverted by rotating the connecting tube about ground joint *J*. By applying suction over flask *B* the liquid was filtered through the fritted glass plate. Thus any dilution from condensation of atmospheric moisture was avoided.

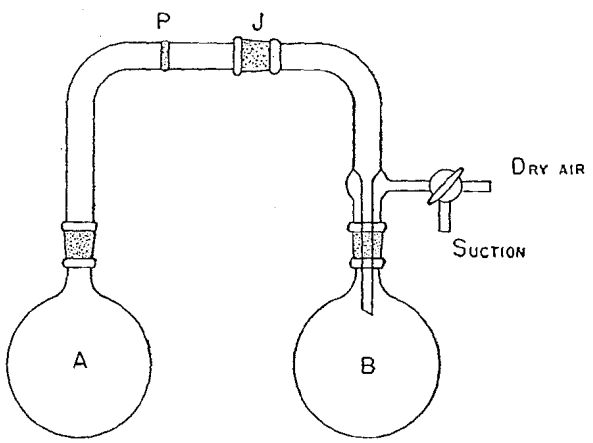

FIG. 1. *Apparatus for concentrating hydrogen peroxide by fractional crystallization.*

About 70 gm. of liquid was needed for a freezing point determination. In one series of determinations about 3 lb. of a 99.6% solution was recrystallized a number of times. The freezing point was measured when about two pounds was left and four times thereafter with at least two fractional crystallizations between successive measurements. The results shown in Table II are believed to be the most reliable to date. The measurements were carried out immediately after a recrystallization except in the case of Run No. 40 where the sample was left standing overnight, which may explain the slight discrepancy.

A second set of experiments was made starting with 1 lb. of concentrated solution, so that only three determinations could be made. The refractive index of the sample used for Run 39 was 1.40669 at 25°C., in perfect agreement with the latest results from this laboratory (4).

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TABLE II

FREEZING POINT OF PURE HYDROGEN PEROXIDE

Run No.	Weight % H_2O_2*	Freezing point, °C.
1st series		
29	99.7_9	−0.479
31	99.9_5	−0.465
38	100.0_3	−0.461
39	99.9_7	−0.461
40	99.9_3	−0.469
2nd series		
30	99.8_3	−0.500
32	99.9_3	−0.492
37	99.9_0	−0.461

* *From volumetric analyses.*

The method of W. P. White (21) for calculating the freezing point at zero impurity from time–temperature curves was applied to the above determinations assuming that traces of water were the only contaminant in the peroxide. The calculations were based on the portion of the cooling curve where from 1/10 to 1/3 of the sample was frozen. The results, summarized in Table III, are rather inconsistent as a whole, apparently owing to the fact that the system was very sluggish in reaching equilibrium. Other investigators (1) have reported that in the case of hydrocarbons equilibrium is attained within four or five minutes. In associated liquids, however, the high viscosity slows down diffusion considerably and this may lead to spurious results.

TABLE III

CALCULATED FREEZING POINT AT ZERO IMPURITY

Run No.	Fraction frozen	Temperature, °C.	Freezing point, °C. (at zero impurity)
30	1/10	−0.508	−0.428
,,	1/5	−0.517	−0.432
31	1/5	−0.469	−0.448
,,	1/3	−0.474	−0.447
32	1/10	−0.495	−0.468
,,	1/5	−0.498	−0.468
,,	1/4	−0.501	−0.465
37	1/5	−0.470	−0.425
,,	1/4	−0.472	−0.428
39	1/10	−0.465	−0.425
,,	1/5	−0.469	−0.429
40	1/5	−0.473	−0.451

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Using the same apparatus and technique the freezing point curve of the system hydrogen peroxide – water was re-examined. Some twenty measurements covering the entire concentration range were carried out, particular attention being paid to the region between 40 and 60%. On the whole the results (Table IV) agree fairly well with those of previous investigators (6, 9, 11) except for the freezing point of the addition compound $H_2O_2.2H_2O$. A comparison of the various values for this latter quantity and the co-ordinates of the two eutectic points is shown in Table V.

TABLE IV

FREEZING POINT OF HYDROGEN PEROXIDE SOLUTIONS

Run No.	Weight % H_2O_2	Freezing point, °C.
43	3.40	− 1.99$_4$
42	5.81	− 3.49$_5$
44	9.40	− 5.93$_8$
52	19.6$_5$	−14.3$_1$
51	28.1$_5$	−23.2$_8$
53	39.1$_4$	−39.9$_7$
55	44.6$_5$	−51.0$_4$
60	46.8$_0$	−52.1$_6$
62	48.5$_1$	−51.9$_9$
56	48.5$_7$	−52.1$_0$
59	48.6$_4$	−52.1$_0$
61	51.9$_2$	−52.4$_0$
50	57.7$_7$	−54.5$_3$
58	60.3$_1$	−56.1$_2$
54	70.9$_4$	−38.8$_4$
48	81.1$_2$	−23.0$_1$
46	91.0$_4$	−10.2$_1$
47	95.3$_3$	− 5.35$_6$
45	95.6$_8$	− 5.05$_1$
27	97.5$_6$	− 3.18$_3$

TABLE V

COMPOUND AND EUTECTICS

1st eutectic		Compound		2nd eutectic		Authors
Weight % H_2O_2	Temp., °C.	Weight % H_2O_2	Temp., °C.	Weight % H_2O_2	Temp., °C.	
45	−53	48.6	−51	59	−56	Maass and Herzberg
46	−51.5	,,	−50.3	60	−56.5	Giguère and Maass
45.8	−52.5	,,	−50.3	59.0	−55.5	Kubaschewski and Weber
45.2	−52.4	,,	−52.10	61.2	−56.5	This work

Solid Solutions

The so-called 'wet-residue' method of Schreinemakers (17) was applied using potassium chloride for the third component. Indeed, it is soluble in both liquids and is easily determined; in addition it does not decompose hydrogen peroxide. Two experiments were done with dilute peroxide solutions and two with concentrated solutions. The ternary mixtures were placed in a constant temper-

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ature bath (5) and crystallization was induced by seeding at a few degrees below the freezing point. Temperature was gradually lowered by about 10 degrees so that a good portion of the sample was solidified. After remaining at least 10 hr. at that temperature the two phases were separated as thoroughly as possible by siphoning the liquid through a filter stick. Both phases were then analyzed, potassium chloride being determined gravimetrically with silver nitrate, and hydrogen peroxide, by the usual titration with permanganate. The results of Table VI were plotted on a tricoördinate graph; the corresponding lines when extrapolated passed exactly through the apex in all four cases, thereby indicating that no solid solution existed on either side of the phase diagram.

TABLE VI

RESULTS OF THE 'WET RESIDUE' METHOD WITH POTASSIUM CHLORIDE

Filtration temperature, °C.	% Composition of mother liquor			% Composition of wet solid		
	KCl	H_2O_2	H_2O	KCl	H_2O_2	H_2O
−15	7.09	17.64	75.3	4.62	10.78	84.6
−15	11.38	15.49	73.13	7.16	9.98	82.9
−23.8	4.48	79.3	16.2	1.24	94.6_4	4.1_2
−23.8	2.12	79.9_5	17.9_3	0.93	93.7_8	5.9_2

An objection to the above method is that addition of a third component in the large amounts needed for significant analysis may disturb considerably the normal equilibrium between the two major components. A solution of this difficulty in the present case was discovered in the use of radioactive tracers. Because of the very minute quantity needed there can be no disturbing effect of such a third component; yet the techniques of radioactivity measurements and the availability of concentrated isotopes result in an accuracy considerably greater than that of conventional chemical analysis. Radioactive phosphorus P^{32} in the form of potassium dihydrogen phosphate was used for this purpose as it fulfilled a number of desirable conditions: solubility in both water and hydrogen peroxide; inertness towards the latter; only one type of particles (β) emitted, and with sufficient energy (1.7 Mev.), to allow use of thin walled glass counters; half life of the right order of magnitude (14.3 days) for the proposed experiments and at the same time presenting no serious problem of contamination. The isotope was obtained from the Atomic Energy Project of the National Research Council at Chalk River. The original sample weighing 0.028 gm. had an activity of 0.95 millicurie when shipped. It was diluted a 100-fold and an amount added to give a concentration of 0.00025 gm. per liter of peroxide solution.

Two determinations were made, one with a 7% and one with a 95% solution of hydrogen peroxide. The phase separation was effected at −10°C. as described above and the activity measured with a Geiger–Mueller counter (Tracerlab No. TGC-5). The plateau of this counter had a slope of the order of 5% per 100 volts; starting voltage, 825 v. The operating voltage was kept at 900 v.±

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0.1% by means of a stabilized power supply. The Geiger tube was mounted in an inverted position so that a test tube of appropriate size containing the solution could be placed around it. Care was taken that the liquid always reached the same level above the thin section of the counter. The latter was carefully cleaned between successive measurements and the background redetermined. This was kept at about 23 counts per minute with the help of a heavy shield of lead blocks. A scaler and a Cenco impulse counter completed the apparatus. The activities given in Table VII are corrected for background,

TABLE VII

RESULTS OF RADIOACTIVITY MEASUREMENTS

Wet solid			Mother liquor		
Weight of sample, gm.	Weight % H_2O_2	Activity, counts/min.	Weight of sample, gm.	Weight % H_2O_2	Activity, counts/min.
76.3	7.67	6911	25.5	15.38	13747
86.4	94.79	5021	70.4	79.23	19650

dead time of counter (100 μsec.), and for decay of the radioactive material during experimentation. The calculations are as follows.

For the 7% solution the ratio of activities in the two phases is 6911/13747 = 0.5027; therefore the per cent of water in the solid phase is:

$$\frac{(100 - 7.67) - 0.5027\ (100 - 15.38)}{(1 - 0.5027)} = 100.1\%$$

Similar calculations for the 95% solution yielded exactly the same result, thereby fully confirming the above conclusions.

Discussion

The freezing point of pure hydrogen peroxide was first reported as being −1.7°C. (10). This is still often quoted in spite of the fact that it was found later to be too low by about 0.8°C. (3). More recent determinations (19) indicated definitely that the revised value, −0.89°C., was still too low. The present result, −0.461°C., is now believed to lie within a few thousandths of a degree from the true value for the following reasons: It is the highest freezing temperature observed in a direct determination; in addition it is the only result that could be duplicated to the limit of accuracy of the measurements (0.001°) and this with two different samples.

The results of calculations at zero impurity will not be considered since at least in one instance (Run No. 32) they lead to a lower temperature than the highest one obtained directly. If the correct freezing point were around −0.43°C. as suggested by runs No. 30, 37, and 39 (Table III), then the above result, −0.461°C., would correspond to a sample containing 0.03% water. Considering the difficulty of removing the last traces of water from hydrogen peroxide this is not a large quantity. However, there is no reason why exactly

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the same amount of impurity should have been present in the three runs No. 37, 38, and 39 (Table II). The present investigation provides the most accurate and reliable method of ascertaining the purity of highly concentrated hydrogen peroxide. Its only drawback is the relatively large sample (70 cc.) necessary for a determination. It is planned to improve the apparatus in that respect, particularly along the lines adopted by Herington and Handley in their recent work (8).

At the time this work was begun the formation of solid solutions in the system hydrogen peroxide – water was considered an open question. In favor was the fact that fractional crystallization is extremely inefficient for concentrating hydrogen peroxide solutions. This observation, first made by Maass and Hatcher (10), has been verified repeatedly, in particular by Giguère and Maass (6), who applied the analytical, or phase separation method, and came to the conclusion that solid solutions were formed. In addition they pointed out that the freezing points of very concentrated peroxide solutions were appreciably higher than those calculated from Raoult's law.

On the other hand, these arguments were opposed by the following ones: the lattice constant of hydrogen peroxide is the same in frozen solutions (82 and 90%) as in the pure compound according to an X-ray investigation (16). More recently it has been observed in this laboratory that hydrogen peroxide solutions on cooling do not always solidify *completely* at temperatures below their corresponding eutectic, a result not easily reconciled with occurrence of solid solutions in the system (5). It is now obvious why these solutions can be supercooled with respect to the addition compound, $H_2O_2.2H_2O$; the limited stability of this hydrate is confirmed both by its low symmetry (16) and the flatness of its freezing point curve (Fig. 2).

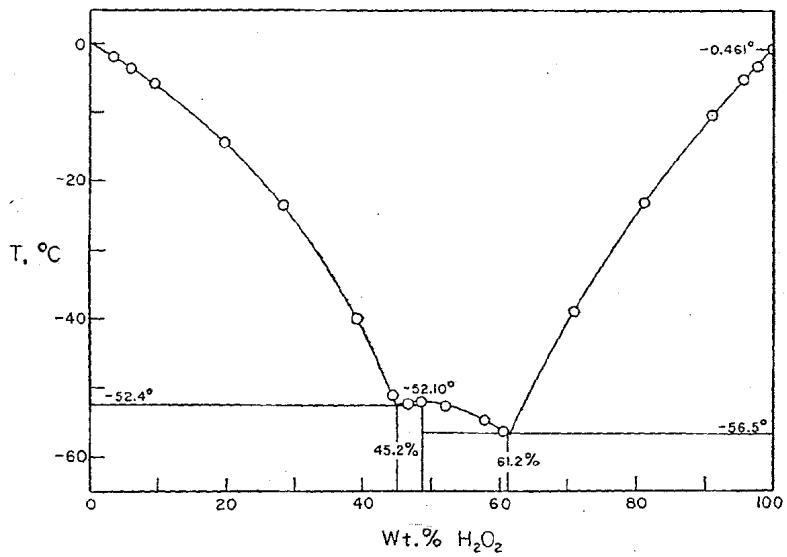

FIG. 2. *Phase diagram of the system hydrogen peroxide – water.*

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From the present study and a similar one made on the system hydrazine–water (14) it must be concluded that the poor results obtained in attempting to freeze out the ice or the pure compound are due entirely to the difficulty of removing the mother liquor from the crystals. Calculations show that in most instances the solid still contained as much as its own weight of liquid although it looked quite dry. The so-called synthetic or 'wet residue' method is certainly superior to the analytical one for such investigations. In particular the use of radioactive tracers as described above should make it still more valuable and more widely applicable in the study of phase equilibria.

Finally there remained the question of deviation from Raoult's law; since dilute peroxide solutions show almost ideal behavior up to concentrations of 10% H_2O_2 it became questionable whether the accepted value, 74 cal. per gm., for the heat of fusion of hydrogen peroxide was not appreciably in error. A check of that datum by means of an ice calorimeter has yielded a value, 85.75 cal. per gm. which leads to very good agreement of the freezing point curve with Raoult's law. A description of this and other thermal measurements will be published shortly.

Acknowledgment

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THE EFFECT OF RELATIVE HUMIDITY ON COAGULATION AND SURFACE LOSSES OF AMMONIUM CHLORIDE SMOKE[1]

By T. Gillespie and G. O. Langstroth

Abstract

Studies have been made of the change with time in the particulate number and rate of loss to surfaces of ammonium chloride smoke at various relative humidities ranging from 15% to 98%. The results are adequately described by the theory given previously with appropriate values for the loss and coagulation constants. The rate of disappearance of the smoke increased with increasing relative humidity, particularly above a value of about 60%. This circumstance is due to an increased loss rate from the system and not to increased coagulation. Though the possibility of 'protecting' an aerosol against coagulation is remote, it would appear possible to render certain aerosols more persistent in humid atmospheres by treatment affecting loss processes rather than coagulation.

Previous studies (1, 2, 6) of the rate of disappearance of aerosols at various humidities have permitted no distinction to be made between the effect of water vapor on the coagulation process and on the mechanism of loss to surfaces. It is possible, however, to determine these separate effects by analysis of appropriate particle number and surface loss data. A suitable analytic procedure and experimental confirmation of it have been described in detail (3, 4) in connection with studies of the aging of ammonium chloride smoke under normal laboratory humidity conditions (at Ralston, 15% to 30% R.H.). This article describes studies with ammonium chloride smoke at various relative humidities ranging from 15% to 98%, leading to a description of the effect of water vapor on the coagulation and surface loss processes.

1. Apparatus and Procedure

Experiments were performed in a 0.6 m. cube chamber in 'still' air. The smoke was produced by heating 108 mgm. of ammonium chloride in an external generator as described previously (3, 4). In general, particle number and surface loss measurements were made periodically for about 100 min., but in two experiments the former were continued for more than four hours. Particle number was determined from assessment of deposits on thermal precipitator slides in the usual manner. The number of particles lost to surfaces during successive intervals in the life of the smoke was calculated from counts on replaceable slides attached to the top, bottom, and each wall of the chamber. Estimates of the apparent particle size distribution of selected thermal precipitator samples were made with the aid of a Patterson–Cawood graticule in some experiments. The details of all sampling and assessment techniques have been described elsewhere (3, 4).

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To maintain the desired relative humidity in the smoke chamber, all surfaces were covered with asbestos paper soaked in water, or in a saturated aquecus solution of an appropriate salt (5). To minimize changes caused by the influx of air during smoke production, the air entering the generator was bubbled through water or the same solution. The relative humidity in the chamber was measured immediately before and after each experiment by means of an attached Assmann wet and dry bulb hygrometer; the difference between these two values never exceeded 4%. In the absence of smoke, the determined relative humidity in the chamber varied by less than 2% over a 24 hr. period both for conditions designed to produce high and low humidity.

2. Experimental Data

Particulate volume data for eight experiments are given in Table I. Surface loss data for seven experiments are given in Table II. The quantity $(\Delta n)_l$ represents the total number of particles lost to the surfaces of the chamber from the beginning of the experiment up to the time in question, divided by the volume of the chamber. It was obtained by adding together the determined losses to each surface for each successive period up to the time stated. The procedure has been described previously (3). Values of the tabulated quantities as calculated by the methods of Section 3 have been included in Tables I and II for comparison with observed results. Typical apparent particle size distributions at early and late stages in the life of a smoke are given in Fig. 1 for relative humidities of 46% and 96%.

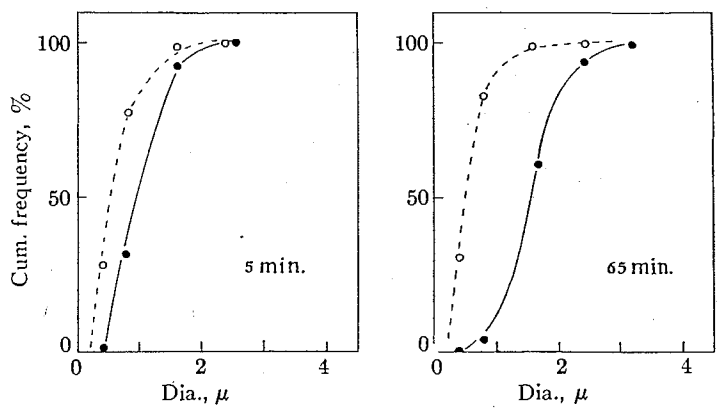

FIG. 1. *A comparison of apparent particle size distributions at relative humidities of 46% (solid lines, Expt. 15) and 96% (dashed lines, Expt. 8). The ordinates represent the percentage of particles with an apparent diameter less than the corresponding abscissa value.*

3. Analysis of the Data

It has been shown previously (3, 4) that experimental data obtained at relative humidities of 15% to 30% are adequately described by equations based on quite general grounds, i.e.,

$$\ln(1/n + k/\beta) = \beta t + \ln(1/n_0 + k/\beta) \quad (1)$$

$$\ln(n) + \beta t = -k/\beta(\Delta n)_l + \ln n_0 \quad (2)$$

$$(\Delta n)_l = \beta \int_0^t n \, dt. \quad (3)$$

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TABLE I

PARTICULATE VOLUME VS. TIME DATA

Tabulated values are $10^6/n$*

Exp. #	7		8		10		11		12		14		15		17	
Relative humidity	96%		96%		96%		82%		78%		53%		46%		15%	
Time (min.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	0.95	0.85	1.12	1.06	0.7	0.7	0.6	0.6	0.76	0.74	0.73	0.8	0.78	0.9	1.10	1.10
15	1.10	1.23	1.28	1.4	1.14	1.14	0.89	1.0	0.94	1.0	1.18	1.2	1.6	1.5	1.85	1.60
25	1.7	1.6	1.8	1.9	2.0	1.6	1.2	1.3	1.18	1.3	1.8	1.5	2.5	1.9	2.2	2.1
35	2.1	2.1	2.5	2.4	1.9	2.2	1.4	1.6	1.6	1.6	1.8	1.9	2.5	2.5	2.9	2.6
45	2.0	2.6	2.2	2.9	2.2	2.8	1.7	1.9	1.8	2.0	2.3	2.3	2.1	2.8	2.6	3.1
55	2.9	3.3	3.5	3.6	3.7	3.5	2.4	2.3	2.4	2.3	2.6	2.6	3.2	3.4	3.1	3.6
65	4.1	4.0	4.1	4.3	4.1	4.3	2.4	2.6	2.3	2.7	4.1	3.1	3.9	3.9	3.1	4.1
75	4.7	4.8	5.2	5.2	5.4	5.1	2.9	2.9	3.3	3.1	4.2	3.4	3.2	4.5	5.3	4.7
85	5.1	5.7	7.6	6.1	6.1	6.1	3.8	3.3	3.8	3.5	4.1	4.1	5.4	5.1	4.8	5.2
95	8.1	6.8	8.0	7.2	7.8	7.5	5.0	3.8	4.5	3.9	3.7	4.3	5.4	5.6	5.0	5.7

* *Values under the heading 'Calc.' were obtained from Equation (1) using the constants given in Table III.*

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TABLE II

SURFACE LOSS DATA

Tabulated values are $(\Delta n)_t \times 10^{-4}$ cc.$^{-1}$ *

Exp. #	8		10		11		12		14		15		17	
Relative humidity	96%		96%		82%		78%		53%		46%		15%	
Time (min.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	6.1	5.2	7.0	5.5	2.5	2.2	2.8	2.8	1.3	0.9	1.5	1.4	0.9	0.95
10	10.5	8.6	13.4	12.0	4.5	6.0	5.4	4.9	2.2	2.2	2.9	3.3	1.7	2.2
20	21.2	16.6	22.7	22.4	8.0	9.6	10.0	10.8	3.8	3.6	5.0	5.5	2.8	3.1
30	28.3	27.0	28.5	27.6	11.4	14.4	14.3	15.0	5.2	4.9	6.7	7.0	3.8	4.0
40	34.5	25.6	33.3	32.0	14.2	16.6	17.9	18.2	6.3	6.2	8.0	8.5	4.5	4.5
50	39.3	35.4	36.6	35.6	17.0	17.2	21.1	20.4	7.5	6.9	9.1	9.7	5.0	5.1
60	42.7	38.8	39.2	40.0	19.4	18.9	23.7	22.6	8.4	7.5	10.1	10.5	5.3	5.4
70	43.4	42.4	41.0	41.4	21.1	19.7	25.8	25.4	9.6	8.6	11.0	11.0	5.7	5.9
80	43.6	45.2	—	46.6	22.9	20.6	27.5	26.6	10.4	9.2	11.8	11.8	6.0	6.3
90	—	—	—	—	23.9	21.4	29.0	27.1	11.3	9.5	12.7	12.3	6.3	6.6

* *The values under the heading 'Calc.' were obtained using Equation (2) and the constants as given in Table III.*

The definition of $(\Delta n)_l$ has been given in Section 2; n and n_0 denote respectively the number of airborne particles per cubic centimeter at t and at $t = 0$. The coagulation and loss constants are represented by k and β, and are defined by "coagulation rate per cc. $= kn^2$" and "average loss rate per cc. $= \beta n$".

Analysis of new data obtained under conditions differing from those previously studied entails (*a*) demonstration that the equations provide an adequate description of the results, and (*b*) determination of the coagulation and loss constants. Certain detailed tests of the adequacy of the theory have been described (3); a comparison of observed values of n and $(\Delta n)_l$ with those calculated using determined k, β, and n_0 values constitutes an "over-all" test. Such a comparison is made in Tables I and II. As in reference (3), the value of β was determined from the slope of the $(\Delta n)_l$ vs. $\int_0^t n\,dt$ curve, and that of k from the slope of the $\ln(n) + \beta t$ vs. $(\Delta n)_l$ plot. In a few experiments for which $(\Delta n)_l$ data were lacking, k and β were found from particle number data as in reference (4) (cf. Equation 1). The values found for the various constants are summarized in Table III, and a plot of β vs. relative humidity is given in Fig. 2.

TABLE III

A SUMMARY OF THE DETERMINED VALUES OF THE CONSTANTS IN EQUATIONS (1) TO (3)

Exp. #	Relative humidity, %	$n_0 \times 10^{-6}$	$\beta \times 10^3$ min.$^{-1}$	$k \times 10^8$ cc./min.	$k/\beta \times 10^6$
17	15	1.24	1.77	4.7	6.8
15	46	1.25	2.9	4.3	14.8
14	53	1.43	1.9	3.3	17.2
12	78	1.66	5.2	2.4	4.7
11	82	2.0	3.5	2.5	7.3
10	96	2.0	10.0	3.4	3.4
8	96	1.1	12.8	2.2	1.8
7	96	1.4	13.0	2.2	1.7
6	98	1.5	12.4	2.5	2.0
5	96	1.8	14.0	2.7	1.9

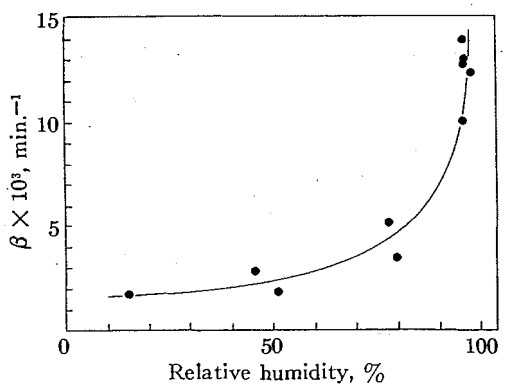

FIG. 2. *The effect of variations in relative humidity on the loss constant* β.

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4. Discussion

The results show that the rate of disappearance of ammonium chloride smoke depended on the relative humidity of the atmosphere in which the particles were dispersed. For example, the number of particles remaining after 1.5 hr. at a relative humidity near 50% was about twice as great as that at a relative humidity of 96% (Table I); the number of particles lost to surfaces in this time was only about 1/4 as great (Table II). These differences are attributed to changes in the characteristics of the particles caused by sorption of water vapor.

A comparison of the calculated and observed values for particulate number and cumulative surface loss shows the agreement to be satisfactory in view of the uncertainties inherent in aerosol assessments (Tables I and II), and plots of $\int_0^t n\,dt$ and $\ln(n) + \beta t$ against $(\Delta n)_t$ were found to be linear in accordance with Equations (3) and (2). It follows that k and β remained essentially constant during an experiment as assumed in the theory, regardless of whether the relative humidity was low or high. This indicates in turn that the particles quickly reached an approximately stationary condition with respect to sorbed water vapor, since a gradual sorption would be expected to cause a gradual but marked change in β at least (cf. Fig. 2 and the remarks below). In support of this view, unpublished studies of the rate of increase in the mass of ammonium chloride smoke particles exposed to a humid atmosphere on the pan of a microbalance indicate that the sorption process is practically complete in less than 10 min.

As may be seen from Fig. 2, the loss constant β was not greatly affected by changes in relative humidity below about 60%, but thereafter increased strongly with increasing relative humidity and became nearly five times as great at 96%. This marked effect is caused presumably by an increased sedimentation rate resulting from the increased apparent density of particles on sorption of water vapor. The smokes at high relative humidity were characterized by a smaller particle size than those at low humidity, and the difference was more apparent with older smokes (Fig. 1). It could be accounted for in part by a more rapid sedimentation of the larger particles in the presence of considerable water vapor. It is interesting to note also from Fig. 1 that the median apparent particle diameter increased from about 1.1 to about 1.6μ in one hour at a relative humidity of 46%, but remained nearly constant ($\sim 0.6\mu$) at a relative humidity of 96%.

In contrast to the changes caused in β, the effect of variations of relative humidity on the coagulation constant k were not marked (Table III). There appears to be some trend, however, toward a smaller value at the high humidities. For example, the average value at 96% R.H. was 2.6×10^{-8} cc. per min. compared to 3.8×10^{-8} cc. per min. near 50% R.H. No attempt to account for this is justified at the moment in view of our lack of knowledge of the parts played by the various coagulation mechanisms.

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To sum up, the rate of disappearance of ammonium chloride smoke increases with increasing relative humidity, though not strongly at values below about 60%. This circumstance is due to an increased rate of loss from the system, while the effect on the coagulation constant (if any) favors less rapid coagulation. The possibility of partially 'protecting' an aerosol against coagulation by introduction of some vapor therefore seems most remote (cf. reference (1)), but it should be possible to increase appreciably the persistence of hygroscopic aerosols in a humid atmosphere by some treatment that renders the particles incapable of sorbing moisture. Such a possibility depends on affecting loss processes other than coagulation.

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THE ALCOHOL–GLYCEROL METHOD FOR THE DETERMINATION OF FREE LIME[1]

By E. G. Swenson[2] and T. Thorvaldson

Abstract

A study was made of the alcohol–glycerol method of determining free lime in Portland cement and in mixtures of some aluminates and silicates of calcium.

Strontium chloride is an effective accelerator. Calcium chloride is effective for mixtures of the pure silicates, but with Portland cement both it and calcium acetate give reduction of the total time required only at low concentrations and produce low values for free lime at higher concentrations of the salts. Lithium chloride produces acceleration, but magnesium chloride masks the presence of free lime. Addition of water in small amounts reduces the time required for the determination; larger amounts cause high values for free lime in the presence of tricalcium silicate.

Lime heated to high temperatures becomes too inert to be determined without reactivation by suitable accelerators.

The presence of 5:3 calcium aluminate and alumina interfere with the determination of free lime. The method is not satisfactory for underburnt lime–alumina–silica systems low in tricalcium silicate but is more suitable for such systems high in this compound. The higher values obtained with accelerators are probably more accurate than those obtained without accelerators. High precision may be attained with mixtures of dicalcium silicate, tricalcium silicate, and tricalcium aluminate.

The alcohol–glycerol method (4, 8) or this method in modified form, (1, 3, 5) is probably the one most generally used for the determination of free lime in Portland cement. Extensive co-operative work (5, 6) in the evaluation of these and other methods has indicated preference for the method of Lerch and Bogue (8) on the basis of precision. The length of time required is a disadvantage, but this may be at least partly remedied by the use of barium chloride (1, 3) or sodium chloride (5) as accelerators. The wide variation in the results obtained by cement chemists in different laboratories (5), however, indicates that there are still difficulties in the execution of all these methods.

The object of the present work was to study the effect of varying conditions, the use of accelerators, and the use of the method in determining free lime in mixtures of the aluminates and silicates of calcium.

The Method

The experimental details were essentially those described by Lerch and Bogue (8). The refluxing apparatus consisted of an electrically heated double-walled asbestos board box, accommodating six 125-ml. florence flasks. Slotted

[1] *Manuscript received September 15, 1950.*

Contribution from the Department of Chemistry, University of Saskatchewan. This paper constitutes part of a thesis submitted by one of us (E.G.S.) to the Faculty of Graduate Studies, University of Saskatchewan, in partial fulfillment of the requirements for the degree of M.A., together with additional work carried out while Assistant Professor of Chemistry at Regina College (U. of S.), Regina, Sask.

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asbestos covers fitted the necks of the flasks which were attached to 50 cm. condensers, set at an angle of 45°, the upper ends being protected by soda-lime tubes. The heating was regulated so as to keep the alcohol–glycerol solution boiling gently, and small unglazed porcelain chips were added from time to time to prevent bumping. Both corks and chips were boiled in alcohol–glycerol solution, washed and dried before use.

Unless otherwise stated, 20-min. refluxing periods were used and the final end point taken when one hour of refluxing produced no pink color in the hot solution.

Both the ethanol and the glycerol used had a water content of less than 0.3% unless otherwise stated. The latter was prepared by vacuum distillation of reagent glycerol, the middle fraction being used. Reagent grade ammonium acetate was used without being first dried, as it was found that the salt became quite acidic on drying. With reasonable protection of the ammonium acetate against absorption of moisture from the atmosphere, the amount of water thus introduced in an ordinary determination is negligible. The accelerators were anhydrous salts.

The Standardization of the Ammonium Acetate Solution

Pure reprecipitated calcium carbonate was ignited to constant weight in a platinum capsule at about 950°C., the oxide cooled in a desiccator over lime, transferred along with the emptied capsule to the dry reaction flask, shaken immediately with 60 ml. of the alcohol–glycerol (5 to 1 by volume) to prevent caking, and the solution refluxed with titrations at 20-min. intervals. Table I indicates typical results obtained with two acetate solutions, without the addition of accelerators, and with the addition of the chlorides of barium, strontium, and calcium.* In Series A, the salts were added in equal weights, while in Series B equivalent molecular proportions were used.

TABLE I

THE EFFECT OF ACCELERATORS ON THE STANDARDIZATION OF AMMONIUM ACETATE SOLUTIONS

Series	Accelerator, gm.	CaO, gm.	Initial titer, ml.	Total titer, ml.	Total time, hr.: min.	Normality obtained
A	None	0.1067	2.0	19.03	4:20	0.200
	$BaCl_2$–0.10	0.1119	6.2	20.29	3:40	0.197
	$SrCl_2$–0.10	0.1009	9.4	18.46	3:00	0.195
	$CaCl_2$–0.10	0.1013	12.3	18.29	3:20	0.197
B	None	0.1010	2.3	16.80	4:20	0.214
	$BaCl_2$–0.375	0.1007	11.4	17.12	3:00	0.210
	$SrCl_2$–0.285	0.1003	13.1	16.89	3:00	0.212
	$CaCl_2$–0.200	0.1016	13.5	16.91	4:20	0.214

* *The accelerating action of calcium chloride was observed by Mr. D. J. Trevoy in this laboratory and recorded in his Graduation Thesis, 1944.*

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The accelerating effect of the salts is evident both in the increased titers at the end of the first 20-min. period of boiling and in the shorter time required to reach the final end point. While calcium chloride is very effective in increasing the first titer, it does not reduce the total time required at high concentrations. The total time is, however, subject to variations due to uncontrollable factors affecting interaction of solids and liquids.

There is a slight tendency towards lower values for the calculated normalities of the acetate solutions when the salts are used as accelerators. The differences between the normalities obtained on averaging all the experimental data available were: for calcium chloride, about 1% lower, and for barium and strontium chlorides 1½% lower than the normalities obtained in the absence of an accelerator. In the calculations of the percentage of free lime given in this paper these corrections are made where applicable.

The determinations with calcium chloride gave the poorest end points, perhaps owing to the formation of a heavy white precipitate in alcohol–glycerol solution in the presence of this salt. Strontium chloride appeared to have a slight advantage over barium chloride in the definiteness of the end point.

It was found that magnesium chloride, instead of acting as an accelerator, inhibited the process. With increasing amounts of this salt, up to a molar ratio of approximately 1½ for magnesium chloride to calcium oxide, the amount of titratable lime decreased to zero.

Increase in the length of the initial refluxing period increases the total time required and appears to increase slightly the value for the normality obtained. In a series with 0.375 gm. barium chloride present (0.1 gm. samples of CaO), and initial refluxing periods of 20, 40, and 60 min., the normality values obtained were 0.2114, 0.2123, and 0.2135, respectively. These variations, while possibly significant, are, however, of the order sometimes obtained in standardizations done at different times.

The effect of varying the weight of lime in a given volume of alcohol–glycerol solution is shown in Table II.

TABLE II

THE EFFECT OF VARYING THE WEIGHT OF LIME IN THE STANDARDIZATION OF AN AMMONIUM ACETATE SOLUTION

(0.142 gm. strontium chloride present in each instance)

CaO, gm.	Total ml. NH_4OAc solution used			Total titer, ml.	Total time, hr.: min.	Normality obtained
	1st titer	2nd titer	3rd titer			
0.0354	3.2	4.2	4.8	5.80	2:00	0.218
0.0709	5.8	7.9	10.0	11.76	2:00	0.215
0.1045	8.1	11.6	14.8	17.42	3:40	0.214
0.1380	7.5	11.5	15.8	23.00	3:40	0.214

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It was also found that the addition of slightly less than the total calculated required volume of ammonium acetate solution on the first titer had no appreciable effect on the normality value obtained or on the total time. Addition of small amounts of water accelerated the process without affecting the value materially.

It is evident that considerable latitude in conditions during the standardization may be allowed without reducing the precision usually attained in the determination of free lime.

Determination of Free Lime in a Portland Cement and a Portland Cement Clinker

The alcohol–glycerol method (8) has been used in this laboratory for many years for determining free lime in Portland cement and in preparations of silicates and aluminates of calcium. In the present study no extended work with commercial cements was undertaken. For comparison, two cements were used, one a dark-colored commercial Portland cement (containing 4% ferric oxide) which had been stored in closed containers in the laboratory for 12 years, and a light-colored commercial Portland cement clinker obtained freshly burnt and unground from a cement plant.

The aged cement gave a loss on ignition of 2.33%. When this cement was received from the mill, the loss had been 0.96% and the value for free lime 1.47%. The new values for free lime were: on the unignited cement, 1.03%, thus showing a drop of almost one-third during storage, and on the cement ignited at 950°C., 2.01%. All the determinations were made without accelerators. It would thus appear that approximately one third of the original free lime had been fixed by carbon dioxide during storage, this reappearing on ignition, while an additional one half of one per cent of free lime was liberated on ignition, probably through decomposition of superficially hydrated tricalcium aluminate (9) and tricalcium silicate (7). Practically all the increase in free lime on ignition appeared as increases in the first two 20-min. titers. The time of determination for the ignited and unignited samples was practically the same: without accelerators seven to eight hours, with accelerators two to three hours. In six individual determinations done at random over a period of two years on the ignited cement, using no accelerator, the maximum free lime obtained was 2.18%, the minimum 1.87%, the mean 2.01%, and average deviation from the mean, 0.09%. Carefully conducted series of determinations gave greater precision.

In agreement with published reports (1, 3, 5) it was found that the addition of barium chloride reduced the time per determination to less than one half, but gave free lime values somewhat higher than those obtained with no accelerator present. Strontium and lithium chlorides were found to have much the same effect. Calcium chloride gave acceleration when used in low concentrations, but the free lime values were low when more than 0.5 gm. of the salt was

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present with no decrease, or even an increase, in the time required. A heavy flocculent precipitate obscures the end point. The addition of small amounts of calcium acetate,* a product of the titration, produced acceleration, but larger quantities gave a gelatinous precipitate and low values for free lime, suggesting a possible weakness in the method when free lime is present in some quantity. The addition of 0.3 gm. of magnesium chloride per determination, or an equivalent amount of magnesium acetate, completely masked the presence of free lime.

The introduction of water in small quantities to the reaction mixture reduced the total time and caused no appreciable increase in free lime values. On addition of more than 0.5 ml. of water per 60 ml. of alcohol–glycerol solution the free lime values obtained increased gradually with increase in the total time, apparently owing to the progressive hydrolysis of cement compounds.

The freshly burnt cement clinker which was ground to pass 200 mesh and which gave an ignition loss of 0.19% was found to have a free lime content of 0.40%. The values for the ignited and unignited samples agreed within experimental error. With various amounts of the chlorides of barium, strontium and calcium as accelerators, and with water, the results obtained were analogous to those for the cement.

Determination of Free Lime in Mixtures of Tricalcium and Dicalcium Silicates

These two silicates constitute about 75% of normal Portland cement clinkers. The sample used was an underburnt mixture of lime and silica of high purity containing only the two silicates and calcium oxide. The average of eight determinations without an accelerator gave 1.72% free lime. The average time was about $4\frac{1}{2}$ hr. and the end points were very definite.

The chlorides of barium and strontium showed about the same accelerating effect as with Portland cement. Calcium chloride was just as effective as, or more effective than, the other salts; thus its behavior with the silicates differed from its behavior with Portland cement, but the flocculent precipitate produced made the determination of the end point more difficult. Strontium chloride gave the best end points. Addition of magnesium chloride masked the presence of free lime. The free lime values were slightly higher with barium and strontium chlorides than with no accelerator. The bromide and nitrate of strontium are also effective accelerators. Table III shows the effect of strontium chloride on the process.

The substitution of "reagent" glycerol, containing 4.4% water, for the distilled glycerol (less than 0.3% H_2O) shortened the time to about the same extent as using 0.5 to 1.0 gm. of the chlorides and gave a normal free lime value of 1.73%.

* *The accelerating action of calcium acetate was observed by Herbert Johnson in this laboratory. Can. J. Res. B, 21: 236. 1943.*

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TABLE III

EFFECT OF STRONTIUM CHLORIDE ON THE DETERMINATION OF FREE LIME IN A SAMPLE OF CALCIUM SILICATES

$SrCl_2$, gm.	Sample weight, gm.	Initial titer, ml.	Total titer, ml.	Total time, hr.: min.	% Free lime obtained
None	1.0094	0.1	2.96	6:00	1.73
0.50	1.0033	1.6	3.00	3:20	1.74
1.00	1.0026	2.0	3.03	4:00	1.76
1.50	0.9957	2.2	3.14	1:40	1.84
2.00	1.0030	2.3	3.11	2:20	1.81

The addition of water produced similar results with this sample as with the cement and the cement clinker, indicating that the increase in the free lime values above a limiting quantity of water is due to the hydrolysis of the silicates in the cement.

The use of excess of the ammonium acetate solution at the first titration had no apparent effect on the values obtained for free lime or any marked effect on the total time, nor was there any significant difference when the sample was ground to pass a 100 or a 200 mesh sieve. The determination of free lime in a mixture formed by the addition of calcium oxide to the above sample of silicates gave the expected calculated value.

In general, the determination of free lime in this type of solid material was found to be considerably easier than in the cement and cement clinker. End points were more definite than with commercial cements and the precision was much greater.

Determination of Free Lime in Solid Systems containing Calcium Aluminates

In a properly fired Portland cement the alumina is probably present partly as tricalcium aluminate and partly as a calcium aluminoferrite. At temperatures above the incongruent melting point of tricalcium aluminate the 5:3 aluminate is probably produced. The 5:3 aluminate may also be present in "underburnt" systems. The effects of the presence of these aluminates on the determination of free lime was studied using mixtures in the form of clinkers or the pure compounds prepared in the laboratory.

All ignitions were made in platinum, below 1000°C. in an electric muffle furnace and above this temperature in an induction furnace. Unless otherwise stated, each firing at the higher temperature was for a period of 45 min. to one hour. After each ignition, the product was ground to pass a 200-mesh sieve and remixed thoroughly.

Pure alumina and calcium carbonate were proportioned by weight to give, if properly combined, tricalcium aluminate and about 2% free lime. After a preliminary ignition at 950°C., Sample A was heated for one-half hour to

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partial fusion at above 1535°C. for the purpose of forming some 5:3 calcium aluminate. Sample B was fired twice at about 1480°C. Sample C was part of Sample B given a third ignition at about the same temperature. After the last ignition the sample was softly sintered and probably contained only tricalcium aluminate plus free lime.

Table IV gives the data for the determination of free lime in these samples. For A, the total time was exceedingly long even with accelerators present; end points were hard to judge, and the final end points were rather uncertain. In Sample B, which had been given two ignitions below the transition point, the alumina being probably mostly in the form of tricalcium aluminate, the time was still very long but was greatly reduced with barium chloride and calcium chloride present, and the end points were much improved. Sample C, with three ignitions, also required an excessively long time when no accelerator was present, but with large amounts of strontium chloride the time was radically reduced and the end points were quite good.

TABLE IV

EFFECT OF IGNITION TREATMENT ON DETERMINATION OF FREE LIME IN LIME–ALUMINA MIXTURES

Sample and ignition temperature	Accelerator, gm.	Sample weight, gm.	Initial titer, ml.	Total titer, ml.	Total time hr.: min.	% Free lime obtained
A	None	0.5220(*a*)	0.5	8.89	61:00	10.1
> 1535°C.	None	0.5362	0.5	9.63	61:00	10.6
	$BaCl_2$–0.526	0.5261	3.9	9.61	20:00	10.7
	$SrCl_2$–0.511	0.5113	4.9	9.52	20:00	10.9
B	None	0.5026	0.1	2.15	24:30	2.53
1480°C.	None	0.5264	0.0	2.01	24:30	2.26
(twice)	$BaCl_2$–0.501	0.5007	1.3	2.15	3:00	2.50
	$CaCl_2$–0.506	0.5064	2.0	2.07	1:40	2.40
C	None	0.9945	0.0	2.52	22:20	1.50
1480°C.	$SrCl_2$–0.100	1.0019	0.6	2.51	22:20	1.46
(thrice)	" –0.500	0.9974	1.3	2.86	5:00	1.67
	" –1.000	1.0014	1.7	2.83	2:30	1.65
	" –1.000	1.0055(*b*)	2.2	2.90	1:40	1.68

(*a*) *100-mesh.* (*b*) *Re-ignited at 950°C.*

Several possible explanations may be proposed for the extremely long time required for the determinations reported in Table IV and for the differences in the behavior at the end points:

(*a*) The physical condition of the material brought about by partial fusion.

(*b*) The formation of "hard-burnt" unreactive calcium oxide at the high temperature.

(*c*) That the presence of the 5:3 aluminate by some unknown mechanism lengthens the time required and obscures the end point.

As to (*a*), it was found that the fineness of the sample had only a minor effect on the time required and on the value for free lime obtained. Thus the sample

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in the first determination of Table IV was ground to pass a 100-mesh sieve, the second and all other samples were ground to pass a 200-mesh sieve.

As to (*b*), inactivation of calcium oxide at high temperatures has been reported by several experimenters (2). To test this further a sample of lime was ignited at about 1535°C. and its behavior compared with a sample ignited at 950°C. Table V gives the results of the comparison.

TABLE V

THE EFFECT OF IGNITION AT HIGH TEMPERATURES ON THE TITRATABILITY OF LIME IN ALCOHOL–GLYCEROL SOLUTION
(0.1 gm. samples of lime)

Ignition treatment	Accelerator, gm.	Total time, hr.: min.	Normality obtained for acetate solution
Ignition at 950°C. for 17 hr.	$SrCl_2$–1.0	1:00	0.205
	None	4:20	0.205
Ignition at 1535°C. for 20 min.	$SrCl_2$–1.0	1:00	0.204
	None	40% lime titrated after 5½ hr. of boiling.	

It is evident that at high temperatures calcium oxide becomes very unreactive to the alcohol–glycerol mixture but is readily reactivated by the presence of strontium chloride, thus behaving like samples B and C of Table IV. Other experiments indicated that this inactivation of calcium oxide is noticeable at a temperature of 1150°C.

The behavior of Sample A of Table IV only partly fits this pattern. It seemed possible that the presence of the 5:3 calcium aluminate has an adverse effect both on the time required and the definiteness of the end point. This question was further investigated.

In preliminary experiments, a sample of tricalcium aluminate which was deficient in lime and therefore contained some 5:3 aluminate was used. One-gram samples of this were mixed with 0.1 gm. of pure ignited calcium oxide and the usual determination of free lime made on the mixture. With no accelerator the determination was only 64% completed in 11 hr. as against a normal total time for completion for lime alone of about four hours under the same conditions. The end points were also more difficult to judge. With barium chloride or strontium chloride, the time was reduced but was longer than normal. After three ignitions with excess of lime at 1450°C. to transform all the 5:3 aluminate into tricalcium aluminate, the determination of free lime, using 1 gm. of strontium chloride, became normal both as to the time required and the definiteness of the end point.

Three series of experiments were carried out with mixtures of calcium oxide and 5:3 calcium aluminate, the latter ground to pass a 200-mesh sieve. In Series A (Table VI, Expts. 1, 2, 3, and 4) the amount of the 5:3 compound

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was varied, the amount of calcium oxide (ignited separately at 950°C.) being almost constant. During the first two 20-min. periods of refluxing, no accelerator was present. This showed that the initial titer obtained decreased with the increase in the 5:3 compound present. Then 1 gm. of barium chloride was added and the determination carried to an end point. There was a marked increase in total time owing to the presence of the aluminate and also all the lime added was not accounted for, the deficiency increasing with the amount of aluminate. End points were difficult to judge in all the runs in which this aluminate was present. At the end point accepted, the solid had a red coloration thus suggesting incompleteness while the supernatant liquid remained colorless for one hour of refluxing.

The data of Series A (Table VI) suggest that under the conditions of the determination, the 5:3 aluminate may combine with or in some way neutralize calcium oxide. Series B (Expts. 5, 6, 7, 8, and 9) was designed to determine whether such disappearance of free lime is increased by increasing the length of the refluxing period before titration, or by using no accelerator, or by delaying its addition. It is evident that using no accelerator (No. 7 vs. No. 6) accentuates the disappearance of free lime; that using long refluxing periods at the start and delaying the addition of the catalyst (Nos. 8 and 9 vs. nos. 5 and 6) both increases the total time and the disappearance of free lime. The statements re the end points in Series A apply here also. Another sample of 5:3 calcium aluminate used in Series C (Expts. 10, 11, 12, 13, and 14) was freshly ignited, a very long initial refluxing period was used, and the amount of lime added increased by steps. This also shows the progressive disappearance of free lime, increasing with the amount of free lime present. In this series, the solid remaining at the end point was not colored, and the end points were easier to determine than in Series A and B.

The presence of the 5:3 calcium aluminate appears to reduce the initial titer, lengthen the total time required, and give lower values for free lime. The length of time which the solution is in contact with the lime and aluminate accentuates, and the presence of accelerators reduces, these effects.

The above observation on the effect of the 5:3 calcium aluminate on the determination of free lime is of interest in connection with the work of Thorvaldson and Schneider (10) on the thermal decomposition of the hexahydrate of tricalcium aluminate and the composition of the aluminate formed. One might suspect that here is the explanation of the low values for free lime obtained by these workers, leading them to favor the formula, $12CaO.7Al_2O_3$, in place of $5CaO.3Al_2O_3$, for the aluminate produced by the thermal decomposition. However, under the conditions they used the determination of free lime in the thermal decomposition product of the hexahydrate was very rapid (most of the free lime being titrated with three five-minute periods of boiling), and the determination had none of the adverse characteristics observed with the mechanical mixture of calcium oxide and 5:3 calcium aluminate prepared by ordinary thermal methods. Thus, the aluminate formed on thermal decom-

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position of the hexahydrate of tricalcium aluminate (10) at temperatures between 550° and 950°C. does not have the same properties as the product formed by the thermal interaction of lime and alumina in the molar ratio 5: 3 at higher temperatures (Table VI).

TABLE VI

THE EFFECT OF 5: 3 CALCIUM ALUMINATE (C_5A_3) ON THE DETERMINATION OF FREE LIME

Expt. No.	Initial reflux period before 1st titer, hr.: min.	Added C_5A_3, gm.	CaO, gm.	Initial titer, ml.	Total titer, ml.	Total time, hr.: min.	% of added lime determined
Series A. 1.0 gm. barium chloride added after two 20-min. refluxing periods							
1	0: 20	None	0.1036	2.3	17.56	3: 20	Taken as 100
2	0: 20	0.5083	0.1019	1.9	16.87	8: 00	98
3	0: 20	1.0027	0.1011	1.0	15.37	6: 00	90
4	0: 20	1.5121	0.1029	0.9	12.51	8: 00	72
Series B. 5 and 6, 1.0 gm. $BaCl_2$ added at start; 7, no accelerator; 8, 1.0 gm. $BaCl_2$ added after 1 hr. 20 min.; 9, 1.0 gm. $BaCl_2$ added after 2 hr. 20 min.							
5	0: 20	None	0.1029	14.2	17.39	1: 40	Taken as 100
6	0: 20	0.9360	0.1048	12.4	17.19	4: 20	97
7	0: 20	0.9996	0.1007	1.3	14.93	9: 40	89
8	1: 20	0.9344	0.1047	3.1	15.75	9: 00	89
9	2: 20	0.8999	0.1005	3.1	12.27	11: 30	72
Series C. 1.0 gm. strontium chloride added at start							
10	0: 20	None	0.1011	16.3	16.98	0: 40	Taken as 100
11	22: 30	0.5004	0.1948	9.2	31.32	6: 30*	95.6
12	22: 30	0.5004	0.2050	8.7	32.11	9: 30*	93.1
13	22: 30	0.5009	0.2168	8.9	33.74	10: 30*	92.5
14	22: 30	0.5002	0.2259	8.7	34.66	10: 00*	91.2

* *Not counting initial refluxing period.*

It was found that the presence of monocalcium aluminate interferes with the determination of free lime, increasing the time required, giving low values and poor end points. The use of barium chloride, however, largely counteracts these effects.

The presence of free alumina also interferes in a similar manner. Hydrated alumina is most effective in lowering the value for free lime. Full values for the lime added are obtained in the presence of alumina which has been ignited at 1300°C. but the time required is still longer than with the lime alone.

The determination of free lime in the presence of tetracalcium aluminoferrite (1 part of lime to 10 parts of compound) presented some difficulty in the observation of the end point, but all the calcium oxide was titratable.

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The Determination of Free Lime in Laboratory Clinkers Containing Lime, Alumina, and Silica

In the preparation of samples, all clinkers were ground after each firing to pass a 200-mesh sieve.

The first sample studied was a clinker made in the laboratory by repeated firings until tests for free lime were negative. By calculation, after allowing for the effect of small amounts of ferric oxide and magnesium oxide, it contained 51% dicalcium silicate, 24% tricalcium silicate and 24% tricalcium aluminate. It was then fired in the induction furnace at slightly above 1535°C. for 16 min. after which 20 hr. of refluxing with the alcohol–glycerol mixture with accelerator gave a value of 0.23% for free lime. After a second such firing for eight minutes, with rapid cooling in air, the same value was obtained in 15 hr. of refluxing. Two other samples fired at about 1600°C. for 15 and 35 min. respectively, the platinum crucible being quenched in water, gave a negative test for free lime in the final product after one hour of refluxing. It appears therefore that, at these temperatures, the lime liberated by the decomposition of the tricalcium aluminate combines very rapidly with the dicalcium silicate or that the method for determining free lime fails with this material. There is also the possibility that at the time of quenching all the tricalcium aluminate had been decomposed to the 5:3 compound and that the dicalcium silicate, of which there is a large excess, had combined with all the lime liberated in the process.

Addition of 1 gm. of the original clinker to 0.05 and 0.10 gm. samples of pure calcium oxide increased materially the time of refluxing required, and the addition of the same amount of the product fired above 1600°C. increased the time required still further.

A second clinker of similar composition was then prepared from pure calcium carbonate, alumina, and silica in such a way as to leave a small amount of free lime in the product. The calculated composition for complete combination was: dicalcium silicate 52%, tricalcium silicate 24%, and tricalcium aluminate 24%. Two consecutive firings, one of 45 min. and the other of 25 min. were made in the clinkering range below 1535°C. A free lime determination on the product with 0.5 or 1 gm. of strontium chloride required over 20 hr. and gave a value of 1.2% calcium oxide. Without an accelerator the time required was more than 30 hr. and the value for free lime 0.9%. The end points were poor and the behavior of the product reminded one of the aluminates of Table IV.

Both the ternary clinkers so far used were by calculation relatively high in dicalcium silicate and low in tricalcium silicate. A third, slightly underburnt clinker high in tricalcium silicate was therefore prepared from pure materials. For complete combination the calculated composition was dicalcium silicate 7.5%, tricalcium silicate 68.5%, and tricalcium aluminate 24%. This was fired twice slightly below 1535°C., first for 45 min. with the production of a hard clinker and then for 35 min. giving a softer sintered mass. Using accelerators the time required for a free lime determination was $3\frac{1}{2}$ to 4 hours and the value 2.5% calcium oxide, and without an accelerator a value of 1.9% was obtained

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after 10 hr. of refluxing. The behavior of this sample did not differ greatly from that of some commercial Portland cements. The end points without an accelerator were poor but improved with the use of the chlorides of either barium or strontium.

On adding 5% magnesium oxide to this clinker and heating for 25 min. between 1450° and 1500°C. with quenching of the crucible in water, the value obtained for free lime (with barium chloride as accelerator) was increased to 5.4%. The time of refluxing required was also increased materially.

The experiments with lime–alumina–silica laboratory clinkers indicate that the alcohol–glycerol method for determining free lime is too lengthy and gives results of doubtful accuracy for underburnt clinkers low in lime, without the use of accelerators, but may give somewhat more reliable results with underburnt clinkers high in lime. It seems probable that the clinkers giving unsatisfactory results contain active aluminum compounds of lower lime content than tricalcium aluminate, possibly the 5:3 calcium aluminate. High temperatures cause the free lime to become inert and lengthen the process of extraction with the alcohol–glycerol mixture. These adverse effects may be accentuated simultaneously by conditions such as the rapid passage of a partly reacted mix from the zone of medium to that of high temperature, as was the case with the samples of Table IV and the ternary clinkers studied above. Through the reactivation of inert calcium oxide and the speeding up of the extraction process, the use of suitable accelerators probably gives more accurate values for free lime in such "difficult" clinkers. One may conclude that, whenever the time of the determination of free lime is abnormally lengthy, the results should therefore be suspect.

The experiments described were all made with a highly anhydrous alcohol–glycerol mixture, usually containing not more than 0.1% water. It is possible that the time required for a determination of free lime could be materially reduced by using a less anhydrous mixture without introducing serious error.

The Mechanism of the 5:3 Calcium Aluminate Effect

The basic chemistry of the alcohol–glycerol determination of free lime, which needs further study, will not be discussed here. Analysis of the solid formed during the digestion of calcium oxide indicated that it is a mixture of mono- and diglycerates of calcium. The presence of the 5:3 calcium aluminate produces three effects. First, the reaction which changes the calcium oxide to a titratable form appears to be retarded as shown by the progressively decreasing first titers with increasing amounts of the aluminate, and by the increase in the total time required. Successive 20-min. titers then increase gradually to a maximum, probably owing to the accelerating action of the calcium acetate and of the water formed during the titration, and then taper off. Second, the amounts of calcium oxide, as measured by titration, tend to be reduced. Third, end points become very difficult to judge. The first two effects are partly counteracted by the use of suitable accelerators.

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The first effect appears to be due to dehydration of the alcohol–glycerol mixture by the aluminate. There are reasons to expect this, as reaction with water produces two substances of extremely low vapor tension, tricalcium aluminate hexahydrate and a monohydrate of alumina. The calculated maximum removal of water by this reaction is equal to about one-third of the weight of the 5:3 aluminate. The accelerating effect of water in the determination of free lime has been mentioned. If the amount of water in the mixture is decreased, the rate of production of the titratable combination of calcium oxide is progressively reduced as a completely anhydrous system is approached. It was found that the reduction in the initial titer with the 5:3 aluminate is most marked with alcohol–glycerol mixtures containing very small but appreciable amounts of water. In parallel determinations of lime with and without the addition of the 5:3 aluminate, starting with a nearly anhydrous alcohol–glycerol mixture, progressive additions of very small quantities of water rapidly increased the first titer for the pure calcium oxide, but had very little effect on the first titer for the mixture of calcium oxide and 5:3 calcium aluminate until a critical ratio for water to aluminate had been reached. This critical ratio varied with different samples of the 5:3 aluminate of practically the same chemical purity, apparently owing to differences in reactivity, produced by conditions during their preparation. Further parallel experiments refluxing pure calcium oxide (1) with an alcohol–glycerol solution which had been given a preliminary refluxing with 5:3 calcium aluminate and decanted, and (2) with the original solution, gave in the first case the 5:3 aluminate effect of the smaller initial titer and longer total time.

The second effect, the low value for free lime, is probably due to a chemical reaction of the calcium oxide with the 5:3 aluminate. When an effective accelerator is used with short intervals between titrations the error thus introduced may not be significant, but when the early titers are small and the determination is prolonged due to the absence of accelerators (including water) the error may become appreciable.

The third effect, the indefinite end point, may be due to a slow reversal of the process by which calcium oxide is removed by the 5:3 aluminate. The difficulty is not due to adsorption of the indicator as increasing its concentration does not give any improvement.

If the first effect of the 5:3 aluminate, the reduction in the initial titer and the lengthening of the time required for the determination, is due to dehydration, it is evident that any powerful dehydrating agent, which is otherwise inert as far as the process is concerned, should slow up the process without introducing error in the final result. This appears to be the case. Addition of tricalcium aluminate to calcium oxide was found to increase the time of refluxing required but the end points were good. Addition of barium chloride brought the time required back to normal. The addition of 1 gm. of a mixture of silicates containing 92% tricalcium silicate to 0.1 gm. of calcium oxide more than doubled the time necessary to titrate the free lime, but the end points

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were not affected and the calculated values for free lime were obtained. The behavior of hydrated alumina on ignition, reported above, indicates that its capacity to combine rapidly with lime is destroyed by heating before it loses its capacity to remove water from the reaction mixture. When cement containing no free lime is introduced into the reaction flask containing the alcohol–glycerol mixture with pure calcium oxide, the time for the titration is greatly increased but all the free calcium oxide is recovered. One would expect the effect to vary considerably with different cements, depending mainly on their content of tricalcium aluminate and tricalcium silicate, the two chief dehydrating agents present, but also probably on the conditions of manufacture of the cement.

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EXCHANGE REACTIONS OF IODIDE ION WITH AROMATIC IODIDES[1]

By A. M. Kristjanson and C. A. Winkler

Abstract

The exchange reactions of iodide ion with *o*- and *p*-nitroiodobenzene in the temperature range about 170°–238°C. were apparently second order with activation energies of approximately 29 and 33.5 kcal. per mole respectively. In the same temperature range the exchange of iodide ion with iodobenzene and *m*-nitroiodobenzene appeared to be first order reactions, with activation energies of approximately 25 kcal. per mole.

Introduction

The use of radioactive isotopes to investigate nucleophilic substitution at an aromatic carbon atom has received only limited attention. It has been reported that bromide ion does not exchange with bromobenzene (1) and that iodide ion does not exchange with iodobenzene, *p*-nitroiodobenzene, or *p*-nitroaniline at 100°C. in ethanol, nor with *m*- and *p*-iodobenzoic acids at 100°C. in acetone (5). With diphenyl iodonium iodide at room temperature in aqueous ethanol, only the negatively ionizing iodine exchanges with iodide ion (4). Exchange of bromine has been observed between bromobenzene or 1-bromonaphthalene, and aluminum bromide, but no reaction of these aromatic bromides occurred with potassium, cupric, or antimony bromides (7). Both iodine and iodide ion have been found to exchange with *l*-diiodotyrosine in aqueous solution and with 3,5-diiodo-*p*-cresol, 2,6-diiodophenol, 4,6-diiodophenol, and 2,4,6-triiodophenol in aqueous methanol (6).

The only kinetic study of exchange between halide ion and an aromatic halide is that of Sugden and Lu (9), who determined the second order velocity constants and activation energy for the exchange between lithium bromide and 2,4-dinitrobromobenzene in ethylene glycol diacetate solution in the temperature range of 70.3° to 130.1°C.

In the present investigation the exchange reactions of sodium iodide with iodobenzene and with *o*-, *m*-, and *p*-nitroiodobenzenes have been studied kinetically by working at temperatures higher than those used in previous unsuccessful attempts to effect such exchanges.

Experimental and Results

Radioactive I^{131} was obtained as carrier-free sodium iodide from the National Research Council Atomic Energy Project, Chalk River. Merck reagent grade sodium iodide, dried at 120°C. for several days, was used as diluent for the radioactive material.

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Iodobenzene from Brickman and Co., Montreal, was fractionated to obtain an experimental sample boiling at 189.1–189.2°C. The nitroiodobenzenes were also from Brickman and Co., and had the following characteristics after recrystallization:

o–Nitroiodobenzene — m.p. 51°C., b.p. 284°C.
m–Nitroiodobenzene — m.p. 37°C., b.p. 280°C.
p–Nitroiodobenzene — m.p. 171°C., b.p. 284°C.

The rate of reaction was followed by determining the change in specific activity of a silver iodide precipitate obtained from appropriately treated solutions of the inorganic or organic iodide. The silver iodide, after being washed with hot nitric acid, was slurried in anhydrous methanol and poured into a glass collar ground to a leak-proof fit on the surface of a glass plate. After evaporation of the methanol and removal of the collar, a uniform deposit of silver iodide remained, the activity of which was determined with standard counting equipment. The weight of silver iodide taken was 20 to 60 mgm., over which range experiment showed errors from weighing and self-absorption to be less than 1%.

Reaction mixtures were contained in sealed Pyrex glass tubes. Vapor thermostats were used, the temperatures of which were determined by the boiling points of pure liquids. From time to time a tube was removed, the contents extracted with benzene, and the iodide in the aqueous layer precipitated with silver nitrate. If it was desired to determine the activity of the aromatic iodide, the benzene layer was washed with water until free of halogen and the aromatic iodide then converted to inorganic iodide by catalytic hydrogenation in alkaline solution as described by Schwenck, Papa, and Ginsberg (8). After hydrogenation, the catalyst was removed by centrifuging, and filtering, and the clear filtrate treated with nitric acid and silver nitrate.

Preliminary experiments with ethylene glycol diacetate as solvent showed exchange to occur between sodium iodide and iodobenzene at temperatures of 150–250°C., but the solvent was simultaneously attacked by sodium iodide. Ethanol and acetonitrile were found to be unaffected by sodium iodide in the same temperature range during periods of more than 200 hr. Acetonitrile was chosen as the solvent for further work owing to its lower vapor pressure at the relatively high temperatures used.

The value of the rate constant recorded for a given temperature is, with a few exceptions, the average of individual values for different reaction times with the particular concentration conditions indicated. Two or more reaction times were generally used. The mean deviation of the individual values of k from the average was usually less than $\pm$ 10%, but seldom less than $\pm$ 5%.

Exchange of Sodium Iodide with o-Nitroiodobenzene

In Table I are given the results for the exchange of sodium iodide with *o*-nitroiodobenzene, the aromatic iodide which exchanged the most rapidly of those studied, and for which the experimental results are the most extensive.

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TABLE I

THE EXCHANGE OF SODIUM IODIDE WITH *o*-NITROIODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^2$ liter-mole^{-1} hr.$^{-1}$
	NaI	o-$NO_2.C_6H_4I$		
238	0.037	0.147	87.5	596
	0.147	0.037	65.5	319
207	0.076	0.038	62	70.5*
	0.038	0.076	72	89
	0.038	0.153	50	93
	0.153	0.038	42	65
	0.076	0.153	34	88 (single value)
185	0.039	0.158	85	30
	0.158	0.039	59	13.6
	0.079	0.158	62	25.5
157	0.041	0.164	63	7.1
	0.164	0.041	24	2.3
	0.082	0.164	36	4.4
	0.082	0.328	98	12.4
	0.328	0.082	55	1.8*
122	0.086	0.171	42	1.0
100	0.088	0.176	30	0.26
	0.044	0.176	43	0.46
	0.176	0.044	6	0.05

* *Determined from increase in activity of organic iodide.*

It will be noted that the calculated constant increased as the ratio of aromatic to inorganic iodide was increased, this increase being more pronounced the lower the temperature. Empirically, log k at a given temperature varies in approximately linear manner with the square root of the ratio of aromatic iodide concentration to inorganic iodide concentration.

A plot of log k against $1/T$, for a given ratio of aromatic iodide to inorganic iodide concentrations, gives a straight line in the temperature range about 170°C. to 238°C., corresponding to an activation energy of approximately 29 kcal. per mole. At lower temperatures there is distinct curvature of the Arrhenius line in the sense of a smaller temperature dependence of the reaction rate, but the data are inadequate for a proper evaluation of the activation energy in the lower temperature range, where the rate of exchange became inconveniently slow.

Assuming reaction to be between the aromatic iodide and iodide ion derived from sodium iodide, error in calculating the rate constants is introduced into the concentration term for the inorganic iodide by ignoring the change in degree of dissociation of sodium iodide in acetonitrile with change of concentration. At the boiling point of acetonitrile (*ca.* 80°C.), sodium iodide is approximately 85% dissociated in 0.05 M solution, and about 50% dissociated

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in 0.20 M solution (2). If it is assumed that the change in degree of dissociation with concentration is the same at the temperatures used in the present study as it is at 80°C., correction can be applied to the calculation of the velocity constants. When this is done, the discrepancy between the calculated velocity constants with different ratios of aromatic to inorganic iodides is largely eliminated for temperatures above 185°C. At lower temperatures, however, the calculated values of k still increase with increase in the ratio *o*-nitroiodobenzene: sodium iodide. Since the basis of the correction is somewhat uncertain, corrected k values are not tabulated. However, the fact that such a correction does operate in the sense of improving the second order rate constants makes it seem probable that the reaction is essentially first order with respect to both aromatic iodide and iodide ion in the region of higher temperatures. At sufficiently low temperatures the principal mechanism may be altered, possibly to one with a first order rate-controlling step.

It would appear from the results at 207°C. and 157°C. that the calculated k values increase with increase of aromatic iodide concentration at given sodium iodide concentration. This effect, which seems to be more marked at the lower temperature, is further indication, perhaps, of the occurrence of some reaction other than a second order exchange.

During the exchange of sodium iodide with *o*-nitroiodobenzene, traces of free iodine (5×10^{-7} mole) were formed after about 30% exchange. There was no indication that its presence had any influence on the velocity constant for the exchange reaction.

Exchange of Sodium Iodide with p-Nitroiodobenzene

An exception to the general method of analysis was made for *p*-nitroiodobenzene. The contents of a reaction tube was transferred to a 50 cc. centrifuge tube containing 25 cc. of cold water, and cooled to promote nearly complete crystallization of *p*-nitroiodobenzene. The mixture was centrifuged and the clear liquid decanted and analyzed for sodium iodide activity if desired. The solid *p*-nitroiodobenzene was washed with water until the wash water gave no test for halogen, and was then reduced to inorganic iodide by catalytic hydrogenation. Silver iodide was then precipitated as before for determination of activity. Experiment showed that analysis for either reactant gave concordant results.

The range of *p*-nitroiodobenzene concentrations used in the experiments was limited by its solubility in acetonitrile. The data obtained for the exchange rate at various temperatures and concentrations of inorganic and aromatic iodide are summarized in Table II. There is little doubt that the reaction at higher temperatures is of the same order in respect of both reactants. The experiment at 207°C. with 0.037 M sodium iodide and 0.190 M aromatic iodide clearly indicates that the reaction is second order over-all, hence first order with each reactant.

TABLE II

THE EXCHANGE OF SODIUM IODIDE WITH *p*-NITROIODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^2$ liter-mole^{-1} hr.$^{-1}$
	NaI	p-$NO_2.C_6H_4I$		
238	0.037	0.074	66	178
	0.074	0.037	55	128
207	0.076	0.037*	53	17.5
	0.037	0.076*	61	19.3
	0.076	0.037	64	17.4
	0.037	0.076	64	21.7
	0.076	0.037	53	17.1
	0.037	0.190	48	18.0
185	0.039	0.079	50	4.6
	0.079	0.039	39	3.5
157	0.041	0.082	20	0.76
	0.082	0.041	13	0.52
100	0.044	0.088	12	0.16
	0.088	0.044	0.25	0.003

* *p-Nitroiodobenzene sublimed.*

At the higher temperatures, the increase in velocity constant with increased ratio of aromatic iodide to sodium iodide is largely eliminated if correction is applied for the change in degree of dissociation of sodium iodide, on the basis indicated previously for *o*-nitroiodobenzene.

The Arrhenius line for given concentrations of inorganic and aromatic iodides is straight over a temperature range of about 170° to 238°C., corresponding to an activation energy of 33.5 kcal. per mole. At lower temperatures, the line is markedly curved in the sense of smaller temperature dependence but the results at 100°C. are not sufficiently accurate to permit evaluation of the activation energy in this temperature region.

Exchange of Sodium Iodide with m-Nitroiodobenzene

The results obtained for the exchange of sodium iodide with *m*-nitroiodobenzene in acetonitrile are summarized in Table III. The values at 238°C. are subject to uncertainty from secondary reactions which produced appreciable amounts of free iodine as well as trace amounts of black precipitate.

It is evident that the first order constants (last column), calculated on the assumption that the rate depended only on the concentration of aromatic iodide, show much better agreement than the second order constants for varying concentrations of reagents. The activation energy calculated from the first order constants was found to be 25 kcal. per mole.

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TABLE III

THE EXCHANGE OF SODIUM IODIDE WITH *m*-NITROIODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^4$ liter-mole^{-1} hr.$^{-1}$	$k \times 10^4$ hr.$^{-1}$
	NaI	m-$NO_2C_6H_4I$			
238	0.037	0.368	89	826	30.4
	0.074	0.368	77	543	39
	0.147	0.147	37	220	32*
207	0.038	0.382	67	107	4.1
	0.076	0.382	55	59.7	4.6
	0.153	0.153	18	29	4.5*
185	0.039	0.394	60	33	1.32
	0.079	0.394	33	14.2	1.12
	0.158	0.158	19	9.4	1.4*
157**	0.041	0.410	14	5.4	0.2
	0.082	0.410	12	4.1	0.35
	0.164	0.164	3.5	1.8	0.3

* *Analyses for gain in activity of aromatic iodide.*
** *Only one value of k at each concentration was obtained.*

Exchange of Sodium Iodide with Iodobenzene

Results for the exchange of sodium iodide with iodobenzene are shown in Table IV. At 238°C., free iodine was observed in all samples, as well as small amounts of a black precipitate. The results at 157°C. are only approximate, owing to the small percentage exchange. First order velocity constants cal-

TABLE IV

THE EXCHANGE OF SODIUM IODIDE WITH IODOBENZENE

Temp. °C.	Reactant conc., molarity		Maximum exchange, %	$k \times 10^4$ liter-mole^{-1} hr.$^{-1}$	$k \times 10^4$ hr.$^{-1}$
	NaI	C_6H_5I			
238	0.037	0.662	88	240	8.9
	0.074	0.662	74	148	10.9
	0.147	0.294	18	33	5.0
207	0.038	0.688	48	20.5	0.79
	0.076	0.688	42	14.3	1.1
	0.153	0.306	14	5.6	0.86
185	0.039	0.719	22	5.7	0.22
	0.079	0.719	11	2.5	0.20
	0.158	0.315	6	1.8	0.25
157	0.041	0.736	2.7	0.44	0.018
	0.082	0.736	3.4	0.5	0.04
	0.164	0.328	2.9	0.6	0.10

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culated on the assumption that the rate was independent of sodium iodide concentration (last column) give a much better representation of the behavior with varying concentrations than do the second order constants. The variation with temperature of the first order constants corresponds to an activation energy of 24 kcal. per mole.

Comparison of the rates in normal reaction mixtures with those for similar mixtures to which small amounts of iodine (5×10^{-5} gm.) were deliberately added showed that the presence of iodine accelerated the reaction 10–15%. The presence of water (0.5 gm.) retarded the reaction, as did also the presence of sodium sulphite, to the extent of about 15%.

These results indicate that the formation of free iodine during reaction may lead to values of the rate constant that are too large. However, no significant increase in k with time was observed in any of the experiments where free iodine was formed, perhaps because the amount formed was too small to cause a detectable effect.

Discussion

The exchange reactions involving *o*- and *p*-nitroiodobenzenes, in the temperature range of approximately 170°–238°C., may be satisfactorily interpreted as bimolecular reactions between the aromatic iodide and iodide ion. In the same temperature range, however, it appears that the comparable reactions of *m*-nitroiodobenzene and iodobenzene must be regarded as involving a first order rate-controlling step, independent of the sodium iodide concentration. The same may well be true for the *o*- and *p*-nitroiodobenzene reactions at lower temperatures.

It does not seem possible to offer a satisfactory explanation of the first order kinetics in the two systems where such behavior apparently prevails. A rate-controlling ionization of the aromatic iodide is improbable from theoretical considerations (3), while there is no direct evidence for a homolytic fission to produce free radicals, a process that would not be favored in the highly polar solvent used (10, p. 15). Further study of analogous systems might enable an opinion to be expressed on this matter.

The difference in behavior between *o*- and *p*-nitroiodobenzene on one hand and *m*-nitroiodobenzene and iodobenzene on the other is presumably the result of differences in electron density at the site of reaction. A substituent group affects this electron density by inductive and resonance effects. A nitro group in the ring confers electropositivity to the carbon atom bonded to iodine in the order ortho > para > meta. The approach of a negative iodide ion should therefore be facilitated in the order ortho > para > meta, and the activation energy of the corresponding second order reactions should increase in the same order. In the present study, the two reactions that are second order behave as expected. With *m*-nitroiodobenzene and the unsubstituted iodobenzene, second order behavior apparently is not observable, even at 238°C.

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THE SYNTHESIS OF SOME STEREOISOMERIC DERIVATIVES OF DECAHYDRONAPHTHALENE[1]

By A. Zlatkis[2] and E. A. Smith

Abstract

Both racemic forms of *trans* 2-chlorodecalin have been prepared and separated in pure form. The reaction between these chlorodecalins and ethylmagnesium bromide has been studied and two racemates of *trans* 2-ethyl decalin have been isolated. Some progress has been made in the preparation of the 9-chlorodecalins. A new method for converting *cis* decalin to *trans* decalin rapidly in high yield using tertiary butyl chloride and anhydrous aluminum chloride is indicated.

Introduction

The preparation of the monoalkyl derivatives of decahydronaphthalene (decalin) has not been extensively investigated. One approach to the synthesis of this group of hydrocarbons has been the hydrogenation of the corresponding naphthalene derivative. Three isomers of 1-methyldecalin have been prepared in this manner (9).

The present work describes a new route by way of the reaction of the monochlorodecalins with ethylmagnesium bromide. The two racemic forms of *trans* 2-ethyldecalin have been prepared from the corresponding chlorodecalins.

Experimental*

Preparation of trans Decalin

Commercial decalin (Eastman Kodak Co.) (500 ml.) was treated twice with 200 ml. of concentrated sulphuric acid with vigorous agitation. The purified product was then dried for 24 hr. over sodium hydroxide pellets. Refractometric measurements indicated that the decalin contained 70% of the *cis* isomer and 30% of the *trans* isomer (8).

The conversion of *cis* to *trans* decalin in the presence of anhydrous aluminum chloride has been reported by Zelinsky (10), who obtained low yields. It was found since by the author that by using a 10% catalytic mixture of 3:1 anhydrous ferric chloride and anhydrous aluminum chloride, complete isomerization could be effected in three hours (11). Final purification of the *trans* decalin was accomplished by vacuum distillation at 10 mm. pressure through a Stedman column. The physical constants of the resultant product were: b.p.$_{10}$ 63.7°C., n_D^{20} 1.4696, d_4^{20} 0.8699. These agreed closely with those reported in the literature by Seyer and Walker (8): b.p.$_{10}$ 63.7°C., n_D^{20} 1.4697, d_4^{20} 0.8695.

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* *All boiling points are uncorrected.*

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The Chlorination of trans Decalin

The procedures of Gysin (5) and Borsche and Lange (2) have been modified as follows to give higher yields.

The reaction vessel consisted of a one-liter three-necked flask. Chlorine, previously moistened by passing through a wash bottle containing water, was passed in through a tube which was pulled out to a capillary. A dropping funnel at the center of the flask permitted decalin to be dropped in slowly. The capillary part of the chlorine tube was placed 1/2 in. from the end of the dropping funnel so that an atomizing effect could be produced when the decalin and chlorine met. A glass tube extending to the bottom of the vessel and leading to a receiver, at a level below the reaction flask, acted as a siphon and captured the product.

The decalin was sprayed in the form of a fine mist, with chlorine under pressure, against the walls of the reaction vessel which was immersed in an ice–salt bath. The system was kept slightly below atmospheric pressure to prevent the escape of chlorine, and to facilitate removal of the product from the reaction vessel to the receiver. Decalin was passed through the apparatus at the rate of 100 ml. per min. The chlorinated product was recycled until the desired degree of chlorination, as determined by checks on the specific gravity, was obtained. The reaction was stopped when the specific gravity of the chlorinated product reached unity. As a rule, seven to nine cycles were required. The crude chlorodecalin was washed first with 15% sodium carbonate solution, then with water. This was dried over calcium chloride and finally distilled. Five hundred milliliters of decalin could be fully treated in one hour using this atomizing procedure, with an over-all yield of 80% or better.

The following conditions appeared to be most favorable for the reaction:
(*a*) Intimate mixture of the chlorine with the decalin,
(*b*) The use of a small amount of iodine (1/2%) as a catalyst,
(*c*) Moistening the chlorine before passing it into the reaction chamber,
(*d*) The use of a strong light source to catalyze the reaction,
(*e*) Stopping the reaction before appreciable dichlorination set in.

Distillation of the halogen products was carried out in a large fiber glass packed fractionating column (3 ft. by 1 in.) under vacuum. The still was tested at total reflux at atmospheric pressure, and gave a result of 20 theoretical plates. Several distillations were necessary to obtain the isomers in their pure forms. Table I shows the properties found for these chlorodecalins. The *trans* isomer

TABLE I

Property	*trans* 2-chlorodecalin A	*trans* 2-chlorodecalin B
b.p.$_{15}$, °C.	115	117
n_D^{20}	1.4946	1.4970
d_4^{20}	1.0234	1.0377
% C : H : Cl calc.	69.56 : 9.86 : 20.58	69.56 : 9.86 : 20.58
% C : H : Cl found	69.62 : 9.88 : 20.50	69.48 : 9.92 : 20.60

of 2-chlorodecalin corresponding to the chlorodecalin derivable from 2-decalol (m.p. 75°C.) (4) has been designated as *trans* 2-chlorodecalin A, the one derivable from 2-decalol (m.p. 53°C.) *trans* 2-chlorodecalin B.

The values found compare favorably with those of the literature (4, 6). The chlorodecalins are colorless, but turn light yellow on standing.

Twenty milliliters of *trans* 2-chlorodecalin A was heated for six hours in 25 ml. of diethyl ether in the presence of 5 gm. of magnesium, resulting in the decalylmagnesium chloride. The latter, on treatment with oxygen at 0°C. and followed by decomposition with water, resulted in the decalol m.p. 74°C. The same procedure with *trans* 2-chlorodecalin B produced the decalol m.p. 53.5°C.

Synthesis of the 9-Chlorodecalins

Bartlett's work (1) on the catalyzed exchange of hydrogen and halogen offered a convenient method of preparing a pure 9-chlorodecalin. Pure isomers of decalin were used to facilitate identification of the products.

Three hundred milliliters (1.89 moles) of pure *trans* decalin was mixed with 115 ml. (1.05 moles) of tertiary butyl chloride in a two-liter separatory funnel. To this was added 15 gm. of anhydrous aluminum chloride, and the mixture was then shaken for a period of 30 sec. A reaction took place as soon as the aluminum chloride came in contact with the solution. The solution turned dark amber in color and the sides of the vessel became black. On quenching the reaction with three times the volume of water, two layers were formed. The top oily, amber layer was washed with water and dried with phosphoric anhydride. This solution now had a blue fluorescence and on distillation gave a small yield (14%) of a 9-chlorodecalin: b.p.$_7$ 83°C., n_D^{20} 1.4937, d_4^{20} 1.0007. Calc. % Cl = 20.58. Found % Cl = 20.67.

The use of *cis* decalin in a similar procedure produced a more violent reaction and the 9-chlorodecalin yield was greater (20%). During the course of the reaction (40 sec.), the *cis* decalin had almost completely isomerized to the *trans* form. This is rather remarkable in view of the authors' earlier experience in a study of this isomerization (11). The 9-chlorodecalin from this reaction had the following properties: b.p.$_7$ 85°C., n_D^{20} 1.4946, d_4^{20} 1.0645. Found % Cl = 20.60 This was probably a mixture of *cis* and *trans* 9-chlorodecalins due to the simultaneous occurrence of the isomerization.

Dehydrohalogenation with Pyridine

In order to identify the chlorinated product obtained with *trans* decalin, the corresponding 9, 10 octalin was prepared: 20 ml. of the chlorodecalin n_D^{20} 1.4937 was refluxed in an equal volume of dry pyridine for three hours, at the end of which time a white precipitate of pyridine hydrochloride had formed. The red solution was decanted off, washed with water, then dried with phosphoric anhydride. The product was now colorless and had the following properties: b.p.$_{13}$ 74°C., n_D^{20} 1.4984. The literature reports (7) for 9, 10 octalin: b.p.$_{12}$ 75°C., n_D^{20} 1.4996. Three milliliters of the octalin was converted to the

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blue nitrosochloride. A solution consisting of the octalin, 10 ml. glacial acetic acid, and 6 ml. of isoamyl nitrite was cooled to −30°C. and then treated with 6 ml. of concentrated hydrochloric acid in a dropwise manner. The resulting blue precipitate was washed with acetone and had a melting point of 90–91°C. The melting point for 9, 10 octalin nitrosochloride is reported as 92°C. in the literature (3).

Synthesis of the trans 2-Ethyldecalins

Eighty-five milliliters (0.5 mole) of the colorless *trans* 2-chlorodecalin A was added to 0.75 mole of ethylmagnesium bromide in 100 ml. of isoamyl ether over a period of one hour. The Grignard reagent had been prepared in the usual manner. After refluxing for one hour, the solution was allowed to stand overnight. The reaction mixture was then poured into a beaker containing 300 ml. of 1:1 sulphuric acid solution and about 200 gm. of chopped ice. The ether layer was distilled in a fiber glass-packed column. Although the yield was low (10%) 5 ml. of a pure product was obtained: b.p.$_8$ 70°C., n_D^{20} 1.4716, d_4^{20} 0.8583. Calc.: C, 86.64, H, 13.36%. Found: C, 86.26; H, 13.53%.

A similar procedure was followed for the preparation of the other isomer of *trans* 2-ethyldecalin. In the latter case, *trans* 2-chlorodecalin B was used. The resulting product (5 ml.) showed the following characteristics: b.p.$_8$ 72°C., n_D^{20} 1.4809, d_4^{20} 0.8803. Calc.: C, 86.64; H, 13.36%. Found: C, 86.26; H, 13.52%.

Conclusions

While the Grignard reaction with the chlorodecalins has not produced good yields in the preparation of the *trans* 2-ethyldecalins, the racemic forms of the chlorodecalins isolated are of interest for further investigation. Particular significance may be attached to the isomerization occurring when *cis* decalin was treated with tertiary butyl chloride in the presence of anhydrous aluminum chloride. The catalyzed exchange of hydrogen and halogen offers a simple, convenient method for the conversion of *cis* decalin to *trans* decalin. Complete isomerization is effected in only 40 sec.

Acknowledgment

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PARTICLE SHAPE IN THIXOTROPIC SUSPENSIONS[1]

By A. F. Sirianni, G. B. Moses, and I. E. Puddington

Abstract

Several equations have been proposed that predict the shape of suspended particles when the viscosity of a suspension of known concentration is measured. These are not applicable to suspensions showing thixotropy, owing to the dependence of the measured viscosity on the shear rate used. However, by using viscosity values that have been extrapolated to infinite rate of shear, good agreement has been found between the predicted and measured shapes for particles in thixotropic systems, and the method appears to be suitable for submicroscopic particles. A scheme is also proposed for comparing the degree of thixotropy of different systems.

When the viscosities of most homogeneous liquids are measured at different rates of shear, constant values are obtained unless the shearing is sufficiently great to cause turbulence. The same is true of suspensions provided the particles of the solid phase are sufficiently separated to avoid mutual interference. The increase in viscosity due to the suspended particles has been shown theoretically and practically to be proportional to the volume concentration. With spheres at low concentrations the proportionality factor is 2.5. As the particles depart from the spherical shape larger factors are required. The various equations that have been derived to account for the effect of the shape of the particles, their rigidity, and the effect of Brownian movement have been excellently reviewed (1, 10).

In actual suspensions, however, it is more common that the solid phase particles do interfere mutually, in many cases at low volume concentrations, and the experimental value that one obtains on measuring the viscosity is markedly dependent on the rate of shear used during the measurement. It frequently happens that the system as a whole may be a solid at zero rate of shear and yet have a viscosity only slightly higher than that of the suspension medium at high rates of shear. When this phenomenon occurs isothermally and reversibly the system is said to be thixotropic, and it is obvious that the usual equations relating viscosity and volume concentration no longer hold.

When some thixotropic suspensions are examined microscopically, the solid phase will be seen to exist in agglomerates that may be readily broken up by agitation but that re-form, enmeshing large volumes of liquid phase when left undisturbed. In some cases this re-formation is virtually instantaneous; in others considerable time may elapse before rest equilibrium is again established. It seems likely, however, that under any constant rate of shear, a steady state will be set up when the rate of formation of agglomerates due to mutual inter-

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ference of the particles will be equal to their rate of disintegration due to shear. Goodeve and Whitfield (7) have derived the following equation, based on this conception, relating viscosity and shear

$$\eta - \eta_0 = \frac{\theta}{s},$$

where η is the apparent viscosity of the system,

η_0 the residual viscosity $\left(\text{i.e., when } \frac{1}{s} = 0\right)$

s the rate of shear,

θ the coefficient of thixotropy.

From the derivation, the coefficient of thixotropy is the rate of growth of structure with time divided by the probability of the viscosity being reduced in unit time by unit shear and has the dimensions of force per unit area (dynes per cm.^{2}). It may be measured, as seen from the equation, by the limiting slope of the viscosity vs. reciprocal shear curve. The extrapolation of this curve to $\frac{1}{s} = 0$ gives the value of η_0, that is, the viscosity that the system would have at infinite shear when no thixotropy can be present. This reasoning ignores, of course, any effects peculiar to very high rates of shear that might appear if one were to attempt experimental measurements in this region.

Goodeve's theory also predicts the effect of solids concentration on θ from the following considerations: The rate of formation of thixotropic links due to any one particle will be proportional to the concentration of particles in the layer passing over it, and the number of particles forming links from the passing layer will also be proportional to the concentration. Thus the total rate of link formation will be proportional to the square of the concentration. This was actually the case for carbon black suspended in oil, as Goodeve's data show.

In an effort to get more information from the data than was contained in Goodeve's original communication, it was considered that some idea of the shape of the suspended particles should be available by examining the change in the values of η_0 with increasing solids phase concentration.

The original Einstein equation,

$$\frac{\eta}{\eta_0} - 1 = \frac{5}{2} C$$

or its extension for higher concentrations is valid only for spheres and would probably have limited application. Various other equations have been developed which contain "f" or axial ratio terms and are thus applicable to other than spherical particles. Most of these equations agree reasonably well amongst themselves provided "f" is not too high (i.e., about 50) but diverge at high axial ratios. In their derivation it is usually assumed that the particles are unoriented and are acted on by Brownian forces. While it is doubtful whether

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Brownian movement is a factor under conditions of high shear, it is also doubtful if orientation exists to any great extent in particles of the shape and size about to be described, since a fluid velocity gradient across the short axis of the particle is almost certain to result in a torque. Indeed, it has recently been shown by Mason (11) that rotation actually does take place with visible particles in a shear field. In view of the lack of adequate knowledge of conditions prevailing at infinite shear, the choice of equations did not seem to be critical and the rather simple Kuhn equation

$$\frac{\eta}{\eta} - 1 = \left(\frac{5}{2} + \frac{f^2}{16}\right) C$$

was used in the present work. The values of "f" actually found using it agreed well, in the cases examined, with those obtained with the more complicated Guth and Gold equation, which was derived for moderate concentrations of rigid rods unaffected by Brownian movement, and its use seems to have been justified. In some cases where microscopy was practicable "f" could be measured directly and compared with those values found viscometrically.

Results of the application of Kuhn's equation to Arnold and Goodeve's (2) viscosity data on carbon black in oil and also to Robinson's (14) experimental results with glass spheres in oil are shown in Fig. 1. Robinson's system showed no viscosity dependence on rate of shear but Goodeve's was definitely thixotropic. In both cases "f" depends on concentration but approaches linearly a value of unity on extrapolation to zero concentration.

These results were sufficiently encouraging to warrant an extension of the investigation to highly thixotropic systems where the solid particles might be highly anisodimensional.

When applied to two independent sets of data on the viscosity of dispersions of lime soaps in hydrocarbon oil (3, 12) Kuhn's equation produced some interesting results. Arveson's data indicated a substantially constant value for "f" of 17 for 3 to 14% volume concentration of soap. Two master samples of similar dispersions were used by Moses and Puddington (12) and intermediate concentrations were obtained by dilution. One of these samples gave an "f" of 15 in the concentration range 11–16%, the other a value of 23 for 18 to 30% of soap. Comparison of these values with electron micrographs of calcium soap fibers from similar systems shows these figures to be of the correct order although the viscometrically measured "f" values would be expected to be low if appreciable shear orientation had taken place.

Two electron micrographs of soap particles from lime base greases are shown in Figs. 2 and 3. These are taken from the work of Ellis (5) and of Farrington and Birsdall (6). Fig. 2 shows the soap still dispersed in the oil while in Fig. 3 the oil has been leached out and the sample shadow cast. The obvious conclusion is reached after comparing these figures that remarkable similarity exists in the size and shape of the lime soap particles of greases from different sources where different procedures were probably used in their preparation.

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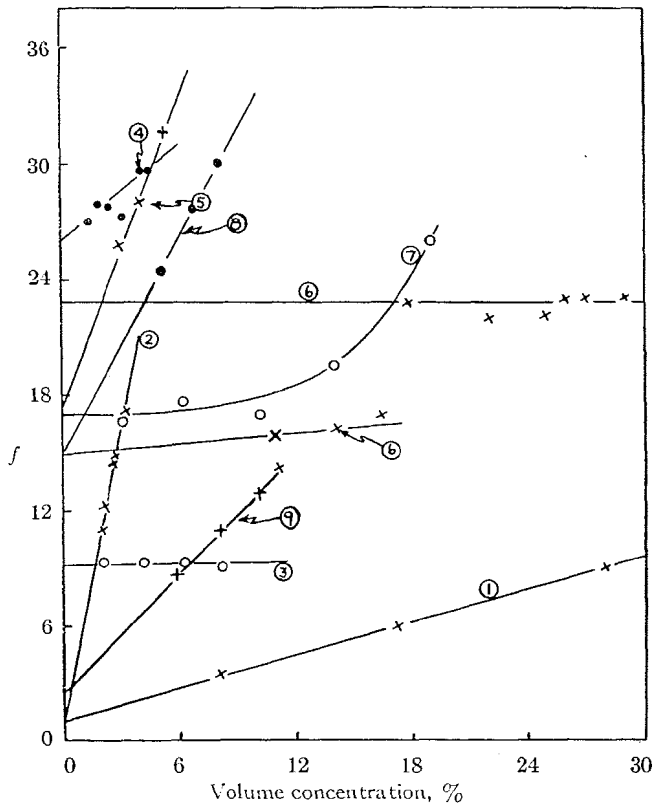

FIG. 1. *Relation between particle axial ratio and volume concentration. Curve 1, glass spheres in oil (Robinson); 2, carbon black in oil (Arnold and Goodeve); 3, rice starch in carbon tetrachloride–toluene (Hatschek and Jane); 4, silica aerogel × 0.5 in oil; 5, Shawinigan black in oil; 6, calcium soap in oil (Moses and Puddington); 7, calcium soap in oil (Arveson); 8, polythene in oil; 9, barium sulphate in oil.*

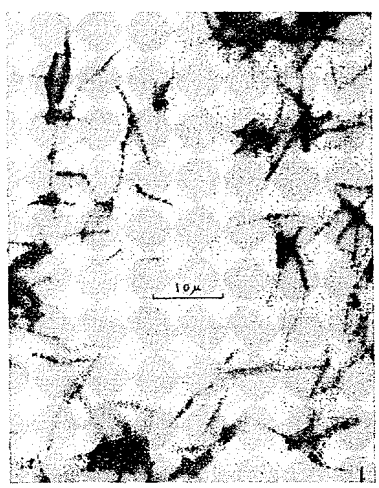

FIG. 2. *Electronmicrograph of calcium soap in oil (Ellis).*

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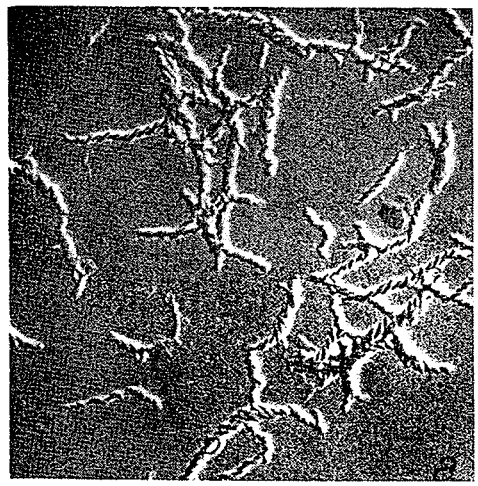

FIG. 3. *Electronmicrograph of calcium soap petroleum ether washed and gold shadowed (Farrington and Birsdall).*

Applying this treatment to the viscosity of rice starch suspended in a hydrocarbon – carbon tetrachloride solution as measured by Hatschek and Jane (8), a constant "f" of 9 in the concentration range of 2 to 8% is found. This is surprising since rice starch particles are essentially spherical. However, there is some evidence (13) that agglomerates that are substantially spherical in the undisturbed state are first elongated on shearing, and only after very high shear rates are applied do they break down to individual particles. Absolute shear rates used in this work could not be found and it is probable that the extrapolation to $\frac{1}{s} = 0$ was made from data obtained when the agglomerates were still in the ellipsoidal shape.

Using this procedure with dispersions of Shawinigan black in hydrocarbon oil, an extrapolated "f" equal to 17 was obtained. This again seems very high, but Shawinigan black is known to form extremely tenacious chains (4) and it is quite probable that these were stable under the conditions of shear that were obtained in the capillary tube used in the measurements. The samples had been passed through a colloid mill during preparation and it is likely that the shears exerted there (about 7×10^5 sec.$^{-1}$) fixed the minimum "f" values that could be reached later in the capillary.

The results on dispersions of silica in hydrocarbon oil in concentrations of 1–4% are of special interest. The silica used in this case was an aerogel prepared from a 2% aquagel according to the method of Kistler (9). The particles are supposed to be in substantially the same condition as found in the original gel and are undoubtedly fibrillar, with a high axial ratio. The system is also highly thixotropic. Since the ultimate particles are subelectronmicroscopic no direct measurement is possible; however, the "f" values of 55–60 found are not unduly high.

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Thixotropic suspensions of polyethylene were prepared by dissolving the solid in hot lubricating oil and allowing the system to cool. In concentrations of 4–8% by volume a solid of greaselike consistency was produced. Pigment grade barium sulphate in volume concentrations of 6–10% gave dispersions of similar consistency in oil. About 0.5% of water added to the latter system increased the amount of thixotropy considerably. Values of "f" obtained from viscometric measurements on these dispersions are also shown in Fig. 1. The extrapolated "f" values of 15 for polyethylene and 2–3 for barium sulphate agree well with microscopic observations.

While the data presented here are perhaps too meager to be conclusive, they certainly suggest that this approach could be of considerable value in thixotropic systems that do not lend themselves readily to microscopy.

In checking Goodeve's postulation that the coefficient of thixotropy should be proportional to the square of the solids concentration a graph was constructed and shown in Fig. 4 where the log coefficient of thixotropy is plotted against log concentration. If the postulate is correct, a straight line with a slope of 2 should result with each system. That this was the case with the data discussed above is readily seen. The figure also illustrates that it is possible to compare the degrees of thixotropy of the various systems by comparing the concentrations required to produce any selected value of θ. It also should be possible to prepare systems having a predicted value of θ from a knowledge of the properties of the system at any one concentration. It is again interesting

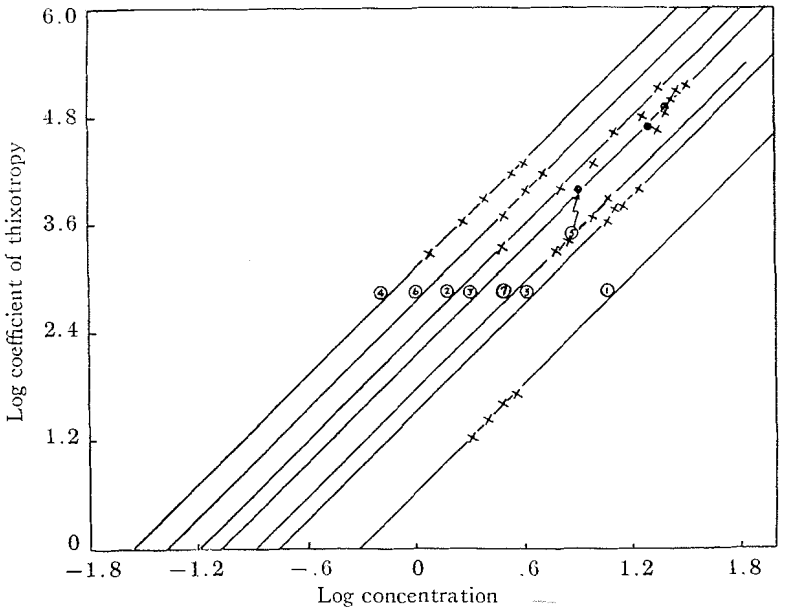

FIG. 4. *Relation between coefficient of thixotropy and concentration for suspensions in oil. Curve 1, carbon black (Arnold and Goodeve); 2, calcium soap (Arveson); 3, calcium soap (Moses and Puddington); 4, silica aerogel; 5, calcium soap (Tapp, unpublished); 6, Shawinigan black; 7, barium sulphate.*

to note the similarity in degree of thixotropy shown by the lime soap greases from several independent sources.

Such a series of curves could be of considerable practical use in correlating data on thixotropic suspensions provided that the slope of 2 is general. While there may be exceptions, this value was faithfully followed in all the data used here and the approach seems to warrant further investigation.

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HYDROGEN PEROXIDE AND ITS ANALOGUES

I. DENSITY, REFRACTIVE INDEX, VISCOSITY, AND SURFACE TENSION OF DEUTERIUM PEROXIDE – DEUTERIUM OXIDE SOLUTIONS[1]

By M. K. Phibbs and Paul A. Giguère

Abstract

Some deuterium peroxide containing less than 0.3% ordinary hydrogen was produced both by the persulphate and the electric discharge methods. By means of fractional distillation, solutions of deuterium peroxide in deuterium oxide of various concentrations up to 90% were obtained, of which the following properties were measured: refractive index at 25°C., density, viscosity and surface tension at 0°C. and 20°C. Measurements of the last two properties were also extended to solutions of ordinary hydrogen peroxide. The physical constants of the two isotopic peroxides are compared and discussed. The density, viscosity and surface tension of supercooled heavy water at 0°C. were also measured for the first time.

The deuterium analogue of hydrogen peroxide, D_2O_2, has attracted relatively little attention so far owing, no doubt, to the difficulty of obtaining it in a pure state. A number of kinetic and other investigations have been made by diluting concentrated hydrogen peroxide in various amounts of heavy water (1,2,4,5,8,12,15,21,29). Obviously this procedure yields rather complex mixtures of the following molecular species: H_2O, HDO, D_2O, H_2O_2, HDO_2, and D_2O_2. The first work dealing with substantially pure deuterium peroxide, that is, free of contamination by ordinary hydrogen, was that of Fehér (9,10,11) who prepared some 15–20 cc. of this compound by the persulphate method in order to measure its Raman spectrum. More recently Taylor (25) has reported preliminary results on the infrared absorption of the fairly pure compound in the liquid state. Now that heavy water is available in larger quantities than before, it is deemed worth while to prepare the pure isotopic peroxide in sufficient amount to enable accurate measurement of its physical properties.

Experimental Methods and Results

An important part of this project consisted in the actual preparation of the deuterium peroxide. The potassium persulphate method was first tried, since it had proved workable (11). Fehér had reported some difficulty due to frothing of the persulphate mixture on hydrolysis. With this in mind a number of improvements were effected in his original apparatus. In particular an anti-foaming device (7) was added on top of the reaction vessel. In spite of this the process remained extremely tedious and awkward to operate. Furthermore it turned out to be rather wasteful of the scarce heavy water because an appreciable portion of the deuterium is eventually transformed into potassium deuterium sulphate from which it cannot be recovered quantitatively.

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Therefore that method was soon discarded in favor of the electric discharge through water vapor (22,23). An apparatus was built in which the vapor of heavy water could be dissociated in an electrodeless discharge operating at 22 megacycles. The dissociation products were condensed in a liquid air trap. Under optimum conditions a 60% solution of deuterium peroxide in deuterium oxide was obtained which was concentrated further by fractional distillation. This part of the project will be described in a subsequent paper. The material made by both methods amounted to about 10 cc. of a 90% solution and 10 cc. of a 50% solution by weight. Although they seemed very stable these solutions were found to decompose at a rather high rate, very likely because their large surface-to-volume ratio favored the heterogeneous catalysis. To overcome that difficulty the samples were kept at low temperature, and once a solution had been prepared and analyzed, the four properties were determined in rapid succession.

The small amount of material available made it necessary to build special instruments. All glassware was thoroughly cleaned following the procedure recommended by Huckaba and Keyes (16). Contamination of the deuterium compounds by atmospheric moisture during handling was carefully avoided. A test of the liquid by means of its infrared spectrum made after the physical measurements showed no significant increase in hydrogen content over the original amount present in the heavy water used, viz., 0.25%. The peroxide content of the solutions was determined by the standard volumetric titration with permanganate using samples of about 0.1 gm.; the estimated accuracy was of the order of 1 in 1000. A constant temperature bath controlled to $\pm$ 0.05°C. was used for the measurements at 20°C. while those at 0°C. were done in a well agitated ice bath. Heavy water freezes at 3.8°C. but it supercools readily enough to enable easy measurement of its physical properties at 0°C.

Density

A U-tube type pycnometer of conventional design with a capacity of 2.9344 ml. at 20°C. was constructed for these measurements. In order to increase the accuracy of this small container the oblique arms were made of fine bore capillary tubing, 0.2 mm. radius for the inlet tube and 0.5 mm. radius for the other arm. The usual weighing corrections were neglected because of the small size of the instrument and the negligible dead space.

As in most measurements with hydrogen peroxide the accuracy was largely limited by formation of oxygen bubbles due to spontaneous decomposition. At 0°C. there was little trouble on that account but at 20°C. it was almost impossible to avoid it completely in spite of repeated cleaning of the pycnometer. After a number of trials the following procedure was adopted and found to give fairly reliable results: the filled pycnometer was allowed to reach temperature equilibrium in a bath at 20°C. Then by applying gentle pressure on one arm the excess liquid was forced out, while tapping, until the liquid level dropped to the reference mark. Thus any stray bubbles formed during

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temperature equilibration were swept out of the liquid for the short time required to measure the volume of sample.

The experimental results are presented in Table I along with those for the three other properties measured. The density curves need not be reproduced here as they are closely similar to those for hydrogen peroxide. In Fig. 1 the molecular volumes of the solutions are plotted as deviation from ideal solution relationship, which is more significant for that sort of data. The value found here for the density of 99.75% pure heavy water at 20°C. is in good agreement with the most recent data, 1.1053 gm. per ml. (27,28). No data could be found in the literature for the density of the supercooled liquid but the present result, 1.1046 gm. per ml. at 0°C. falls quite closely on the density–temperature curve extrapolated below the freezing point. The values for pure deuterium peroxide (Table III) were obtained by extrapolation, a fairly accurate procedure in this case because of the very slight curvature of the density–composition (in weight %) curves. A straight line was drawn through the two higher concentration points and a small correction was applied, equal to that for the hydrogen peroxide curves which are known with good precision (14,16).

TABLE I

DENSITY, REFRACTIVE INDEX, VISCOSITY, AND SURFACE TENSION OF DEUTERIUM PEROXIDE SOLUTIONS

D_2O_2		d_4^t (gm./ml.)		n_D	η centipoises		γ, dynes/ml.	
Weight %	Mole %	0°C.	20°C.	25°C.	0°C.	20°C.	0°C.	20°C.
0.00	0.0	1.104_6	1.105_6	1.32806	2.35_0	1.24_4	76.1	73.3
9.05	5.24	1.141_4	1.137_0	1.3340	2.23_0	1.25_5	76.5	73.5
20.02	12.22	1.185_7	1.178_0	1.3414	2.18_4	1.26_8	77.0	74.1
33.6_8	22.0_3	1.244_0	1.232_0	1.3510	2.18_2	1.30_0	77.9	75.2
43.2_5	29.7_9	1.286_0	1.270_1	1.3579	2.19_3	1.32_5	78.7	75.8
56.6_8	42.1_3	1.344_7	1.328_4	1.3678	2.19_2	1.37_2	79.8	77.0
73.7_8	61.0_2	1.423_6	1.403_3	1.3809	2.14_9	1.39_7	81.4	78.7
91.6_5	85.9_3	1.513_0	1.490_8	1.3955	2.04_7	1.37_9	82.7	80.0

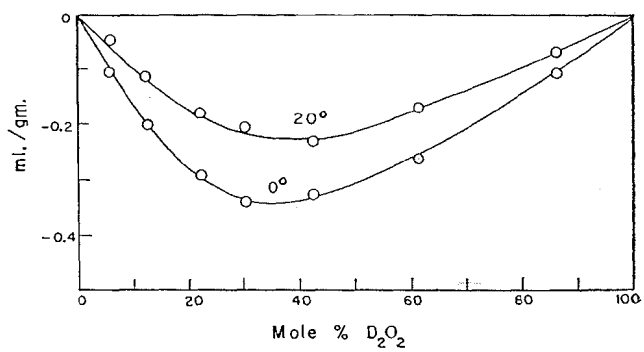

Fig. 1. Deviation from a straight line of molecular volume of D_2O_2–D_2O mixtures at 0° and 20°C.

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Refractive Index

The measurements were made with a Precision Abbé Refractometer (Bausch and Lomb), the technique being generally the same as previously reported for hydrogen peroxide solutions (13). These measurements required very small samples, one drop or two of liquid, which was fortunate since no recovery was possible, contrary to the other three properties. Measurements at another temperature besides 25°C. were not possible with the time and material available. It is hoped they can be completed in the near future in view of the great convenience of this method for analyzing solutions of deuterium peroxide. In addition to the small amount of liquid needed, the refractive index can be measured very quickly and it is less affected by slight decomposition than most other physical properties.

The plot of deviation from a straight line, Fig. 2, shows that the measurements were internally as consistent as those for hydrogen peroxide solutions. The refractive index of heavy water was taken from the literature (19) as it fell beyond the range of the instrument used; that of pure D_2O_2 is based on extrapolation as described under 'density'.

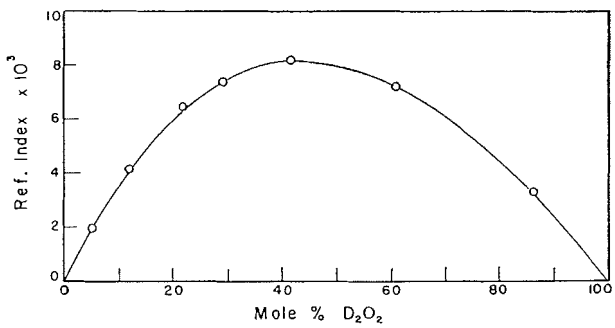

Fig. 2. Deviation from a straight line of refractive index measurements of D_2O_2–D_2O mixtures at 25°C.

Viscosity

An Ostwald type viscometer of small dimensions was made according to the specifications of Cannon and Fenske (3). The upper bulb had a volume of about 1 cc., and a determination could easily be made with 3 cc. of liquid. The instrument was so designed that no surface tension correction was necessary; the capillary was fine enough so that flow times were always greater than 180 sec. and the kinetic energy corrections were negligible. The viscometer was calibrated with pure water at 20°C. For measurements on the same volume (3cc.) of liquid at 0°C. it was necessary to correct for the change of driving head due to contraction of the liquid on cooling. This correction was calculated from the formula:

$$C_{t_2} = C_{t_1}\left[1 - \frac{(V_2 - V_1)}{0.785\ Hd^2}\right],$$

where C is the viscometer constant at the two temperatures, V the volume of liquid sample, d the diameter of the lower bulb in centimeters and H the mean

driving head in the same units. In fact the correction amounted only to 2–4 units in the fourth decimal place. The viscosity measurements were not appreciably affected by the presence of a few minute bubbles in the peroxide solution as was shown by the following checks: It was found that after degassing a solution the formation of bubbles was delayed long enough to allow a viscosity determination to be made. In all cases the results agreed quite well whether or not this precaution was taken.

The curves in Fig. 3 are based on extrapolated values for 100% deuterium peroxide and on the results of actual determinations for heavy water. The latter agree very well with those of Lewis and McDonald (18): 1.26 centipoises at 20°C. and 2.35 cp. (by extrapolation) for the supercooled liquid at 0°C. In that connection the more recent data of Lemonde (17) appear to be in error as they lead, on extrapolation, to a much higher value, 2.75 cp. at 0°C. Indeed, if his results are plotted in the form log η vs. $1/t$ there is a sharp break at 8°C.; above that temperature the curve extrapolates to 2.38 cp. at 0°C.

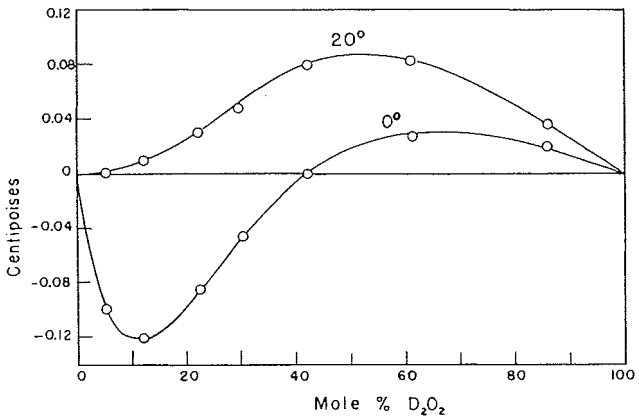

Fig. 3. Deviation from a straight line of viscosity determinations of D_2O_2 solutions at 0° and 20°C.

Since the necessary material was available the viscosity measurements were extended to hydrogen peroxide solutions over the whole concentration range. The results at 0°C. (Table II) confirm generally those of Maass and Hatcher (20), the only ones to be found in the literature, although their noted discontinuities in the viscosity–composition curves have now disappeared (Fig. 4). The present values are believed to be more accurate owing to the availability of purer hydrogen peroxide and to the revision in the viscosity constant of water, 1.798 cp. instead of 1.778 at 0°C.

Surface Tension

Measurements of this property were hindered more seriously than the others by the small volume of solutions available; they were also more sensitive to the slightest bubble formation in the liquid. The capillary rise method was applied, the above described viscometer serving for this purpose as well. This was possible because of the careful selection and calibration (by means of a

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TABLE II

VISCOSITY AND SURFACE TENSION OF HYDROGEN PEROXIDE SOLUTIONS

Weight % H_2O_2	η, centipoises		Weight % H_2O_2	γ, dynes/cm.	
	0°C.	20°C.		0°C.	20°C.
0.00	1.792	1.005	0.00	75.65	72.75
8.68	1.746	1.011	17.05	76.36	73.41
19.06	1.746	1.045	26.31	76.95	74.12
25.11	1.783	—	37.33	77.69	74.67
37.3_3	—	1.120	49.7_6	78.41	75.68
42.7_2	1.844	1.140	64.3_3	79.62	76.65
49.0_8	—	1.170	71.5_5	80.48	77.36
51.9_3	1.884	—	84.1_2	81.92	78.61
62.3_7	1.917	1.219	95.7_5	82.93	79.87
69.7_3	—	1.234	97.8_6	82.81	79.88
71.5_5	1.933	—	——	——	——
81.2_1	1.919	1.266	——	——	——
91.7_6	—	1.262	——	——	——
95.7_5	1.854	1.259	——	——	——
100.0	1.819	1.249	——	——	——

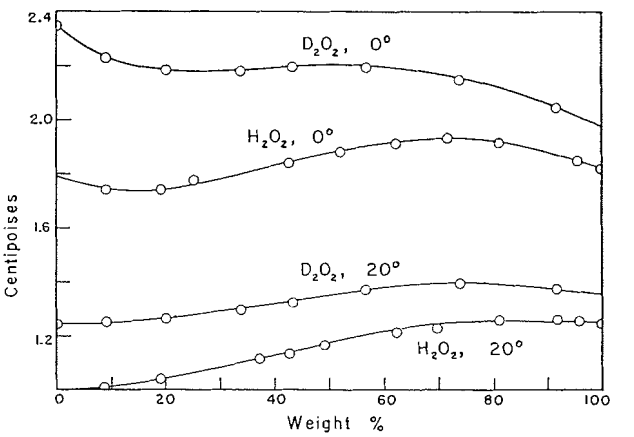

Fig. 4. Viscosity at 0° and 20°C. of H_2O_2–H_2O and D_2O_2–D_2O mixtures.

mercury index) of the capillary, a Tru-Bore tube with a remarkably constant radius: 0.1976 ± 0.0002 mm. over the usable section. This apparatus could not give absolute measurements of surface tension, however, because of the small section of the reference surface, 1 cm. Calibration was done with distilled water, the obvious choice in this case, since its surface tension at 20°C. is almost exactly the same as that of heavy water, and that of the peroxide solutions is of the same order of magnitude. The value found for heavy water at 0°C. is again in good agreement with extrapolation of other data found in the literature (6, 26). On the other hand the limited accuracy of the present measurements, especially with concentrated solutions, render the extrapolated value for the surface tension of 100% deuterium peroxide less accurate than the other three properties, as shown in Fig. 5.*

**This plot, as well as those in Fig. 2 and 3, has no particular significance other than showing the internal consistency of the measurements.*

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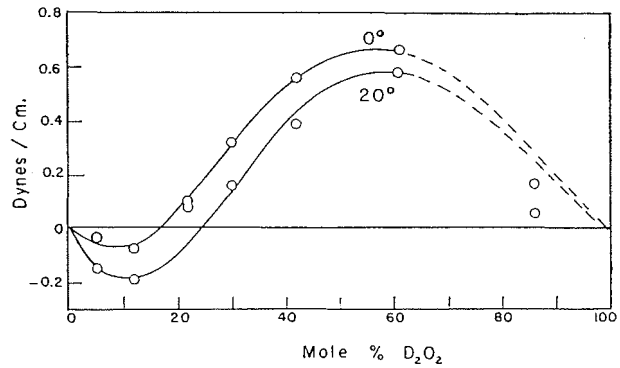

Fig. 5. Deviation from a straight line of surface tension measurements of D_2O_2 solutions at 0° and 20°C.

By analogy with water and heavy water one would expect the two isotopic peroxides to have nearly the same surface tension. In this respect the present results for deuterium peroxide are completely at odds with those of Maass and Hatcher (20). To check this point the surface tension of hydrogen peroxide solutions was measured at 0° and 20°C., again by the capillary rise method but with a much larger reference surface (30 cm.²). The results shown in Table II are appreciably higher than the previous ones, which is easily understood since, for their pioneer work, Maass and Hatcher had to start with an impure and very dilute solution (3%) and mere traces of most impurities would lower the surface tension appreciably. In the present investigation, even with pure 90% hydrogen peroxide available as starting material, only erratic results were obtained at first. This was eventually traced to the presence in the commercial peroxide of some surface active agent arising apparently from the plastic material used for stopping containers. Repeated distillations were not sufficient to remove completely all traces of this impurity. Only by use of uncontaminated peroxide and glassware could consistent results be obtained.

Discussion

By way of discussion the physical properties of the two peroxides may be compared. As illustrated by the various constants in Table III substitution of hydrogen by deuterium generally has the same kind of effect on peroxide as on water molecules. Although the accuracy of the density data for the peroxides is not very high the slight increase in molecular volume on substitution seems genuine. In water this effect is interpreted as due to greater association of D_2O (24) since, as is well known, association of water molecules leads to a more open structure. Hydrogen peroxide shows no such anomalous behavior but the above mentioned effect is certainly related to association; indeed, the molecular volume of unassociated liquids is scarcely affected by deuterium substitution. In order to learn more about that question the infrared spectrum of deuterium peroxide is now being studied in this laboratory.

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TABLE III

PHYSICAL CONSTANTS

	H_2O	D_2O	H_2O_2	D_2O_2
Molecular weight	18.015	20.028	34.015	36.028
Density, d_4^0	0.99987	1.1046	1.4730	1.5574
Density, d_4^{20}	0.99823	1.1056	1.4502	1.5343
Molecular volume, $(V)^0$	18.02	18.13	23.09	23.13
Molecular volume, $(V)^{20}$	18.05	18.12	23.45	23.48
Refractive index, n_D^{25}	1.33251	1.32806	1.4067	1.4026
Specific refraction, r_D^{25}	0.2054	0.2029	0.2460	0.2438
Molecular fraction, $[R]$	3.712	3.680	5.764	5.746
Polarizability, $\alpha \times 10^{24}$	1.472	1.459	2.286	2.279
Average molecular radius, in Å	1.14	1.13_5	1.32	1.32
Viscosity, η^0	1.798	2.35	1.819	1.975
Viscosity, η^{20}	1.005	1.25	1.219	1.358
Surface tension, γ^0	75.6	76.15	83.3	83.6
Surface tension, γ^{20}	72.75	72.73	80.2	81.2
Parachor	52.7	52.9	70.0	70.4

As in the case of water the decrease in molecular refraction and polarizability is indicative of tighter binding in D_2O_2 than in H_2O_2. A glance at Fig. 4 reveals that viscosity is considerably affected by isotopic substitution, in the same way as it is by temperature changes. It is easily understood why an increase of mass has the same effect as a lowering of temperature. Because of its lower zero-point energy the deuterium compound must be brought to a higher temperature than the hydrogenic compound in order to be in an equivalent situation as far as molecular motion is concerned. For the same reason the melting point of D_2O_2 should be higher than that of H_2O_2. Finally no real significance can be attached to the difference in surface tension because the values for D_2O_2 are too uncertain, as explained above.

Acknowledgment

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Résumé

A partir d'eau lourde à 99.7% de pureté l'on a préparé des solutions de peroxyde de deutérium, D_2O_2, par voie chimique (hydrolyse du persulfate de potassium) et par voie physique (décharge électrique à haute fréquence). Cette dernière méthode s'est avérée supérieure à l'autre tant par la simplicité d'opération que par le rendement. Les solutions ont été purifiées et concentrées par distillation et l'on en a mesuré l'indice de réfraction à 25°, la densité, la viscosité et la tension superficielle à 0° et 20° en fonction de la teneur en peroxyde. On a également repris les mesures de viscosité et de tension superficielle des solutions de peroxyde d'hydrogène. Les résultats obtenus conduisent à des considérations intéressantes sur les effets de la substitution de l'hydrogène par le deutérium dans des molécules simples.

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THE SYNTHESIS AND ULTRAVIOLET SPECTRA OF SOME PYRAZOLONES[1]

By Paul E. Gagnon, Jean L. Boivin,[2] Paul A. Boivin,[3] and R. Norman Jones

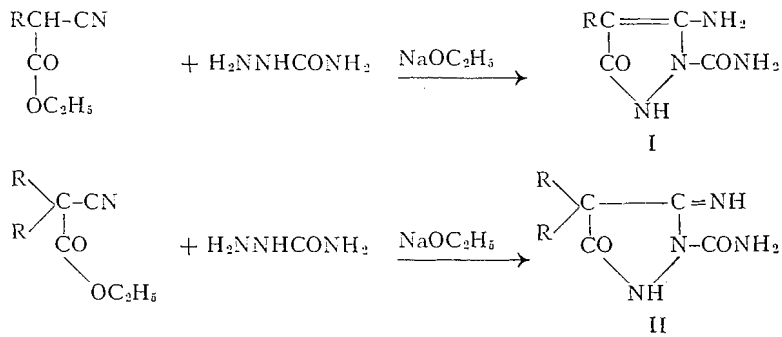
Abstract

Twenty-five pyrazolones were prepared by reacting mono- or disubstituted cyanoacetic esters with hydrazine, phenylhydrazine and semicarbazide. 4-Benzyl-3-amino-1-phenyl-5-pyrazolone has been synthesized and its properties have been compared with those of the corresponding 2-phenylpyrazolone derivative. The ultraviolet absorption spectra of several pyrazolones have been determined.

Introduction

The investigation of the reaction of ethyl cyanoacetate with hydrazine and hydrazine derivatives has been reviewed in earlier publications (2, 3, 4). Gagnon, Savard, Gaudry and Richardson (4) have studied the behavior of substituted cyanoacetic esters with hydrazine and observed that crude substituted cyanoacethydrazides yielded 4-substituted-3-amino-5-pyrazolones in excellent yield. Later, Gagnon, Boivin and Jones (2, 3) reinvestigated this transformation and prepared several 4-monosubstituted-3-amino-5-pyrazolones and 4, 4-disubstituted-3-amino-5-pyrazolones. They also synthesized some 4-monosubstituted-3-amino-2-phenyl-5-pyrazolones and 4, 4-disubstituted-3-imino-2-phenyl-5-pyrazolones.

In the present work, the preparation of other 4-monosubstituted-3-amino-5-pyrazolones and 4-monosubstituted-3-amino-2-phenyl-5-pyrazolones is described. A new series of 4-monosubstituted-3-amino-2-carboxamido-5-pyrazolones (I) and 4, 4-disubstituted-3-imino-2-carboxamido-5-pyrazolones (II) have also been synthesized by the method of Conrad and Zart (1).



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This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.
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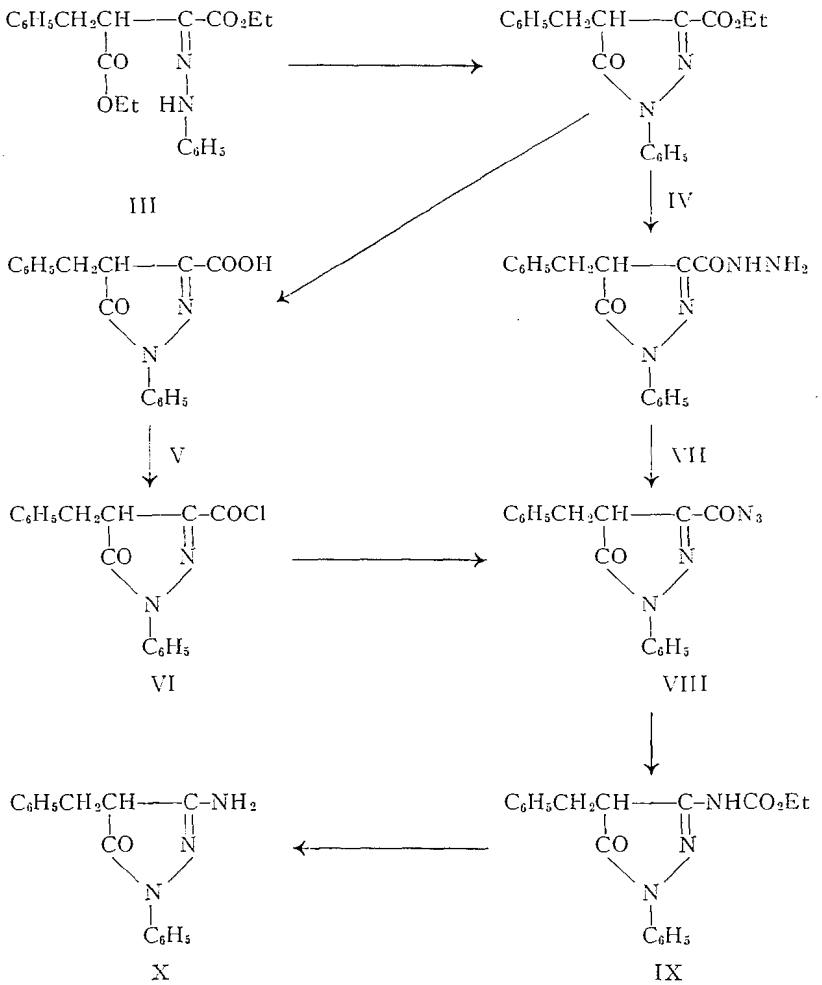
The position of the N-phenyl group in the phenylpyrazolones has been established and it has been shown that the reaction of phenylhydrazine with substituted cyanoacetic esters under the conditions described yielded 2-phenylpyrazolones, whereas unsubstituted cyanoacetic ester yielded 1-phenyl derivatives (6).

The position of the phenyl group was established by the following synthesis in which a representative 4-substituted-3-amino-1-phenyl-5-pyrazolone was prepared according to the following scheme:



Benzyl oxalacetic ester was heated with phenylhydrazine to prepare the phenylhydrazone of the ethyl ester of benzyloxalacetic acid (III), which was transformed into 4-benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (IV) in an almost quantitative yield (5). The conversion of the carbethoxy group into an amino group (X) was effected through the hydrazide (VII), azide (VIII) and urethane (IX) by the Curtius degradation.

However, since the hydrazide could not be isolated in the crystalline state, the urethane was obtained also by another method. The Wislicenus pyrazolone (IV) was boiled in alcoholic potash to give the 3-carboxyl derivative (V). This acid was transformed into the acid chloride (VI) by means of thionyl chloride. The resulting crude acid chloride was treated with sodium azide to give the corresponding azide (VIII) which after treatment with ethanol yielded the same urethane (IX). This was identified by a mixed melting point determination with the sample previously obtained.

The methods outlined above for the synthesis of 4-benzyl-3-amino-1-phenyl-5-pyrazolone leaves no doubt as to the position of the phenyl group. Moreover, the melting point of this pyrazolone, 206–207°C., is much higher than that of the corresponding 2-phenylpyrazolone, 160–161°C. (2).

Derivatives of both the 1-phenyl- and 2-phenylpyrazolones were prepared. The two 3-benzoylamino derivatives obtained also had melting points differing by some 30 degrees.

By analogy to the phenylhydrazine reaction with substituted cyanoacetic esters, it may be presumed that semicarbazide will react in the same manner. This implies that the carboxamido group of pyrazolones just reported above (I and II) is in position 2.

Experimental*

Starting Materials

Ethyl α, α-Disubstituted-α-cyanoacetates

To a cooled solution of sodium ethoxide (400 ml. of absolute alcohol and one mole of sodium) a half equivalent of ethyl cyanoacetate and one equivalent of organic halide were added. The mixture was boiled under reflux on a water bath until it was neutral to litmus paper. The alcohol was removed by distillation and the residue poured into cold water and extracted with ether. The ethereal solution was washed with 5% sodium hydroxide solution to remove the monosubstituted esters, dried over anhydrous sodium sulphate, evaporated, and the residue fractionally distilled under reduced pressure.

The properties and yields of the disubstituted esters are summarized in Table I.

TABLE I

ETHYL α, α-DISUBSTITUTED CYANOACETATES, $RR(CN)COOC_2H_5$

R	Starting material	Yield, %	B.p., °C.	Formula	Nitrogen, %	
					Calc.	Found
2-Pentyl	$C_5H_{11}Br$	50	153–156 (13 mm.)	$C_{15}H_{27}O_2N$	5.53	5.60
n-Hexyl	$C_6H_{13}Br$	50	176–178 (13 mm.)	$C_{17}H_{31}O_2N$	5.00	4.92
n-Heptyl	$C_7H_{15}Br$	51	198–201 (13 mm.)	$C_{19}H_{35}O_2N$	4.53	4.52
n-Octyl	$C_8H_{17}Br$	48	152–155 (6 mm.)	$C_{21}H_{39}O_2N$	4.16	4.22
n-Nonyl	$C_9H_{19}Br$	45	170–174 (6 mm.)	$C_{23}H_{43}O_2N$	3.83	3.89

* *All melting points are uncorrected.*

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Ethyl α-Cyano-α-cinnamylacetate

Ethyl cyanoacetate (113 gm.; 1 mole) and cinnamyl bromide (98.5 gm.; 0.5 mole) were added to a solution of sodium (11.5 gm.; 0.5 mole) in absolute alcohol (200 ml.). The mixture was refluxed on a steam bath for two hours. After removal of the alcohol the product was shaken with water and ether, and the dried ethereal extract evaporated and fractionally distilled under reduced pressure: b.p. 206° to 208°C. (12 mm.). Yield, 68.7 gm. (60%). Calc. for $C_{14}H_{15}O_2N$: N, 6.11%. Found: N. 6.00%.

α-Cyano-α-cinnamylacetic Hydrazide

Ethyl α-cyano-α-cinnamylacetate (22.9 gm.; 0.1 mole) was stirred with hydrazine hydrate (5.0 gm. of 100%). The two layers disappeared with evolution of heat, and after five minutes a white solid was formed. It was recrystallized from ethanol: m.p. 94° to 95°C. Yield, quantitative. Calc. for $C_{12}H_{13}ON_3$: N, 19.5%. Found: N, 19.2%.

4-Monosubstituted-3-amino-5-pyrazolones

These pyrazolones were prepared by treatment of the corresponding substituted cyanoacethydrazides with strong alkalies (2).

4-Monosubstituted-3-amino-2-phenyl-5-pyrazolones

Three compounds were synthesized by heating the substituted cyanoacetic esters with phenylhydrazine in the presence of sodium ethylate (2).

4-Monosubstituted-3-amino-2-carboxamido-5-pyrazolone

This pyrazolone was prepared by a method similar to that outlined above for the 4-monosubstituted-3-amino-2-phenyl-5-pyrazolones, except that semicarbazide hydrochloride was used instead of phenylhydrazine and the time of heating in an oil bath was 18 hr.

This compound was soluble in alkalies and strong acids. It is insoluble in sodium carbonate and can be precipitated from its alkaline solution by carbon dioxide.

4, 4-Disubstituted-3-imino-2-carboxamido-5-pyrazolones

To a solution of sodium ethoxide (0.3 mole of sodium and 120 ml. of absolute ethyl alcohol) a mixture of ethyl disubstituted cyanoacetates (0.1 mole) and semicarbazide hydrochloride (0.1 mole) was added. The reaction mixture was heated at 160°C. in an oil bath for 24 hr. The solvent was removed under reduced pressure, the residue dissolved in hot water (100 ml.) and extracted with ether to remove unchanged esters. A viscous product separated on acidification with acetic acid and soon solidified. The products were recrystallized from ethanol or acetic acid.

The pyrazolones were soluble in alkalies and insoluble in strong acids. They can be precipitated from their alkaline solution by means of carbon dioxide.

The physical constants and elemental analyses are given in Table II.

TABLE II

PROPERTIES OF INDIVIDUAL PYRAZOLONES

Compound	Formula	M.p., °C.	Analysis % Nitrogen Calc.	Analysis % Nitrogen Found	Ultraviolet absorption maxima Neutral‡ Å	Neutral‡ log E_m	Acid+ Å	Acid+ log E_m
4-Monosubstituted-3-amino-5-pyrazolones								
4-(*n*-Nonyl)-	$C_{12}H_{23}ON_3$	222–223	18.7	18.5	2840	3.58	2770	3.59
4-(*n*-Stearyl)-	$C_{19}H_{37}ON_3$	200–202	13.0	12.7	2830	3.56	2760	3.57
4-(β-Cyclohexyl-ethyl)-	$C_{11}H_{19}ON_3$	203–205	20.1	20.1	2840	3.57	2770	3.59
4-Cinnamyl	$C_{12}H_{13}ON_3$	198–200	19.5	19.3				
4-Monosubstituted-3-amino-2-phenyl-5-pyrazolones								
4-(*n*-Nonyl)-	$C_{18}H_{27}ON_3$	167–168	14.0	13.8	2680			
4-Acetyl	$C_{11}H_{11}O_2N_3$	217–219	19.4	19.6	2490	4.33	2600	4.28
4-(β-Cyclohexyl-ethyl)-	$C_{17}H_{23}ON_3$	154–155	14.7	14.4	2500			
4-Monosubstituted-3-amino-2-carboxamido-5-pyrazolone								
4-(α-Naphthyl)-	$C_{14}H_{12}O_2N_4$	273–275	20.9	20.6	2910 2810 2710 2240	3.80 3.96 3.88 5.04	2920 2810 2710 2240	3.80 3.96 3.89 5.04
4-Disubstituted-3-imino-2-carboxamido-5-pyrazolones								
4, 4-Dipropyl	$C_{10}H_{18}O_2N_4$*	304–307	24.3	23.9	2880 2680 2340	3.98 3.95 4.24	2800	4.11
4, 4-Dibutyl	$C_{12}H_{22}O_2N_4$†	278–280	22.0	21.8	2860 2700 2360	3.96 3.94 4.31	2800	4.09
4, 4, *bis*-(2-Pentyl)-	$C_{14}H_{26}O_2N_4$	300	19.9	19.9	2880 2690 2360	3.94 3.89 4.26	2820	4.08
4, 4-Diamyl	$C_{14}H_{26}O_2N_4$	273–275	19.9	19.6	2880 2700 2340	3.96 3.93 4.44	2800	4.13
4, 4-Dihexyl	$C_{16}H_{30}O_2N_4$	261–263	18.1	18.5	2900 2700 2340	3.89 3.86 4.13	2800	4.06
4, 4-Diheptyl	$C_{18}H_{34}O_2N_4$	270–272	16.6	17.0	2880 2700 2360	3.93 3.91 4.21	2820	4.06
4, 4-Dioctyl	$C_{20}H_{38}O_2N_4$	266–268	15.3	15.8	2880 2700 2360	3.93 3.91 4.22	2820	4.07
4, 4-Dinonyl	$C_{22}H_{42}O_2N_4$	259–261	14.2	14.8	2880 2690 2350	3.93 3.90 4.19	2810	4.06

* *Calc. C, 53.1%; H, 8.00%. Found: C, 53.0%; H, 8.10%.* † *Calc. C, 56.7%; H, 8.66%. Found: C, 56.5%; H, 8.80%.*

‡ *Solvent, 95% ethanol.*

\+ *0.1N HCl in 95% ethanol.*

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4-Benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (*IV*)

This pyrazolone was obtained by the method described by Wislicenus (5), but since the yield was low it was prepared also by another method. To the ethyl ester of the benzyloxalacetic acid (27.8 gm.; 0.1 mole) was added phenylhydrazine (10.8 gm.; 0.1 mole). Reaction occurred with evolution of heat. To complete the reaction, the mixture was warmed on a steam bath for one hour; during this time water was liberated. The temperature of the bath was gradually raised to 210°C. when ethyl alcohol was evolved. The solid residue was recrystallized from a large volume of ethanol: m.p. 194° to 195°C. (yield 95%).

4-Benzyl-3-carboxyl-1-phenyl-5-pyrazolone (*V*)

4-Benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (32.2 gm.; 0.1 mole) was heated on a steam bath with alcoholic potash for one hour. The product was poured into ice water (600 ml.) and the solution treated with an excess of hydrochloric acid (50%). The white precipitate that separated was recrystallized from ethanol: m.p. 233° to 234°C. When the hydrolysis was attempted with an aqueous potassium hydroxide solution, the starting material was recovered. Calc. for $C_{11}H_{14}O_3N_2$: N, 9.52%. Found: N, 9.60%.

4-Benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone (*VI*)

4-Benzyl-3-carboxyl-1-phenyl-5-pyrazolone (29.4 gm.; 0.1 mole) was added to an excess of thionyl chloride (28 ml.) and the solution heated on a water bath for one hour. The excess of thionyl chloride was evaporated under reduced pressure, leaving the 4-benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone as a brown viscous liquid.

4-Benzyl-3-carbohydrazide-1-phenyl-5-pyrazolone (*VII*)

4-Benzyl-3-carbethoxy-1-phenyl-5-pyrazolone (16.1 gm.; 0.05 mole) was heated with an excess of hydrazine hydrate (16 ml.) at 140°C. for six hours. There was liberation of ethanol. The product was poured into water (400 ml.), and the solution neutralized with acetic acid. A white solid was obtained consisting of unreacted ester. To eliminate impurities, the solid was dissolved in concentrated hydrochloric acid at 0°C. The hydrazide passed into solution leaving a residue of insoluble starting material. The acid filtrate was neutralized at 0°C. with sodium hydroxide solution (5%). The brown resinous material, which was very soluble in alcohol, ether, and benzene, could not be crystallized.

4-Benzyl-3-carboxazide-1-phenyl-5-pyrazolone (*VIII*)

The solution of the 4-benzyl-3-carboxhydrazide-1-phenyl-5-pyrazolone in hydrochloric acid was extracted with ether to eliminate impurities. Then, it was covered with ether (200 ml.). At the beginning, it was observed that the ether layer was clear and colorless. The mixture was cooled at 0°C. and mechanically stirred while adding dropwise an aqueous solution of sodium nitrite for two hours. The 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone passed immediately

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into the ether layer, which became green. The ether was decanted and the aqueous solution extracted three times with ether. The extracts were washed with sodium carbonate, dried over anhydrous sodium sulphate and poured into absolute alcohol (200 ml.). A portion of the ethereal solution was evaporated to dryness. A crystalline residue of 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone was obtained: m.p. 134°C. (with deflagration).

4-Benzyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (IX)

This pyrazolone was obtained in two ways: (*a*) from 4-benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone (VI) and (*b*) from 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone (VIII).

(*a*) A solution of 4-benzyl-3-chlorocarbonyl-1-phenyl-5-pyrazolone (20 gm.) in ether (300 ml.) was added to a solution of sodium azide (20 gm.) in water (30 ml.) The mixture was cooled at 0°C. and mechanically stirred in an ice bath for two hours. The ether layer was decanted, washed with sodium carbonate, and finally with ice water. The green ethereal solution was dried over anhydrous sodium sulphate and poured into absolute ethanol. The ether was distilled off with liberation of nitrogen and the alcoholic solution was heated to boiling for 12 hr. The solution was cooled overnight, when a crystalline solid separated out. It was recrystallized from ethanol: m.p. 178° to 179°C. Calc. for $C_{19}H_{19}O_3N_3$: N, 12.5%. Found: N, 13.0%.

(*b*) A solution of 4-benzyl-3-carboxazide-1-phenyl-5-pyrazolone in a mixture of ethanol and ether was heated in a flask with a fractionating column; the ether distilled off and the alcoholic solution heated to boiling for 12 hr. The solution was concentrated and a solid separated out. It was recrystallized from ethanol: m.p. 178° to 179°C. A mixed melting point of this product with the urethane above described showed no depression.

4-Benzyl-3-amino-1-phenyl-5-pyrazolone (X)

A suspension of 4-benzyl-3-carbethoxyamino-1-phenyl-5-pyrazolone (2 gm.) in sodium hydroxide was refluxed for two hours. The solution was then cooled and neutralized with acetic acid. A white solid precipitated and was recrystallized from ethanol: m.p. 206° to 207°C. Calc. for $C_{16}H_{15}ON_3$: N, 15.8%. Found: N, 15.5%.

4-Benzyl-3-benzoylamino-1-phenyl-5-pyrazolone

A mixture of 4-benzyl-3-amino-1-phenyl-5-pyrazolone (2 gm.) and benzoyl chloride (2 ml.) in anhydrous dioxane (25 ml.) was heated on a water bath for 18 hr. The solution was evaporated to dryness under reduced pressure to eliminate the benzoyl chloride. The residue was recrystallized twice from ethanol: m.p. 225° to 227°C. Calc. for $C_{23}H_{19}O_2N_3$: N, 11.4%. Found: N, 11.1%.

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4-Benzyl-3-benzoylamino-2-phenyl-5-pyrazolone

This 3-benzoylamino derivative was prepared by the method outlined above from 4-benzyl-3-amino-2-phenyl-5-pyrazolone (2). The compound was recrystallized from a large volume of ethanol: m.p. 197° to 198°C. Calc. for $C_{23}H_{19}O_2N_3$: N, 11.4%. Found: N, 11.3%.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were determined on a Beckman Model DU spectrophotometer, and the experimental details have been reported previously (4). The intensities of the absorption maxima are given in Table II.

The spectra of several 4-monoalkyl-3-amino-5-pyrazolones have been measured and the curves found to agree closely with those of the 4-methyl and 4-ethyl derivatives reported previously (2, 3). In Fig. 1 the spectra of 4-benzyl-3-amino-1-phenyl-5-pyrazolone (X) and the corresponding 2-phenyl derivative (XI) are shown. On acidification of the solution the spectrum of the 1-phenyl derivative is unchanged but that of the 2-phenyl is displaced to longer wave lengths. The spectrum of 4-benzyl-2-phenyl-3-amino-5-pyrazolone resembles those of the 4-methyl-2-phenyl and 4-ethyl-2-phenyl derivatives (2, 3); the spectrum of the 4-acetyl-2-phenyl derivative is also similar (Fig. 2).

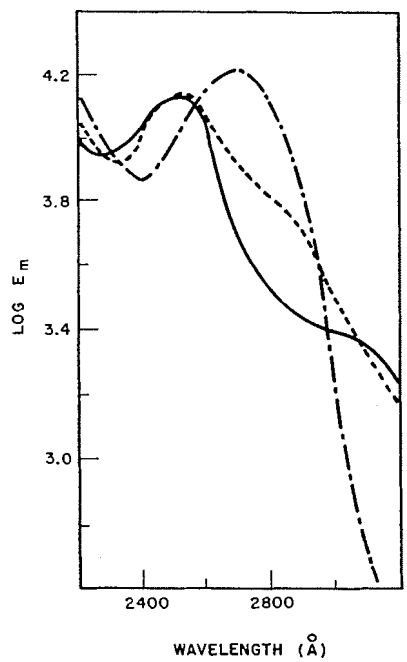

FIG. 1. ———— *4-Benzyl-3-amino-1-phenyl-5-pyrazolone (neutral).*
— — — — *4-Benzyl-3-amino-2-phenyl-5-pyrazolone (neutral).*
— - — - — *4-Benzyl-3-amino-2-phenyl-5-pyrazolone (acid).*

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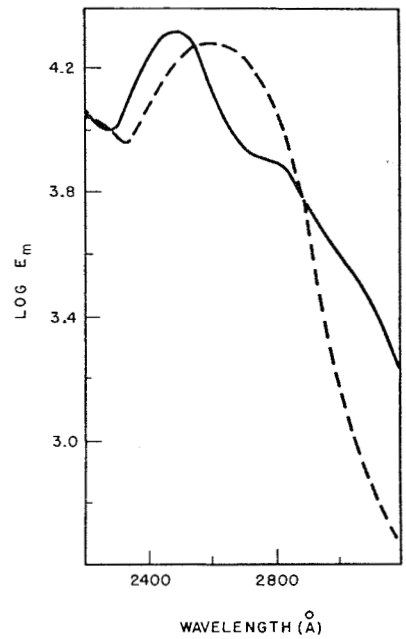

FIG. 2. ———— *4-Acetyl-3-amino-2-phenyl-5-pyrazolone (neutral).*
— — — — *4-Acetyl-3-amino-2-phenyl-5-pyrazolone (acid).*

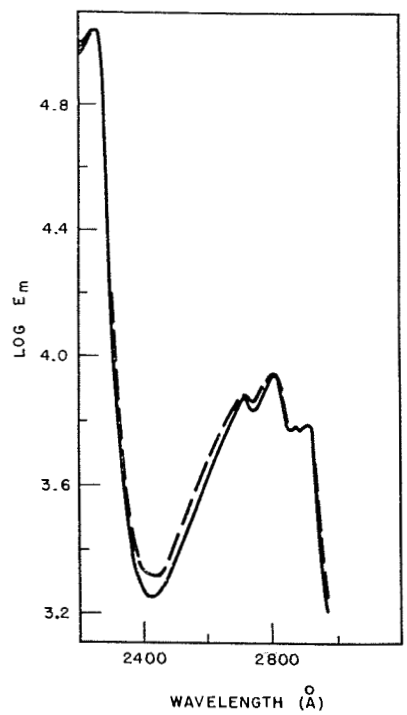

FIG. 3. ———— *4-(α-Naphthyl)-3-amino-2-carboxamido-5-pyrazolone (neutral).*
— — — — *4-(α-Naphthyl)-3-amino-2-carboxamido-5-pyrazolone (acid).*

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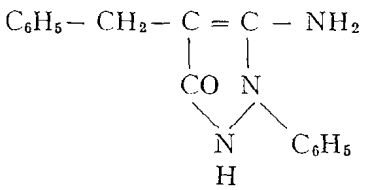

XI

Several carboxamide and carboethoxy pyrazolones have also been examined. The curve for 4-(α-naphthyl)-3-amino-2-carboxamido-5-pyrazolone shown in Fig. 3 is dominated by the naphthalene chromophore. The 3-imido-2-carboxamido-5-pyrazolones disubstituted at position 4 give absorption curves which are all very similar (Table II and Fig. 4). In the case of the 4, 4-diamyl derivative, measurements have been made also in alkaline solution and maxima observed at 2520 Å (log $E_m = 4.19$) and 2950 Å (log $E_m = 3.70$).

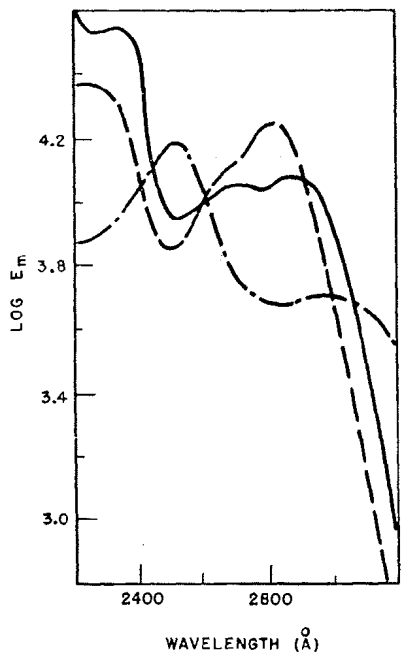

FIG. 4. ———— *4, 4-Diamyl-3-imino-2-carboxamido-5-pyrazolone (neutral).*
— — — — *4, 4-Diamyl-3-imino-2-carboxamido-5-pyrazolone (acid).*
— - — - — *4, 4,-Diamyl-3-imino-2-carboxamido-5-pyrazolone (alkaline).*

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C^{13} ISOTOPE EFFECT IN THE DECARBOXYLATION OF NORMAL MALONIC ACID[1]

By J. G. Lindsay,[2] A. N. Bourns, and H. G. Thode

Abstract

An investigation has been made of the relative rates of decarboxylation of two isotopic species of malonic acid, one containing only C^{12} carbon atoms and the other containing a C^{13} in a carboxyl position. Two effects were observed using malonic acid containing a normal abundance of C^{13}—(1) a 3.3% faster rate of reaction for the molecule containing only C^{12} carbon atoms; (2) a 2% greater probability of rupture of a C^{12}–C^{12} bond than a C^{12}–C^{13} bond in the molecule containing a C^{13} carbon. The latter effect was found to be independent of temperature. The magnitude of the isotope effect is in reasonable agreement with theoretical predictions.

Introduction

Until recently isotope effects in nonequilibrium processes were believed to be negligible except in those cases where deuterium was involved. During the past two years, however, isotope effects in unidirectional processes have been reported for compounds containing isotopic atoms other than deuterium, namely, C^{13}, C^{14}, and N^{15}. Stevenson, *et al.* (1), while investigating propane-1-C^{13} in a mass spectrometer, found that the probability of rupture of C^{12}–C^{13} and C^{12}–C^{12} bonds differed by about 20%. In the thermal cracking of propane-1-C^{13} the effect was smaller, an 8% more frequent rupture of C^{12}–C^{12} than of C^{12}–C^{13} bonds being observed (13). More recently, Yankwich and Calvin (15) found that the specific activity of the CO_2 produced from the decomposition of malonic acid containing C^{14} in a carboxyl group was significantly less than that calculated on the basis of equal probabilities of rupture of C^{12}–C^{12} and C^{12}–C^{14} bonds. Bigeleisen and Friedman (4) have reported a much smaller effect with C^{13} using normal malonic acid. Isotope effects of a similar nature have also been observed in the decomposition of normal oxalic acid (9) and in the hydrolysis of C^{14} labeled esters (12). In this laboratory a 1–2% greater probability of rupture of C^{12}–N^{14} bonds than of C^{12}–N^{15} bonds has been found in the deammonation of phthalamide.*

The case of malonic acid is particularly interesting. Calvin, using C^{14} labeled malonic acid, obtained a 12% isotope effect. Bigeleisen and Friedman, using normal malonic, found a much smaller effect with C^{13} than one would expect from Calvin's results, if the assumption is made that the effect with C^{13} should be one-half that found with C^{14}. A theoretical treatment, based on the postulates of statistical mechanics and the absolute reaction rate theory, (6) has been developed by Bigeleisen (2) to account for these effects. Calculations

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A contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario.
[2] *Holder of a National Research Council of Canada Studentship.*
* *The results of this investigation are to be reported in a later paper.*

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based on this theory agree to some extent with his experimental results, but give values much too small to account for the results reported by Calvin. Pitzer (10), using Bigeleisen's method, but making different approximations, has produced a value which is substantially in agreement with Calvin's experimental results.

The disagreement among the various workers on the magnitude of the effect with malonic acid containing C^{13} and C^{14} atoms, as well as the need for conclusive results to corroborate or disprove any theory advanced to explain these effects, suggests the need for further careful work on this problem. This paper presents the results of an investigation carried out in this laboratory to determine the relative probabilities of rupture of C^{12}–C^{13} bonds as compared to C^{12}–C^{12} bonds in malonic acid containing a normal abundance of C^{13}.

Theory

The thermal decomposition of normal malonic acid may be represented by the following equations:

$$C^{12}H_2(C^{12}OOH)_2 \xrightarrow{k_1} C^{12}O_2 + C^{12}H_3C^{12}OOH \quad (1)$$

$$C^{13}H_2(C^{12}OOH)_2 \xrightarrow{k_2} C^{12}O_2 + C^{13}H_3C^{12}OOH \quad (2)$$

$$C^{12}H_2(C^{13}OOH)(C^{12}OOH) \xrightarrow{k_3} C^{13}O_2 + C^{12}H_3C^{12}OOH \quad (3)$$

$$C^{12}H_2(C^{12}OOH)(C^{13}OOH) \xrightarrow{k_4} C^{12}O_2 + C^{12}H_3C^{13}OOH \quad (3')$$

According to Bigeleisen's calculations (2), the approximate ratio of the rate constants $\frac{k_1}{2k_3}$ and $\frac{k_1}{2k_4}$ is given by

$$\frac{k_1}{2k_3} = \left(\frac{m_3^*}{m_1^*}\right)^{\frac{1}{2}}\left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right] \quad (4)$$

and

$$\frac{k_1}{2k_4} = \left(\frac{m_4^*}{m_1^*}\right)^{\frac{1}{2}}\left[1 + \sum_i^{3n-6} G(u_i)\Delta u_i - \sum_i^{3n-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right], \quad (5)$$

where m^*'s are the effective masses of the activated complexes along the coordinates of decomposition and are calculated as being the reduced mass across the bond being broken (3), $\Delta u_i = \frac{hc}{kT}(\omega_{1_i} - \omega_{2_i})$, where the ω's are the vibrational frequencies in cm.$^{-1}$, $G(u_i)$ is a function defined by Bigeleisen and Mayer (5) and ‡ refers to the activated complex.

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The ratio $\frac{k_4}{k_3}$, which determines the relative rates of rupture of C^{12}–C^{12} and C^{12}–C^{13} bonds, is then given by

$$\frac{k_4}{k_3} = \left(\frac{m_3^*}{m_1^*}\right)^{\frac{1}{2}} \Big/ \left(\frac{m_4^*}{m_1^*}\right)^{\frac{1}{2}} = \left(\frac{m_3^*}{m_4^*}\right)^{\frac{1}{2}} **.$$

It is seen that this ratio is independent of temperature and depends only on the reduced mass across the bonds being broken. The ratios $\frac{k_1}{2k_3}$ and $\frac{k_1}{2k_4}$, however, are functions of temperature and should decrease with increasing temperature, $\frac{k_1}{2k_3}$ decreasing to the value $\frac{m_3^*}{m_1^*}$ and $\frac{k_1}{2k_4}$ decreasing to unity, since $m_4^* = m_1^*$.

Calculations

The decomposition of malonic acid has been shown to be of first order (7, 8). Therefore, at any time t

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3 M_3^0 (1 - e^{-(k_3+k_4)})}{(k_3 + k_4)\left[M_1^0(1 - e^{-k_1 t}) + M_2^0(1 - e^{-k_2 t}) + \frac{k_4}{k_3 + k_4} M_3^0\left(1 - e^{-(k_3+k_4)t}\right)\right]}, \quad (6)$$

where M_1^0, M_2^0, and M_3^0 are the initial amounts of the different isotopic species of malonic acid in Equations (1), (2), (3) and (3′) respectively.

When $t = \infty$, Equation (6) becomes

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3 M_3^0}{(k_3 + k_4)\left[M_1^0 + M_2^0 + \frac{k_4}{k_3 + k_4} M_3^0\right]}, \quad (7)$$

and when t is small (6) becomes

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{k_3 M_3^0}{k_1 M_1^0 + k_2 M_2^0 + k_4 M_3^0}. \quad (8)$$

Let α be the atom fraction of C^{13} occurring in the normal malonic acid used. If we assume that the ratio of the carbon isotopes is the same in the methylene and carboxyl positions (see page 198), we can calculate the mole fraction of the three isotopic species of malonic acid in terms of α, i.e.,

$$M_1^0 = (1 - 3\alpha)$$
$$M_2^0 = \alpha$$
$$M_3^0 = 2\alpha.$$

** *Dr. Bigeleisen has pointed out that this is an approximation, the correct value being* $\frac{k_4}{k_3} = \left(\frac{m_3^*}{m_4^*}\right)^{\frac{1}{2}}[1 - \Sigma_i G(u_i^{\ddagger})(u_{4i} - u_{3i})]$. *The term in square brackets, however, is negligible (cf. J. Chem. Phys. 18: 1325. 1950.)*

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Substituting these values in Equations (7) and (8) and making the approximations $k_4 \approx k_3 \approx \frac{k_1}{2}$; $k_1 \approx k_2$ in the denominator we obtain:

At $t = \infty$

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2k_3a}{(k_3 + k_4)(1 - a)}, \tag{9}$$

or rearranging

$$\frac{k_4}{k_3} = \frac{2a}{1 - a}\left[\frac{C^{12}O_2}{C^{13}O_2}\right] - 1. \tag{9'}$$

At t small

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{2k_3a}{k_1(1 - a)}, \tag{10}$$

or

$$\frac{k_1}{2k_3} = \frac{a}{1 - a}\left[\frac{C^{12}O_2}{C^{13}O_2}\right]. \tag{10'}$$

If the thermal decarboxylation of malonic acid is taken to completion, a mass spectrometric analysis of the CO_2 produced gives the values of $\frac{C^{12}O_2}{C^{13}O_2}$ in Equation (9'). The ratio $\frac{a}{1 - a}$ is obtained directly from the $\frac{C^{13}O_2}{C^{12}O_2}$ ratio in the CO_2 produced when a sample of the malonic acid is completely converted to CO_2. The ratio $\frac{k_4}{k_3}$ may be obtained in this way. The same ratio may also be obtained from a mass spectrometric analysis of the CO_2 formed on complete oxidation of the acetic acid produced. The equation obtained for the CO_2 of acetic acid oxidation is

$$\frac{C^{13}O_2}{C^{12}O_2} = \frac{\frac{2k_4a}{k_3 + k_4} + a}{2(1 - 3a) + \frac{2k_4a}{k_3 + k_4} + \frac{4k_3a}{k_3 + k_4} + a}, \tag{11}$$

or solving for k_4/k_3

$$\frac{k_4}{k_3} = \frac{2 - a\left[1 + \frac{C^{12}O_2}{C^{13}O_2}\right]}{3a\left[1 + \frac{C^{12}O_2}{C^{13}O_2}\right] - 2}. \tag{11'}$$

If the first CO_2 evolved from a decomposition experiment is collected and analyzed mass spectrometrically, the $\frac{C^{12}O_2}{C^{13}O_2}$ ratio obtained may be substituted in Equation (10'), together with the previously determined value for $\frac{a}{1 - a}$, and $\frac{k_1}{2k_3}$ obtained. Combination of the values obtained for $\frac{k_1}{2k_3}$ and

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$\frac{k_4}{k_3}$ will give $\frac{k_1}{k_3 + k_4}$, which is a measure of the relative reaction velocities of the two isotopic molecular species M_1^0, and M_3^0.

Experimental

The malonic acid used in the investigation came from two sources. Runs 50–1 to 50–4, including Runs II and *Z*, were made with Eastman Kodak malonic acid. Runs 50–5 to 50–9 involved B.D.H.—C.C. Malonic acid. These chemicals were further purified by recrystallization from water. Three-gram quantities of malonic acid were decomposed in a test tube like reaction vessel, the carbon dioxide and acetic acid produced being swept on by a stream of nitrogen purified by passage through liquid air. The acetic acid was separated in a dry ice–acetone trap and the carbon dioxide collected in barium hydroxide solution as barium carbonate. The reaction vessel was maintained to within ± 0.5°C. of the desired reaction temperature by means of a thermostatically controlled bath.

With the exception of Run *Z*, the oxidation of acetic and malonic acid samples was carried out over hot copper oxide in a quartz combustion tube at 700°–800°C. by a method similar to that described by Rittenberg (11). In Run *Z* the malonic and acetic acids were oxidized using a wet oxidation procedure (14). The carbon dioxide formed was collected and purified in a high vacuum system.

In order to test the validity of the assumption that the ratio of the carbon isotopes is the same in the methylene and carboxyl positions, the methylene carbon atom was converted to carbon dioxide and its $C^{12}O_2/C^{13}O_2$ ratio compared with the average ratio for the three carbon atoms as determined from the carbon dioxide obtained by oxidation of malonic acid. This was done stepwise using Eastman Kodak malonic acid. Acetic acid from a decarboxylation experiment was converted to sodium acetate by means of sodium carbonate. The sodium acetate was heated with soda lime in a stream of pure nitrogen to produce methane of methyl origin. The decomposition products were passed through potassium hydroxide and sulphuric acid bubblers to remove carbon dioxide and any unsaturated hydrocarbon. The methane and nitrogen continued over copper oxide maintained at 750°C. in a quartz tube whereby the methane was oxidized to carbon dioxide and collected as barium carbonate in barium hydroxide solution.

The barium carbonate samples were converted into carbon dioxide for mass spectrometric analysis by acidification with phosphoric acid using standard high vacuum techniques. Experiments in which the decarboxylation reaction was carried to completion were conducted at 138°C. and, where possible, both the carbon dioxide and acetic acid were used in determining the k_4/k_3 ratio. In addition, four decarboxylation reactions were taken to completion at higher temperatures in order to investigate a possible temperature effect. In these experiments the carbon dioxide only was collected.

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As an additional experiment, 100 gm. of malonic acid was decarboxylated at 138°C. and the carbon dioxide sample, formed by the decomposition of the first 1% of the acid, was collected separately as barium carbonate. The results of this experiment permit the calculation of the $k_1/2k_3$ ratio. Combination of this ratio with the previously determined value of the ratio k_4/k_3 gives a value of $\frac{k_1}{k_3 + k_4}$.

Mass Spectrometer Analysis

All carbon dioxide samples were analyzed in a 180° direction focusing mass spectrometer. The ion currents were amplified by a total feedback d-c. amplifier using an 954 electrometer tube in the first stage of amplification. The output was fed into a Leeds and Northrup Speedomax recorder. The $C^{12}O_2/C^{13}O_2$ ratio was obtained from the ratio of mass 44/mass 45 ion currents after applying a suitable correction for the contribution to mass 45 of the molecular species $C^{12}O^{16}O^{17}$. Each CO_2 sample was measured relative to a standard, the standard being a CO_2 sample from a malonic acid oxidation. The absolute C^{12}/C^{13} ratio of the standard varied somewhat from day to day but, since all samples were analyzed relative to that standard, it was assigned a C^{12}/C^{13} ratio of 92.77 and the ratios obtained for the various samples corrected relative to this value. The procedure was to analyze the standard, the sample, and the standard again as rapidly as possible. The analysis was considered satisfactory only if the two standards checked to within 0.1%, the precision of a single analysis. Automatic magnetic scanning was used throughout. A single analysis consisted of six or seven spectrograms, each spectrogram consisting of masses 44 and 45 and then by reversing the direction of scan, masses 45 and 44.

Results and Discussion

In general, the k_4/k_3 ratios calculated on the basis of the acetic acid results are lower than those obtained from the decarboxylation of carbon dioxide. The over-all average value for k_4/k_3, using Eastman Kodak malonic acid, is 1.026 ± 0.002 (cf. Table I).

Using B.D.H. malonic acid the average value obtained at four different temperatures is 1.021 ± 0.002 (Table II), a value in excellent agreement with that found by Bigeleisen and Friedman (4) at 138°C. The magnitude of k_4/k_3 and its temperature independence lends good support to Bigeleisen's calculations as well as to the method of calculating the m^*'s.

The assumption that the methylene carbon had a normal $C^{12}O_2/C^{13}O_2$ ratio appears valid in light of the results in Table III for the E.K. acid. One possible explanation for the lack of agreement between the k_4/k_3 values from E.K. and B.D.H. malonic acid would be that while the E.K. acid was synthesized with no fractionation of C^{13} in the methylene position the B.D.H. chemical had undergone fractionation. If the methylene carbon of B.D.H. malonic acid were

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TABLE I

INTRAMOLECULAR ISOTOPE EFFECT IN NORMAL MALONIC ACID*

Run	$\frac{C^{12}O_2}{C^{13}O_2}$ **		k_4/k_3	
	CO_2 (Decarboxylation)	Acetic acid	CO_2	Acetic acid
50–1	93.96	–	1.026	
50–2	93.87	–	1.024	
50–3	94.22	92.33	1.031	1.019
50–4	94.43	92.24	1.036	1.023
II	–	92.22	–	1.024
Z–3***	93.88	92.06	1.024	1.031
Mean			1.028	1.024
			1.026 ± 0.002	

* *Eastman Kodak malonic acid, runs at 138° ± 0.5°C.*

** *All $C^{12}O_2/C^{13}O_2$ ratios are relative to the $C^{12}O_2/C^{13}O_2$ in a normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e.,* $\frac{(1-a)}{a} = 92.77$.

*** *Acetic and malonic acid samples oxidized by sulphuric acid–phosphoric acid solution.*

TABLE II

INFLUENCE OF TEMPERATURE ON INTRAMOLECULAR EFFECT*

Run	Temperature, °C.	$\frac{C^{12}O_2}{C^{13}O_2}$**	k_4/k_3
50–5	138° ± 0.5	93.70	1.020
50–6	151° ± 0.5	93.70	1.020
50–8	174° ± 0.5	93.88	1.024
50–9	199° ± 0.5	93.74	1.021
Mean			1.021 ± 0.001

* *B.D.H malonic acid.*

** *All $C^{12}O_2/C^{13}O_2$ ratios are relative to the $C^{12}O_2/C^{13}O_2$ in a normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e., $(1-a)/a = 92.77$.*

TABLE III

$\frac{C^{12}O_2}{C^{13}O_2}$ RATIO OF METHYLENE CARBON IN E.K. MALONIC ACID*

Run	$\frac{C^{12}O_2}{C^{13}O_2}$**	
	CO_2 from malonic acid oxidation	CO_2 from methylene carbon
I	92.77	92.79
II	92.77	92.80

**Temperature 138°C.*

***$C^{12}O_2/C^{13}O_2$ ratios are relative to the $C^{12}O_2/C^{13}O_2$ in an normal malonic acid combustion sample arbitrarily chosen as 92.77, i.e.,* $\frac{(1-a)}{a} = 92.77$.

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0.5% less abundant in C^{13} than the average for the three carbon atoms, the results with E.K. and B.D.H. would be consistent.

The value for $\frac{k_1}{k_3 + k_4}$ at 138°C. found with Eastman Kodak acid is somewhat larger than that found by Bigeleisen and Friedman (4). It follows from Bigeleisen's calculations that this effect should decrease to a constant value as the temperature is increased. This was not checked. It is of interest to note in Table IV that there has been a 12% change effected in the ratio of the carbon isotopes between the first and last CO_2 fraction.

Table V compares the results obtained in the present investigation with those of Bigeleisen and Friedman. The agreement is good and lends excellent support to the theory as far as k_4/k_3 is concerned. The disagreement of $k_1/2k_3$ with theory indicates that the model used in calculations of the vibrational frequencies was oversimplified and, as Bigeleisen and Friedman have pointed out, the calculations should be more consistent with experimental results when the vibrational frequencies of malonic acid are known.

TABLE IV

INTERMOLECULAR ISOTOPE EFFECT IN NORMAL MALONIC ACID*

Sample	$\frac{C^{12}O_2}{C^{13}O_2}$	$\frac{k_1}{2k_3}$	$\frac{k_1}{k_3+k_4}$ **
1st CO_2 evolved	97.05	1.046	1.033
Last CO_2 evolved	86.83		

E.K. malonic acid; run at 138° ± 0.5°C.
$\frac{C^{12}O_2}{C^{13}O_2}$ *ratios are relative to malonic acid standard as 92.77.*
***Assuming* $k_4/k_3 = 1.026$.

TABLE V

COMPARISON OF RESULTS

	Bigeleisen & Friedman	Present work		Theory (Bigeleisen)
		B.D.H. Mal.	E.K. Mal.	
$\frac{k_1}{2k_3}$	1.037	–	1.046	1.021
$\frac{k_4}{k_3}$	1.020	1.021	1.026	1.020

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THE AGING OF AMMONIUM CHLORIDE SMOKES[1]

By T. Gillespie and G. O. Langstroth

Abstract

In an extension of earlier work, studies have been made of the time variations in the particle number and size and mass concentration of 'still' ammonium chloride smokes having a wide range of initial mass concentration. Direct measurement of losses to chamber surfaces was an important feature of the experiments since it provided an additional quantity to be satified by theory and permitted a more critical evaluation of the coagulation and loss constants than was previously possible. Satisfactory agreement was found between theory and observation. The dependence of the loss constant on smoke chamber dimensions was found to be in accordance with expectation. The coagulation constant was 4.3×10^{-3} cc. per min. for the least dense, but tended to a larger value for the more dense smokes. A revision of the constants obtained from earlier data indicated that the coagulation constant was little affected by turbulent air motion below a more or less critical value.

It has been shown previously (2) that time variations in the particle number of ammonium chloride smokes in still and moving air are described by equations deduced on the assumption that the rates of coagulation and loss to surfaces are proportional respectively to the square and to the first power of the particle number. Application of the equations to the data permitted evaluation of the loss and coagulation constants. The experiments, however, were limited to an approximately constant initial mass concentration of smoke (40 mgm. per m.^{3}). Furthermore, as was pointed out, the procedure employed in the analysis of data did not lead to a very critical evaluation of the constants for still or slightly moving air, although it was satisfactory for the data obtained with the more rapid air motions.

New experiments have been performed with ammonium chloride smoke in 'still' air over a wide range of initial mass concentration (36 to 420 mgm. per m.^{3}). In many of them the rate of loss of particles to surfaces was determined directly in addition to measurements of particle number and size and mass concentration. These determinations were an important feature since (*a*) they provided data for an additional quantity to be satisfied by theory, and (*b*) they permitted use of a more critical procedure for calculation of the coagulation and loss constants. A special set of experiments was performed with a series of chambers of graded size ranging from 11.8 to 0.0033 m.^{3} in order to test the predicted dependence of the loss constant on the ratio of the wall surface area to the chamber volume.

All the data, including those for the rate of particle loss to surfaces and its dependence on chamber size, were in accord with the theory. In the light of the newer results some revision was desirable in the constants for 'still' and slightly moving air as deduced from earlier data (2). On the basis of this revision it appears that the coagulation constant is little affected by turbulent air motion

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when the average rate of flow through a given small volume is less than 40 m. per min. The increased rate of disappearance of smoke with stirring under these conditions is attributed predominantly to an increased loss rate by impingement of particles on surfaces.

1. Apparatus and Procedure

Three different approximately cubical smoke chambers having volumes of 11.8 m.^{3}, 0.22 m.^{3}, and 0.0033 m.^{3} were used in the experiments. In general the smoke was produced by an external generator in the manner previously described (2), but in some experiments it was formed inside the large chamber by placing a Petrie dish containing a weighed amount of ammonium chloride on a hot plate before a fan. Smoke for the smallest chamber was obtained during the generation of a cloud in the 0.22 m.^{3} chamber. With few exceptions (e.g., Expt. S.B. 10) the reproducibility of smoke production was comparable to that previously reported (2), regardless of the method used; initial particulate numbers and mass concentration varied from the mean for similar conditions by less than 30% and 15% respectively.

Particle number, mass concentration, and surface loss samples were taken periodically over an interval of 4.5 hr. in each experiment. The total volume of smoke drawn from any chamber in flushing and sampling during an experiment did not exceed 2% of the chamber volume. Time was reckoned from a zero at the moment of turning off the mixing fan, i.e., three minutes after generation of smoke was complete.

Particle number was assessed from thermal precipitator deposits in the manner previously described (2). Because of the large value under some conditions, it was desirable to dilute the smoke from the chamber before sampling with the precipitator. A suitable technique was found after considerable study. It involved drawing 170 cc. of smoke from the chamber through a 2.5 cm. diameter valve into a brass vessel containing air by lowering the level of oil in the latter. The smoke and air were mixed by four strokes of a vertical stirrer, and 170 cc. of the mixture was flushed through a short 2.5 diameter tube leading to the precipitator. The mixture was then sampled. The validity of the method was established from the concordance of data for samples taken alternately by direct and dilution methods. The dilution factor was 11.4: 1. The technique was used only for smoke of very large particulate number. It was not used in experiments with the smallest chamber; in these the precipitator was mounted directly on the outside of the box to eliminate the necessity of wasteful flushing.

The electrical precipitators and the technique of obtaining samples with them have been described previously (2). Each deposit was dissolved in 50 cc. of distilled water, and the mass concentration was found from electrical conductivity measurements at 25 ± 0.05°C. with the aid of a calibration curve prepared with known solutions. The conductivity cell had 3.6 cm.^{2} plates 1.5 cm. apart and held 40 cc. of solution; the applied voltage was 110 volts a.c.

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By using freshly boiled distilled water for the solutions the mass of the deposit was determinable with an error of less than 5% over the range 0.1 to 1.5 mgm. The conductivity was directly proportional to the mass.

Direct determinations of the number of particles lost to the chamber surfaces during successive periods throughout an experiment were based on assessment of the number of particles deposited on 19 mm. diameter glass slides placed face up on the bottom of the chamber, face down on the top, and vertically at the midpoint of each side wall. The slides were held flush with the surface on brass or plastic plugs which permitted removal and replacement with a fresh slide at selected times. The intervals between replacements were sufficiently short to avoid deposits characterized by appreciable superposition of particles (1). The technique of counting the particles in each deposit was similar to that used for thermal precipitator slides. The number of particles lost to each surface during each successive period in the life of the smoke was estimated from these counts on multiplying by the ratio of the total area of the surface to the area scanned on the slide.

The procedure used in making the estimates described above involved the assumption that losses were uniform over the area of each chamber surface. A series of subsidiary experiments in which smoke in the 11.8 $m.^3$ chamber was sampled simultaneously at different heights and positions by four thermal precipitators of known characteristics was performed to test this point and for reasons to appear later. The disturbance created by sampling was negligible because of the low sampling rate (3 cc. per min.). No differences were found in the particulate numbers at different heights and positions either in the early or late stages of a smoke. The uniform distribution presumably resulted from the occurrence of convection currents; convective motion of particles was apparent on shining a narrow beam of light into the smoke and examination with a long-focus microscope. Since a uniform distribution of smoke must be accompanied by uniformity in the loss rate over each surface, the results support the assumption made. The necessity of mounting slides flush with a flat surface may be noted also since convective air motion can lead to curious patterns about small obstacles.

Particle size distributions were estimated both for thermal precipitator and for surface loss samples with the aid of a Patterson–Cawood graticule, using substage illumination at a magnification of 950 ×. The former refer to air-borne particles and the latter to particles being lost to surfaces.

2. Experimental Data

The time variation of particulate number is illustrated in Fig. 1. Typical surface loss data are shown in Fig. 2. Each point represents a cumulative loss up to the corresponding time and was obtained by adding together the determined losses for all intervals from the beginning of the experiment. The apparent size distributions of air-borne particles and those being lost to surfaces are compared in Fig. 3 for an early and a late stage in the life of a smoke.

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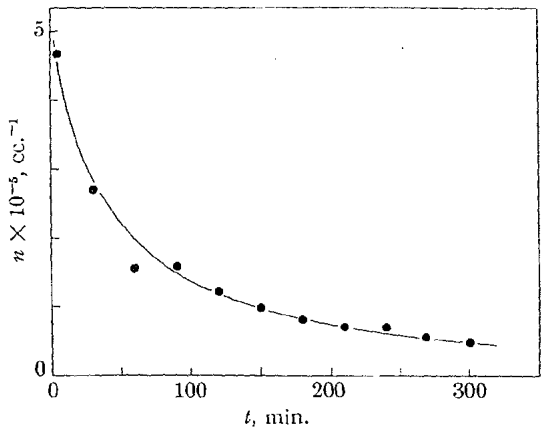

FIG. 1. *Typical particulate number data (Expt. S 29).*

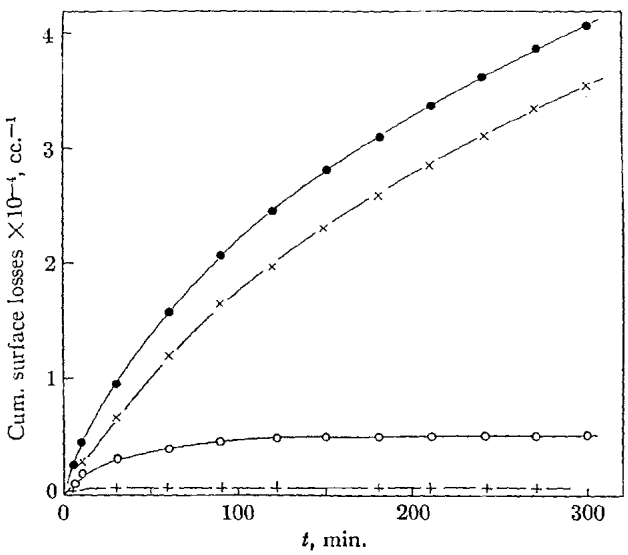

FIG. 2. *Typical surface loss data (Expt. S 29). The plotted points represent the cumulative number of particles lost from the beginning of the experiment to the top (+), side walls (o), and bottom (×) of the chamber, divided by the chamber volume; the sum of the values for all surfaces is indicated by* •.

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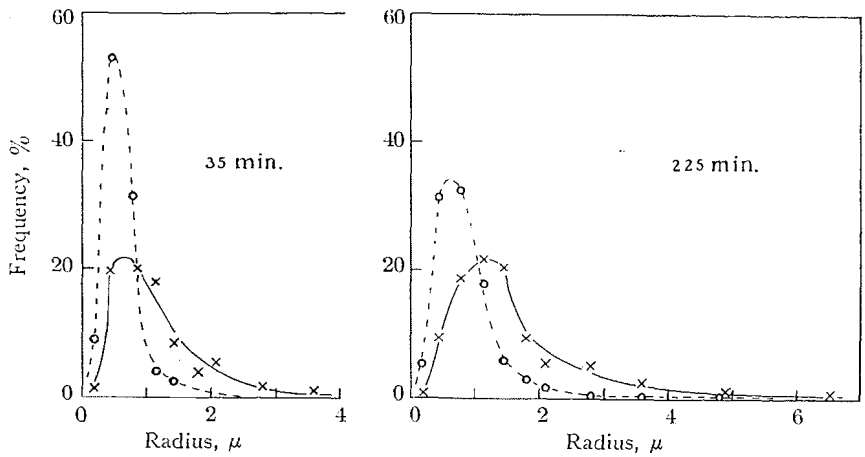

FIG. 3. *Typical size distributions of airborne particles (o) and particles lost to surfaces (×) at early and late stages in an experiment (Expt. S 39). Ordinates represent the per cent frequency of occurrence and abscissas the apparent radii in microns. Each point is plotted at the radius corresponding to the center of its size group.*

Particulate volume and surface loss data for experiments with the 11.8 m.^{3} chamber (Table I*a*), the 0.22 m.^{3} chamber (Table I*b*), and the 0.0033 m.^{3} chamber (Table I*c*), are given in some detail since the method of interpretation differs materially from that used in the past by other workers. Particulate volume data for some experiments in which surface loss was not measured are given in Table II. In these tables, values calculated by the methods of Section 3 are included for comparison with the observed values. Mass concentration data for some of the experiments of Tables I and II are given in Table III.

3. Analysis of the Data

On rather general grounds one may expect (2) that the number of particles per cc. and the mass concentration of a smoke decrease in a time t from initial values of n_0 and m_0 to values given by

$$\ln\left(\frac{1}{n} + \frac{k}{\beta}\right) = \beta t + \ln\left(\frac{1}{n_0} + \frac{k}{\beta}\right), \tag{1}$$

$$\ln(m) = \ln m_0 - \alpha t, \tag{2}$$

where k denotes the coagulation constant, and β and α are constants descriptive respectively of the rate of loss of particles and of mass to adjacent surfaces.

An expression may be obtained easily for the surface loss from systems in which the space distribution of smoke is essentially uniform, as in our experiments (see Section 1). In accordance with the previous treatment (2), the rate of loss of particles to surfaces is taken to be proportional to the number present, i.e.,

$$(dn/dt)_l = -\beta n. \tag{3}$$

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TABLE I(*a*)

EXPERIMENTAL DATA OBTAINED IN AN 11.8 M.^{3} CHAMBER AND A COMPARISON WITH CALCULATED VALUES*

Time (min.)	S 39: M^{**} = 1.02 gm./m.^{3}				S 40: M = 1.02 gm./m.^{3}				S 27: M = 0.5 gm./m.^{3}			
	$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	1.6	1.5	4.3	2.0	1.8	1.7	3.6	2.5	1.9	1.8	2.8	3.4
10	1.8	1.7	8.0	4.8	–	2.0	6.6	5.5	–	–	–	–
30	3.0	2.7	16.2	15.0	3.4	3.2	13.8	16.0	3.5	3.1	13.0	11.5
60	3.8	4.2	24.1	24.8	5.1	5.0	20.5	23.0	4.4	4.8	19.1	18.6
90	5.5	5.8	30.5	33.8	6.5	6.5	26.0	28.3	7.3	6.5	23.5	23.9
120	7.3	7.5	36.6	38.3	7.1	7.0	30.5	28.2	9.1	8.4	27.2	27.5
150	8.8	9.2	41.6	42.2	8.6	10.2	35.5	36.8	10.5	10.2	30.7	30.4
180	10.5	11.0	46.4	46.0	16.8	13.0	39.5	40.5	11.8	12.1	33.9	32.8
210	13.0	13.0	50.3	50.5	14.0	14.0	42.8	41.0	15.3	14.2	36.5	35.8
240	15.7	14.6	53.6	52.4	17.2	16.2	46.0	44.4	20.8	16.2	38.9	37.5
270	17.0	16.7	56.0	54.0	–	–	–	–	18.8	18.4	41.4	39.4

* *From Equations 1 and 4 with constants as given in Table IV.*
** *M denotes the mass of ammonium chloride dispersed per cubic meter.*

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TABLE I(*a*) (*Continued*)

EXPERIMENTAL DATA OBTAINED IN AN 11.8 M.³ CHAMBER AND A COMPARISON WITH CALCULATED VALUES*

Time (min.)	S 29: M^{**} = 0.5 gm./m.³				S 30: M = 0.085 gm./m.³				S 34: M = 0.085 gm./m.³			
	$10^6/n$		$(\Delta n)t \times 10^{-3}$		$10^6/n$		$(\Delta n)t \times 10^{-3}$		$10^6/n$		$(\Delta n)t \times 10^{-3}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	2.4	2.4	2.4	2.8	2.0	2.0	1.4	1.4	1.6	1.6	1.3	1.3
30	3.8	3.7	9.6	10.8	3.1	3.1	4.3	4.3	3.1	2.6	5.6	5.0
60	6.5	5.2	15.6	16.5	4.4	4.4	6.8	7.5	4.3	3.9	8.6	10.0
90	6.4	6.9	20.8	20.5	5.1	6.0	9.0	10.6	5.5	5.0	11.4	12.9
120	8.1	8.3	24.5	24.3	6.9	7.5	11.2	12.6	6.0	6.3	14.1	15.5
150	10.4	10.1	28.1	27.5	10.6	8.0	13.6	13.4	7.7	7.5	16.7	17.7
180	13.0	12.0	31.1	32.0	9.0	10.0	15.4	15.0	8.1	8.6	19.1	18.4
210	14.3	13.6	33.8	32.3	11.0	12.0	17.0	16.8	10.9	9.9	21.0	20.5
240	14.5	15.5	36.3	34.0	14.9	14.0	18.6	18.3	11.0	11.0	22.0	21.5
270	18.9	17.4	38.7	36.0	16.8	15.0	19.9	18.7	12.8	12.4	24.7	22.7

* *From Equations 1 and 4 with constants as given in Table IV.*

** M *denotes the mass of ammonium chloride dispersed per cubic meter.*

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TABLE I(*b*)

EXPERIMENTAL DATA OBTAINED IN A 0.22 M.³ CHAMBER AND COMPARISON WITH CALCULATED VALUES

Time (min.)	R 1 : M = 1.02 gm./m.³				R 2 : M = 1.02 gm./m.³				R 3 : M = 0.085 gm./m.³			
	$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$		$10^6/n$		$(\Delta n)_l \times 10^{-3}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	2.0	2.2	12.8	15.0	1.3	1.2	14.9	14.0	2.4	2.6	3.3	3.1
25	3.9	3.5	45.1	44.0	2.0	2.2	46.9	44.0	3.4	3.5	10.3	10.0
55	6.0	5.7	72.0	75.0	3.7	3.9	74.8	78.0	5.0	4.8	17.4	19.0
85	7.1	8.2	81.7	94.0	6.1	5.9	95.5	100	5.9	6.3	23.9	24.5
115	12.3	11.2	108	107	8.1	8.0	112	113	8.2	7.8	29.5	31.5
145	16.1	14.3	123	119	9.9	10.3	126	124	9.1	9.4	35.2	36.8
175	19.6	18.1	132	126	12.9	12.9	138	132	11.1	11.1	41.3	39.6
205	22.7	21.4	141	131	22.8	15.6	148	135	13.0	12.7	43.8	42.0
235	25.6	27.0	146	140	21.3	18.9	157	140	14.3	14.4	47.1	45.5

See footnote to Table I(a).

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TABLE I(*c*)

EXPERIMENTAL DATA OBTAINED IN A 0.0033 M.³ CHAMBER AND COMPARISON WITH CALCULATED VALUES

Time (min.)	SB 6 : M = 1.02 gm./m.³				SB 7 : M = 1.02 gm./m.³				SB 10 : M = 0.085 gm./m.³				SB 11 : M = 0.085 gm./m.³			
	$10^6/n$		$(\Delta n)_l \times 10^{-4}$		$10^6/n$		$(\Delta n)_l \times 10^{-4}$		$10^6/n$		$(\Delta n)_l \times 10^{-4}$		$10^6/n$		$(\Delta n)_l \times 10^{-4}$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	1.6	1.7	2.8	2.7	1.9	1.9	2.5	2.5	–	–	–	–	3.0	2.9	1.9	1.8
7	–	–	–	–	–	–	–	–	3.0	2.9	2.1	2.6	–	–	–	–
20	3.0	2.9	8.0	9.2	3.7	3.3	8.2	7.8	3.7	3.9	5.2	5.6	4.5	4.0	5.1	5.1
47	5.0	5.2	15.3	15.5	7.3	6.4	14.3	14.8	4.9	6.0	9.2	9.8	5.5	6.5	9.5	10.0
75	9.4	8.4	20.6	19.3	11.2	10.4	18.4	17.8	9.2	9.0	12.0	12.8	9.9	9.9	12.9	12.9
105	13.0	12.7	24.0	22.5	14.5	15.9	21.6	21.2	16.1	12.9	13.7	15.2	14.5	14.7	15.4	15.4
135	16.7	18.6	26.9	24.7	25.0	23.4	23.7	22.6	14.1	17.4	15.2	16.1	16.4	21.1	16.9	16.8
165	27.0	26.4	28.8	25.8	35.3	33.7	25.1	24.2	22.0	23.5	16.6	17.7	22.8	29.5	17.5	18.5
190	29.4	34.4	29.6	26.3	39.0	44.4	25.8	25.5	33.3	29.5	17.8	18.8	47.6	38.3	19.0	18.8

See footnote to Table I(a).

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TABLE II

EXPERIMENTAL DATA OBTAINED IN AN 11.8 M.^{3} CHAMBER WITHOUT DIRECT MEASUREMENT OF SURFACE LOSSES, AND A COMPARISON WITH CALCULATED VALUES

Time (min.)	Mass dispersed, 1.02 gm./m.^{3}				Mass dispersed, 0.5 gm./m.^{3}				M = 0.67 gm./m.^{3}		M = 0.085 gm./m.^{3}	
	S 4 : $10^6/n$		S 5 : $10^6/n$		S 6 : $10^6/n$		S 8 : $10^6/n$		S 10 : $10^6/n$		S 12 : $10^6/n$	
	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)	(Obs.)	(Calc.)
5	1.6	2.1	2.1	1.9	2.2	1.8	1.9	1.9	1.8	1.8	2.7	2.7
35	4.7	4.0	3.3	3.9	3.0	3.2	3.2	3.3	3.0	3.0	3.7	4.0
65	3.0	6.1	6.2	5.9	4.5	4.6	5.5	4.9	5.0	4.8	5.1	5.3
95	8.3	8.3	7.7	8.0	6.9	6.4	6.3	6.4	6.2	6.4	7.6	6.0
125	9.3	10.6	8.8	10.1	6.9	8.0	8.5	8.1	7.5	8.1	8.9	8.2
155	14.8	13.1	12.4	12.4	8.4	9.8	–	9.9	11.4	10.0	10.4	9.0
185	20.8	15.7	15.9	14.9	10.0	11.1	11.4	11.3	11.0	12.0	13.9	11.0
215	20.4	18.3	20.0	17.4	13.2	13.1	14.3	13.1	16.2	14.0	11.2	12.0
245	21.0	21.2	20.0	20.0	14.9	15.0	14.3	15.0	17.3	16.0	14.8	14.0
275	25.1	23.9	23.2	22.9	18.4	17.0	18.6	16.9	18.1	18.1	–	–

See footnote to Table I(a).

TABLE III

MASS CONCENTRATION DATA FOR SOME OF THE EXPERIMENTS OF TABLES I AND II
(The tabulated values are m., (mgm./m.^{3}))

Time, (min.)	S 4	S 5	S 6	S 8	S 10	S 12	S 27	S 44
12	425	357	214	240	325	36.5	235	150
42	336	297	196	189	250	30.0	161	125
72	276	248	157	155	202	29.3	160	107
102	278	228	133	137	187	24.6	148	100
132	221	183	108	115	146	23.8	115	88.2
162	165	173	91.4	96	130	21.6	95	74.0
192	147	131	77.1	83	110	19.7	85.3	69.0
222	137	114	67.3	72.4	93.8	18.3	73.1	60.5
252	118	95	58.0	63.0	82.6	18.5	69.0	52.5
282	96	90	50.3	56.0	72.0	15.4	58.0	46.5

The number of particles lost to surfaces during the period from $t = 0$ to t is then given by

$$(\Delta n)_t = \beta \int_0^t n dt , \tag{4}$$

provided β remains essentially constant. Since both Equations (3) and (4) refer to the average loss per cubic centimeter of the system, $(\Delta n)_t$ is to be interpreted as the estimated loss for the whole system divided by the volume of the chamber. According to Equation (4) a plot of $(\Delta n)_t$ as determined from surface loss measurements against $\int_0^t n dt$ as found from the appropriate area under the n vs. t curve (Fig. 1) should yield a straight line of slope β. The linear character of the curves actually obtained is illustrated in Fig. 4 by examples for three experiments.

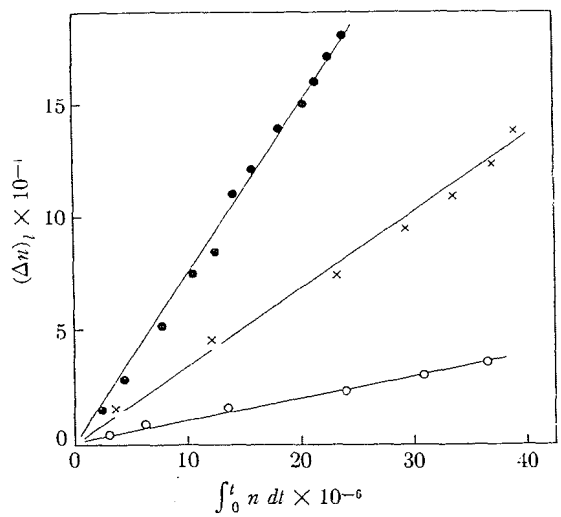

FIG. 4. *Examples of the proportionality between the cumulative surface loss and the area under the particulate number vs. time curve (Expts. SB 10, •; R 2, ×; and S 39, o).*

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Values for k and β were found formerly (2) from plots of $\log\left(\frac{1}{n}+E\right)$ vs. t with the constant E selected by trial and error to yield a straight line. This procedure did not permit a very critical evaluation of the constants for 'still' or slightly moving smoke. With the new data a more critical procedure is possible. It follows from Equations (1) and (4) that

$$\ln(n) + \beta t = -\frac{k}{\beta}(\Delta n)_l + \ln(n_0) . \qquad (5)$$

In accordance with this equation, plots of $\ln(n)+\beta t$, with β found as described above, against $(\Delta n)_l$ yielded straight lines as illustrated in Fig. 5. The value of k was found from the slope of the lines. A few experiments without measurement of surface losses are included in this article; analysis of the data for these was made by the former procedure using an E value consistent with the newer results. Values found for the constants in all experiments are summarized in Table IV.

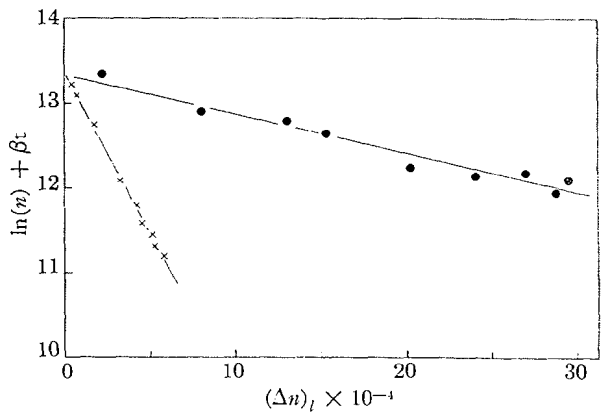

FIG. 5. *Typical* $ln(n)+\beta t$ *vs.* $(\Delta n)_l$ *plots (Expts. S 39,* ×*; and SB 6,* •*).*

4. Discussion

The previous tests (2) of the theory were obtained over a wide range of air motion with smoke of about 40 mgm. per m.^{3} initial mass concentration. It is now apparent from Tables I and II that particulate number data for smokes ranging from 36 to 420 mgm. per m.^{3} initial mass concentration in 'still' air are also adequately described by Equation (1) with experimentally determined values of the constants (Table IV). The average deviation of calculated from observed values was less than 8%. Furthermore, it may be seen from Table I that the cumulative losses of particles to chamber surfaces calculated from Equation (4) using determined β values agree well with observation; the average deviation was less than 6.5%. Two features not previously studied illustrate further the agreement between theory and experiment; (*a*) the direct proportionality between the cumulative surface loss and the area under the particulate number vs. time curve (Fig. 4), and (*b*) the linearity of $\ln(n) + \beta t$

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TABLE IV

A SUMMARY OF THE DETERMINED VALUES OF THE CONSTANTS IN THE EXPERIMENTS OF TABLES I AND II

Expt.	M* (mgm./m³)	m_0** (mgm./m³)	n_0** $\times 10^{-5}$ (cc.$^{-1}$)	$\beta \times 10^3$ min.$^{-1}$	$k \times 10^3$ cc./min.	$k/\beta \times 10^6$	$\alpha \times 10^3$ min.$^{-1}$	α/β	Vol. m.³	$\frac{\text{Surface area}}{\text{Chamber vol.}} \times 10^2$ (cm.$^{-1}$)	$\beta\left(\frac{\text{Chamber vol.}}{\text{Surface area}}\right) \times 10^2$ (cm./min.)
S 12	85	36.0	4.5	0.41	4.1	100	3.0	7.3	11.8	2.62	1.6
S 30	85	–	5.7	0.36	3.9	108	–	–	11.8	2.62	1.4
S 34	85	–	6.7	0.46	3.8	83	–	–	11.8	2.62	1.8
SB 10	85	–	10.9	7.5	5.6	7.5	–	–	.0033	40.5	1.9
SB 11	85	–	3.8	9.0	4.8	5.3	–	–	.0033	40.5	2.2
R 3	85	–	4.4	1.10	3.9	34.8	–	–	.22	10.4	1.1
S 44	250	152	4.2	1.14	5.2	46	4.3	3.8	11.8	2.62	4.4
S 6	500	235	5.8	0.88	4.8	55	5.6	6.4	11.8	2.62	3.4
S 8	500	241	5.3	0.88	4.8	55	5.4	6.1	11.8	2.62	3.4
S 27	500	228	6.9	0.90	5.2	58	4.9	5.5	11.8	2.62	3.4
S 29	500	–	4.8	0.95	4.9	52	–	–	11.8	2.62	3.6
S 10	670	319	8.0	1.23	4.9	40	5.4	4.4	11.8	2.62	4.7
S 4	1020	420	6.2	1.53	6.1	40	5.5	3.6	11.8	2.62	5.8
S 5	1020	375	6.2	1.47	5.9	40	5.4	3.7	11.8	2.62	5.6
S 39	1020	–	8.3	0.99	4.1	40.8	–	–	11.8	2.62	3.8
S 40	1020	–	7.1	1.02	4.8	47.8	–	–	11.8	2.62	3.9
SB 6	1020	–	7.1	9.0	5.1	5.6	–	–	.0033	40.5	2.2
SB 7	1020	–	6.3	8.5	5.6	6.6	–	–	.0033	40.5	2.1
R 1	1020	–	5.6	3.8	5.1	13.3	–	–	.22	10.4	3.7
R 2	1020	–	12.5	3.4	5.1	15.0	–	–	.22	10.4	3.3

* *M signifies the mass dispersed (mgm./m.³).*
** *m_0 and n_0 were obtained by extrapolation of the appropriate time curves.*

vs. $(\Delta n)_t$ plots (Fig. 5). Under all conditions plots of log (m) vs. t for mass concentration data (e.g., those of Table III) yielded straight lines in accordance with Equation (2) and the previous finding (2).

It may be seen from Table IV that the loss constant β for various conditions ranged from 0.36×10^{-3} to 1.35×10^{-3} min.$^{-1}$ with the 11.8 m.^{3} chamber, from 3.4×10^{-3} to 4.4×10^{-3} min.$^{-1}$ with the 0.22 m.^{3} chamber, and from 7.5×10^{-3} to 9.0×10^{-3} min.$^{-1}$ with the 0.0033 m.^{3} chamber. A dependence on chamber dimensions is to be expected since the total rate of loss of particles to surfaces must be proportional to the surface area in contact with the smoke, and also to the product of β and the volume of smoke in accordance with Equation (3). In other words "$\beta \times$ chamber volume/chamber surface area" should be independent of the dimensions of the chamber for smokes having the same characteristics. Some variation in this quantity must be expected for the range of smoke characteristics in our experiments since the loss rate depends on such factors as particle size. Examination of Table IV shows that although the ratio of volume to surface area of the chambers varied by a factor of nearly 16: 1, individual values of the quantity varied by a factor of 2 or less with smokes produced by the dispersal of 85 mgm. per m.^{3} of ammonium chloride, and by a factor of 2.8 or less with those produced by dispersal of 1020 mgm. per m.^{3}

The percentages of the airborne particles and mass lost per minute from the system by impingement on surfaces are given respectively by 100 β and 100 α. These loss rates increased with the initial particle size as shown in Fig. 6. The loss rate of particles of 6×10^{-13} gm. average initial mass, was about 2.5 times greater than that of particles 2×10^{-13} gm. average initial mass, but the mass loss rate was only about 1.4 times greater. The quantity α/β should be equal to the ratio of the average mass of particles lost to surfaces to that of airborne particles (2). Its value lay between 3.6 and 7.3 (Table IV). This is approximately the value estimated from size distribution curves (e.g., Fig. 3), assuming the same density for all particles

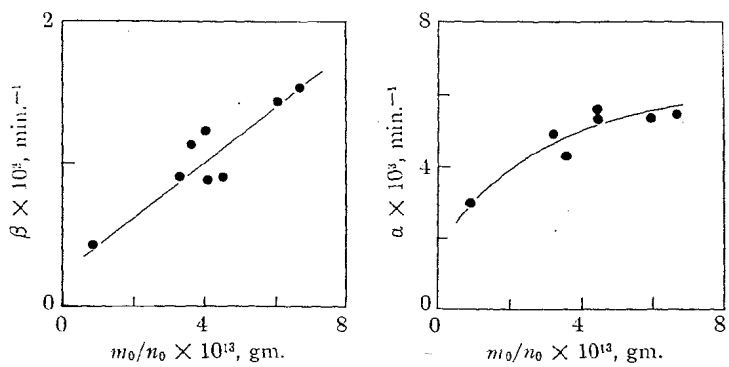

FIG. 6. *The variation of β and α with the average initial particle mass. The data were obtained with the 11.8 m.^{3} chamber.*

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Values obtained for the coagulation constant ranged from 3.8×10^{-8} to 6.1×10^{-8} cc. per min. (Table IV), with an average value of 4.3×10^{-8} cc. per min. for the least dense smoke. Since the average for the most dense smoke was 5.2×10^{-8} cc. per min. there appears to be some tendency for this quantity to increase with increased mass concentration and average particle size. No explanation of this tendency can be advanced at the moment in view of our lack of definite information on the part played by the various mechanisms responsible for coagulation.

The value of the coagulation constant is larger than that previously reported (2) for 'still' air. It is considered more reliable since analysis of the previous data was made by a less critical method. In view of the importance of information on the behavior of systems in moving air, it seemed desirable to re-examine the earlier data to see if they could be described using constants consistent with the newer results. It was found that use of the revised constants as given in Table V led to a slightly better agreement between calculated and observed particulate number data (average deviation 6.0% as compared to the former 6.3%).

The dependence of the revised constants on the degree of air motion (V, m. per min.) is shown in Fig. 7. It appears that the rate of loss of particles to

TABLE V

REVISED CONSTANTS FROM PREVIOUS DATA (2) FOR MOVING AIR

Expt.	V, (m./min.)	$\beta \times 10^3$ (min.$^{-1}$)	$k \times 10^8$ cc./min.	$k/\beta \times 10^6$	$\alpha \times 10^3$ (min.$^{-1}$)	α/β
D 38	0.0	1.13	4.5	40	3.2	2.8
D 40	0.0	1.29	5.2	40	3.4	2.6
W 80	0.0	1.15	4.6	40	3.6	3.1
D 75	1.1	1.8	5.1	28	5.2	2.9
D 74	5.4	3.6	5.4	15	6.2	1.7
D 76	11	4.0	5.6	14	8.3	2.1
D 77	11	3.5	4.9	14	7.4	2.1
W 78	11	3.5	4.6	13	6.8	1.9
W 79	11	3.3	4.6	14	6.2	1.9
D 73	22	5.1	5.1	10	9.0	1.8
D 56	29	5.5	3.9	7	8.1	1.5
D 58	29	5.9	4.2	7	8.5	1.4
D 62	35	7.0	4.2	6	9.6	1.4
D 63	35	7.2	4.3	6	9.6	1.3
D 54	40	8.0	4.8	6	10.8	1.4
D 55	40	8.1	4.8	6	11.0	1.4
W 81	40	8.5	4.3	5	10.8	1.3
D 51	50	9.4	6.6	7	14.0	1.5
D 60	50	9.8	6.9	7	12.8	1.3

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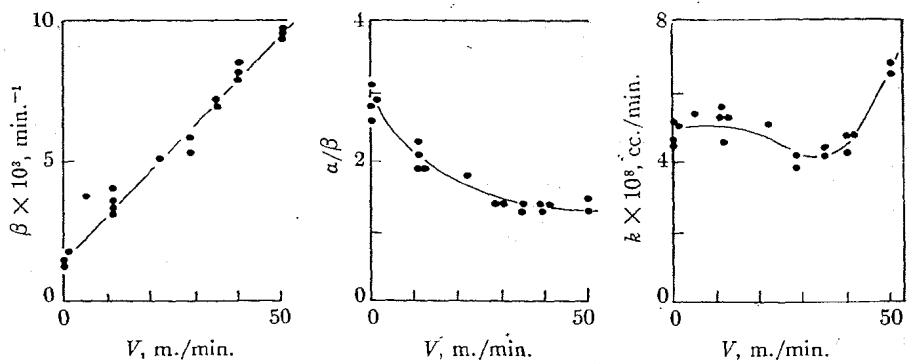

FIG. 7. *Dependence of constants on the degree of turbulent air motion in a 1.12 m³ chamber (from a re-examination of earlier data).*

surfaces increased approximately linearly with the degree of air motion. Since α/β was greater than unity, loss of the larger particles was favored, but since it decreased with increasing air motion this preference was less marked with rapidly moving air. It is not certain that the dip in the k vs. V curve is real. In any event, the coagulation constant was little affected by changes in the degree of air motion until the V value exceeded 40 m. per min.

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THE ESTIMATION OF SOME 17-ALKYL-SUBSTITUTED STEROIDS WITH THE ZINC CHLORIDE – ACETYL CHLORIDE (TSHUGAEV) REAGENT AND A POSTULATED REACTION MECHANISM[1]

By R. H. Cox[2] and E. Y. Spencer

Abstract

The reactivity of a number of 17-alkyl-substituted steroids toward the zinc chloride–acetyl chloride (Tshugaev) reagent has been investigated. Maximum absorption values of reaction products were determined spectrophotometrically. A general parallelism between the Liebermann–Burchard (sulphuric acid–acetic anhydride) and the Tshugaev reagent was confirmed except in the case of 5:6 unsaturated 7-ketosteroids, which reacted to the latter reagent only. Arguments against currently suggested mechanisms for the Liebermann–Burchard reaction are presented, and a new mechanism for color production is postulated which involves ring cleavage. Experimental support is offered.

Introduction

Certain generalizations regarding the relationship between color production and steroid molecular structure have been suggested by Eck and Thomas (9), who determined the reactivity of a number of compounds to the sulphuric acid–acetic anhydride (Liebermann–Burchard) reagent (8, 11). They found that compounds having a double bond at the C_4 or C_5 position with or without an additional double bond or hydroxyl group, and without a ketone group at the C_3 or C_7 position, gave a positive Liebermann–Burchard color reaction. These workers additionally observed (10) that chemical antirachitic activation of sterols by means of such acidic "dehydrating" agents as sulphuric acid–acetic anhydride and zinc chloride–acetyl chloride (Tshugaev reagent) (17) was strictly correlative with color production; all compounds that yielded antirachitically active products gave a positive color test, while those which failed to yield active products did not give a positive test. Such factors as temperature, time, solvent, and proportion and character of reagents used were found to be important in both chemical activation and color production. Eck and Thomas observed a general parallelism as regards color-producing activity between the sulphuric acid–acetic anhydride reagent and the zinc chloride–acetyl chloride reagent.

During the course of collaborative work with Altschul (1) concerning the effect of several steroids on the rabbit, certain 5:6 unsaturated 7-ketosteroids were found to give a positive color reaction with the Tshugaev reagent but no reaction with the Liebermann–Burchard reagent. In the discussion which follows the experimental section, a possible explanation for this exception to the general parallelism observed between these two reagents is offered, based on a new postulate for the mechanism of color production.

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Experimental

Reagents

Zinc chloride reagent: a 20% solution (20 gm. per 100 ml.) of reagent zinc chloride in glacial acetic acid previously refluxed with and distilled from excess potassium permanganate. Acetyl chloride: reagent grade. Chloroform: refluxed with and distilled from excess anhydrous calcium chloride.

Colorimetric Estimation

Zinc chloride reagent (2 ml.) and acetyl chloride (1 ml.) were added to a solution of the steroid in chloroform (1 ml.) contained in a graduated glass-stoppered cylinder (10 ml.). The contents of the cylinder was mixed thoroughly and the resulting solution was heated in a water bath at 65°C. for six minutes to bring about color development; a reagent blank was heated simultaneously. After cooling, both solution and reagent blank were made up to volume (10 ml.) with chloroform.

The use of zinc chloride reagent without acetyl chloride resulted in much slower color development and less color stability. Acetyl chloride hence appeared to be both "sensitizer" and "stabilizer", a dual role suggested in part by Nield, Russell, and Zimmerli (14) from their investigations with an antimony trichloride–acetyl chloride reagent.

Absorption spectra of the color complexes produced with the steroids under investigation were determined over a wave length range of 320 to 600 mμ with the Beckman Model DU quartz spectrophotometer. The λ_{max} and ϵ_{max} values reported in Table I were obtained using steroid concentrations of 0.001%.

In addition to the λ_{max} seen in the table, compounds No. 1-5 showed another absorption maximum at 355 mμ, the value of ϵ_{max} being less than that observed at 525 mμ; compound No. 5, stigmasterol, also gave a further small

TABLE I

λ_{MAX} AND ϵ_{MAX} VALUES OF STEROID COLOR COMPLEXES

No.	Compound (common name)	Chemical name (as derivative of parent hydrocarbon)	λ_{max} (mμ)	ϵ_{max}
1	Cholesterol	Cholest-5-en-3(β)-ol	525	8700
2	Cholesteryl acetate	Cholest-5-en-3(β)-yl acetate	525	8880
3	Cholesterilene	Cholesta-3, 5-diene	525	13,100
4	Dicholesteryl ether	Cholest-5-en-3(β)-yl oxide	525	18,360
5	Stigmasterol	Stigmasta-5, 22-dien-3(β)-ol	525	5900
6	7-Dehydrocholesteryl benzoate	Cholesta-5, 7-dien-3(β)-yl benzoate	390	5850
7	Calciferol	Ergosta-5, 7, 10(19), 22-tetraene-3(β)-ol	395	8500
8	7-Ketocholesterol	Cholest-5-en-3(β)-ol-7-one	445	8360
9	7-Ketocholesteryl acetate	Cholest-5-en-7-on-3(β)-yl acetate	445	8480
10	7-Ketocholesterilene	Cholesta-3, 5-dien-7-one	445	7800

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maximum at 400 mμ. Group No. 8-10, the 7-ketosteroids, gave another absorption maximum at 350 mμ, the ϵ_{max} value in this case being of approximately the same order of magnitude as that measured at 445 mμ. In both groups (No. 1-5 and No. 8-10), the ϵ_{max} at the absorption peak in the region of 350 mμ increased considerably when color development was carried out at a higher temperature or when the heating time was prolonged. Compounds 6 and 7, whose λ_{max} are both somewhat below 400 mμ, still absorbed sufficiently above this wave length to show a noticeable yellow coloration.

The compounds listed above as giving a positive color reaction with the zinc chloride–acetyl chloride reagent also gave a color test with the sulphuric acid–acetic anhydride reagent, except for the three 7-ketosteroids (No. 8-10), which gave no color. The color complexes developed with compounds 1-5 and 8-10 and the zinc chloride–acetyl chloride reagent were highly fluorescent. The fluorescence intensities of the color complexes with cholesterol and 7-ketocholesterol were investigated as a means of quantitative estimation (7).

Discussion

The known vitamers D all possess at the C_{19} position a methylene group formed by an activated (ultraviolet irradiation) rupture of ring B in the sterol precursor used in their preparation. Assuming that all antirachitic activation of sterols involves this same general phenomenon of ring rupture (and all existing evidence suggests that it does), the mechanism of chemical activation and hence color production might be postulated diagrammatically as shown in Fig. 1.

This postulate receives additional support from our observation that calciferol, with a ruptured ring B, gave an immediate color with either reagent, while color development with the other steroids was generally much slower. Color production was also immediate with 7-dehydrocholesteryl benzoate, a

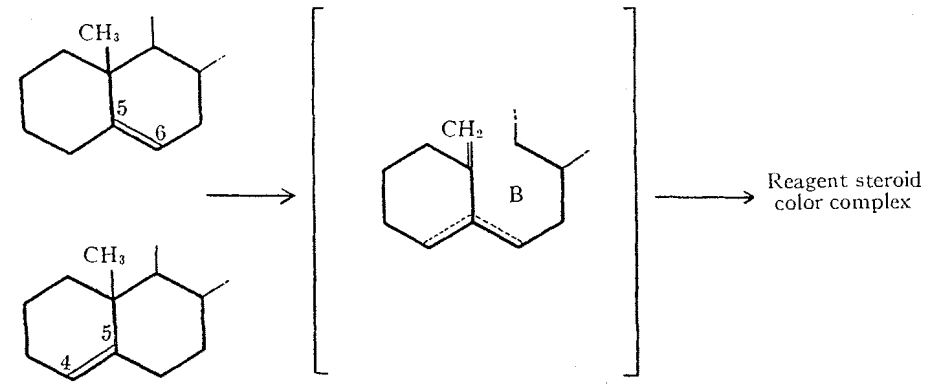

FIG. 1.

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steroid possessing a conjugated (5:6, 7:8) diene system which renders ring B susceptible to cleavage by ultraviolet irradiation. Since antirachitic activation of sterols possessing a single unsaturation (4:5 or 5:6) is possible by chemical means but not by ultraviolet irradiation (10), it appears that chemical agents have the greater activating power. An almost immediate rupture of the more highly susceptible ring B of the 7-dehydrocholesteryl ester, with subsequent rapid color production, would hence be expected on the basis of the postulated mechanism.

Of interest in connection with the foregoing postulate is the observation of Eck and Thomas (10) that color change and antirachitic activation produced by the treatment of cholesterol with sulphuric acid–acetic anhydride were effected in less time when the reaction mixture was irradiated. This suggests a "reinforcement" of the chemical activating force.

The present postulate of ring rupture is substantiated, at least for cholesterol itself, by recent experiments of Raoul and coworkers (15). These investigators showed that cholesterol, in an ionizing medium such as acetyl chloride, was converted to vitamin D_3 through tachysterol as an intermediate, the per cent transformation varying inversely as the cholesterol concentration.

An explanation for the general unreactivity, towards the Liebermann–Burchard reagent, of compounds having a keto group in conjugation with a 4:5 or 5:6 unsaturation (i.e., at C_3 and C_7 respectively) may now be offered, based on the foregoing postulate. The stabilizing influence of an α, β-unsaturated ketone on an alicyclic, six-membered ring system may readily be established in an elementary fashion from its ultraviolet absorption spectrum (5) and optical rotatory power (2). It is suggested that this grouping in either of the previously mentioned positions in the steroid molecule sufficiently stabilizes the particular ring in which the unsaturation occurs that there is no longer sufficient activation of ring B to permit its rupture by the sulphuric acid–acetic anhydride reagent. That is, the 4:5 or 5:6 unsaturation is no longer an "activating" bond but rather a part of a stabilizing influence.

With these observations in mind a possible explanation for color production with the zinc chloride–acetyl chloride reagent and 7-ketocholesterol is offered diagrammatically in Fig. 2.

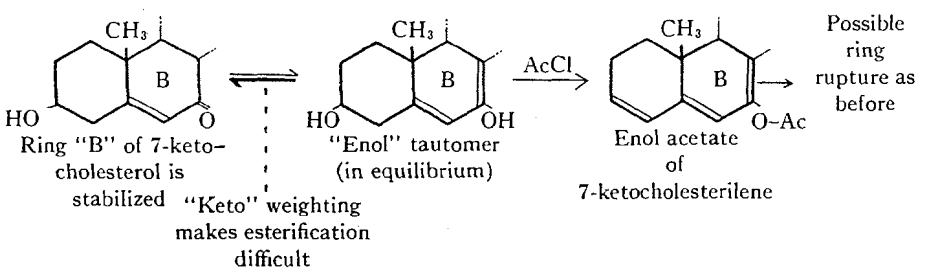

FIG. 2.

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This acetylation of the enol form of 7-ketocholesterol at the C_7 position, together with the simultaneous introduction of an unsaturation in the 3:4 position, has been carried out experimentally by Spencer and Cox (16) using acetyl chloride. However, when 7-ketocholesteryl acetate was refluxed for eight hours with acetic anhydride, it was recovered unchanged, which suggests a possible explanation for the negative color test given with the Liebermann–Burchard reagent.

Although a number of mechanisms have been proposed for color production, none has previously considered ring rupture as a possible factor. The green color of the Liebermann–Burchard reaction has been attributed to the production of cholesteryl esters (4), but cholesteryl acid sulphate in the form of potassium and ammonium salts was found by Eck and Thomas (8) to be antirachitically inactive. Yoder (18) has proposed a mechanism involving dehydration of cholesterol to form dicholesteryl ether, with subsequent cleavage of the ether linkage to give one mole of cholesterilene and one mole of cholesterol, but Nath *et al.* (13) consider that dehydration to cholesterilene occurs directly. McKennis *et al.* (12) have interpreted the observation that on a molar basis the color intensity produced by dicholesteryl ether with the Liebermann–Burchard reagent is essentially twice that of cholesterol itself (a fact also noted with the Tshugaev reagent in the present investigation), as indirect support for Yoder's hypothesis of dicholesteryl ether cleavage by a cholesterol–cholesterilene route. If cholesterilene is a necessary intermediate in the production of color, however, it seems difficult to visualize its rapid formation from cholesteryl acetate by the splitting off of acetic acid in a medium of acetic anhydride—the medium, in effect, which is used to prepare the acetate of cholesterol. Such a phenomenon is even more difficult to accept as fundamental to color development when it is pointed out that both the free alcohol and its acetate show essentially the same rate of color development and the same color intensity.

On the basis of the postulate involving ring rupture, however, such reactions as ether formation and subsequent cleavage, direct dehydration, esterification, and sulphonation (which at the same time exert no appreciable negative effect on the normally activating unsaturation) might all occur to any extent without preventing the simultaneous production of color. Of further importance is the observation that the positive color test given with such compounds as cholestene (cholest-5-ene) and pseudocholestene (cholest-4-ene) (9) could readily be explained, even though these compounds afford no means of introducing the additional unsaturation necessary for the cholesterilene-type intermediates involved in the color mechanisms of other postulates. The twofold value of the ϵ_{max} of dicholesteryl ether would be expected on the basis of the two "B" rings per molecule (i.e., the unusual type of ether cleavage suggested by Yoder would not have to occur at all for color production on the basis of the ring rupture postulate). In addition, the relatively rapid color development noted with cholesterilene and the Tshugaev reagent (also observed by Eck and Thomas (10) with the Liebermann–Burchard reagent) might be attributed to

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a further lowering of the stability threshold of ring B by the introduction of an additional unsaturation in the 3:4 position, rather than to the suggested occurrence of cholesterilene as an intermediate in the process of color production.

Acknowledgments

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STUDY OF NITRATION OF N,N′-DISUBSTITUTED HYDRAZINES[1]

By Jean P. Picard and Jean L. Boivin

Abstract

The nitration of N, N′-disubstituted hydrazines (RNH–NHR) by means of nitric acid – acetic anhydride mixtures has been found to yield, in most cases, the azo derivatives (RN=NR). For example, when R = CH_3, $(CH_3)_2(CN)C$, CH_3CO, or C_2H_5OCO, azo derivatives were formed. When R = HCO, nitrogen, carbon dioxide, and nitrogen oxides were evolved. An exception was observed with N, N′-dibenzoylhydrazine which, under the same conditions, yielded the N, N′-dinitro-N, N′-dibenzoylhydrazine.

Introduction

A recent survey of the literature has revealed the existence of four dinitroso derivatives of substituted hydrazines (3, 4, 12, 13), but the N, N′-dinitro derivatives of disubstituted hydrazines are still unknown. In the light of these facts it was of interest to investigate the formation of nitrate salts and nitro derivatives of some N, N′-disubstituted hydrazines. The substituted hydrazines prepared for the present study are listed in Table I.

TABLE I

Nitration products of disubstituted hydrazines

R–NH–NH–R (I)			R–N = N–R (III)		% HNO_3 in nitrates of I		% N in III	
R	M.p., °C.	Ref.	M.p., °C.	B.p. °C.	Calc.	Found	Calc.	Found
CH_3	168d[a]	5		102	67.7	67.0		
$(CH_3)_2(CN)C$	92–93	12	100–101		43.1	43.9	33.7	34.0
CH_3CO	140	9, 10, 11	104				24.5	24.1
C_6H_5	124	2	68					
HCO	160	8						
C_2H_5OCO	130–131	1	180d[b]	108–110 (15 mm.)				
C_6H_5CO	237–240	5, 7	118–119					

[a] *Isolated as the dihydrochloride.*
[b] *Azodicarbonamide, R = $CONH_2$.*

The N, N′-disubstituted hydrazines (I) were added to nitric acid – acetic anhydride mixture in the ratio of four moles of nitric acid per mole of hydrazo compound. By carrying out the reaction at low temperature, it was found that two of the disubstituted hydrazines used in this study (R = CH_3 and $(CH_3)_2$ C(CN), (Table I) yielded the dinitrate salt (II). As the reaction proceeded, the material went into solution, and simultaneous oxidation took place as seen from the formation of nitrous acid. When the reaction mixture was allowed to warm

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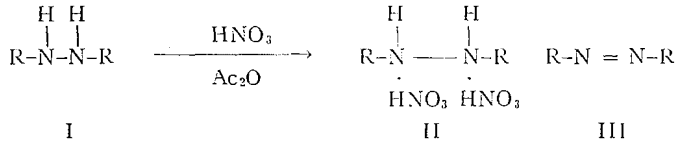
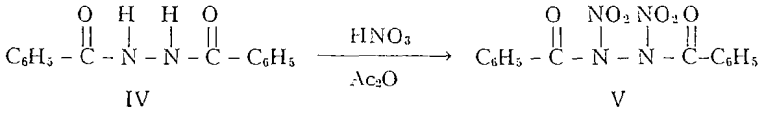
to room temperature, gases were evolved. In most cases the only materials isolated were nitrogen oxides and the azo derivatives (III) of the starting materials.



I II III

For example, N,N′-disubstituted hydrazines, where R = CH_3, C_6H_5, $(CH_3)_2C(CN)$, CH_3CO, or C_2H_5OCO, yielded the azo derivatives only, whereas N,N′-diformylhydrazine (I, R = HCO) was decomposed completely, giving gaseous products.

An exception was observed in the case of N, N′-dibenzoylhydrazine (IV) which, under the same conditions, yielded the N, N′-dinitro-N, N′-dibenzoylhydrazine (V), in admixture with its azo derivative (III, R = C_6H_5CO). This nitrated hydrazine was hydrolyzed by dilute alkalies to benzoic acid and nitrogen oxides. The ultraviolet absorption spectrum of V (Fig. 1), exhibits an absorption band at 2390Å which is characteristic of a secondary nitroamine, as was pointed out by Jones and Thorn (6).



IV V

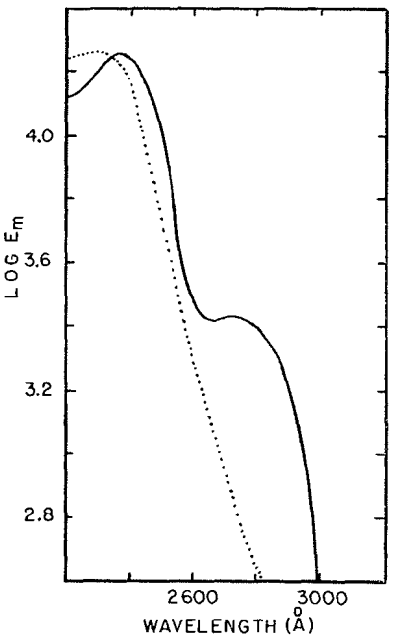


FIG. 1. *Ultraviolet absorption spectra.*
——— *N, N′-Dinitro-N, N′-dibenzoylhydrazine (ethanol).*
..... *1, 9-Diacetoxy-2, 4, 6, 8-tetranitro-2, 4, 6, 8-tetrazanonane (ethanol) (7).*

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This behavior of N,N′-disubstituted hydrazines toward nitric acid – acetic anhydride mixture seems to be dominated by the basic character and reducing power of the hydrazine molecule itself, and appears to be dependent on the substituents employed.

The replacement of two hydrogens of hydrazine by benzoyl groups results in the formation of a weaker base. This effect is not surprising; it is analogous to the effect produced by the replacement of hydrogen in methyl amine by the benzoyl group, whereby a more easily nitrated secondary amine is formed.

Experimental[1]

The action of nitric acid – acetic anhydride mixture on N, N′-disubstituted hydrazines was studied at five different temperatures: –30°C., –20°C., –10°C., 0.5°C., and room temperature. Typical experimental procedures are given below.

Nitrations of N, N′-dimethylhydrazine (I, R = CH_3) and of N, N′-diformylhydrazine (I, R = HCO)

In a flask equipped to catch the gases formed in the reaction mixture were placed nitric acid (100%; 6.3 gm.; 0.1 mole) and acetic anhydride (30 ml.) previously mixed at –30°C. To this solution at –30°C. was added the dihydrochloride of I (3.3. gm.; 0.025 mole) and the mixture was allowed to warm to room temperature over a period of half an hour, during which time gases were evolved and condensed into a dry ice – acetone trap after they had been washed in alkaline solution. The reaction mixture was evaporated at 40°C. (1 mm.) and a trace of unidentified material remained in the flask. In the trap was present a low boiling liquid, b.p. 1–2°C., which was azomethane. When the reaction was held at –30°C., one could isolate from the mixture, by filtration through a sintered glass funnel, a white solid. This crystalline material was very hygroscopic, and after several washings with dry ether was identified as the dinitrate salt of N, N′-dimethylhydrazine. Calc. for $C_2H_{10}N_4O_6$: HNO_3, 67.7%. Found: HNO_3, 67.0%, after making a correction for the water content of the sample.

When N,N′-diformylhydrazine was treated in the same way as above, no nitrate salt could be obtained, and the gaseous product insoluble in alkaline solution was found to be nitrogen. After evaporation of the reaction mixture under reduced pressure, nothing remained in the flask.

Nitrations of Hydrazoisobutyronitrile (I, R = $(CH_3)_2(CN)C$) and Hydrazobenzene (I, R = C_6H_5)

To a solution of nitric acid (100%; 6.5 gm.; 0.1 mole), previously mixed at –30°C. with acetic anhydride (30 ml.), was added I (R = $(CH_3)_2(CN)C$) (4.15 gm.; 0.025 mole) in the solid form. During the addition the temperature was kept at –30°C., then the temperature was allowed to rise slowly. When

[1]*All melting points were corrected against reliable standards.*

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the reaction mixture was held at −25°C. a white solid separated: this was filtered out by suction through a sintered glass funnel. This material, although quite hygroscopic, after several washings with dry ether was identified as a dinitrate salt. Calc. for $C_8H_{16}N_6O_6$: HNO_3, 43.1%. Found: HNO_3, 43.9%, after making a correction for the water content of the sample.

At −20°C. the crystalline compound began to dissolve and a green color appeared. At 5°C., solution was complete. After stirring at 25°C. for half an hour, the solution was poured into 100 gm. of cracked ice and water. The solid that separated out was filtered and washed free from acid with water, m.p. 95–100°C. Recrystallization from ethanol (50%) and from ether raised the melting point to 105°C. Yield 2.5 gm. (60%). Calc. for $C_8H_{14}N_4$: N, 33.7%. Found: N, 34.0%. This compound was identified as the azo derivative by a mixed melting point determination with an authentic sample.

When attempting the nitration of hydrazobenzene in the same manner, the only material isolated was azobenzene, which formed at temperatures as low as −30°C.

Nitration of N, N′-diacetylhydrazine (*I*, $R = CH_3CO$)

To the same proportions of acids as used in the former nitration was added an equivalent quantity of N, N′-diacetylhydrazine. When the reaction temperature was kept at −30°C. for 15 min. a white powder could be isolated by drowning the reaction mixture in ice-water. If the reaction mixture was allowed to warm up, nitrogen and nitrogen oxides were evolved. This white solid material was soluble in ether, and melted at 104°C. with decomposition. A mixed melting point determination with a material prepared by the oxidation of N, N′-diacetylhydrazine with hypochlorous acid at low temperature showed no depression. Calc. for $C_4H_6N_2O_2$: N, 24.5%. Found: N, 24.1%.

Nitration of N, N′-dicarbethoxyhydrazine (*I*, $R = C_2H_5OCO$)

To a solution of nitric acid (100%; 7.0 gm.; 0.11 mole) in acetic anhydride 100 ml.) was added N, N′-dicarbethoxyhydrazine (8.8 gm.; 0.05 mole) at −30°C. The temperature of the colorless mixture was allowed to rise slowly to room temperature while the mixture was stirred. At 0°C. the solid dissolved with production of nitrous acid, and as the temperature rose the color deepened to red. After stirring at 25–30°C. for one hour, the red solution was poured into ice-water (300 gm.). A red oil separated out, ethyl azodicarboxylate, b.p. 108–110°C. (15 mm.). By treatment of this ester with ammonia, azodicarbonamide, a solid, was obtained, m.p. 180°C. with decomposition. Yield, 4.0 gm. (69%).

Nitration of N, N′-dibenzoylhydrazine (*I*, $R = C_6H_5CO$)

The same proportions as in the above described nitrations were used; the precipitated solid in ice-water was extracted with ether. The ethereal solution was washed thoroughly with dilute sodium hydroxide to get rid of the un-

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changed starting material, dried over anhydrous sodium sulphate, and evaporated *in vacuo*. A white crystalline solid remained, m.p. 90–95°C. Recrystallizations from ethanol raised the melting point to 101.5°C. Yield, 2.5 gm. (31%). This compound gave a positive Franchimont test for nitramino groups and reacted with concentrated sulphuric acid, giving off nitrogen oxides. Calc. for $C_{14}H_{10}O_6N_4$: C, 50.9; H, 3.03; N, 16.9%. Found: C, 51.3; H, 3.15; N, 16.0%. From the mother liquor, another compound was obtained as a white powder which, after recrystallization from hot water, has a melting point of 118–119°C. This compound was shown by a mixed melting point determination with an authentic sample to be azodibenzoyl.

Hydrolysis of N, N'-dinitro-N, N'-dibenzoylhydrazine (V)

This compound (0.478 gm.), melting at 101.5°C., was boiled overnight in a solution of 1 gm. of sodium hydroxide in 50 ml. of ethanol (50%). The solution was evaporated to dryness under reduced pressure and the residue dissolved in water (20 ml.). The addition of an excess of concentrated hydrochloric acid to the solution precipitated a solid while nitrogen oxides (mainly NO_2) were evolved. The mixture was extracted with ether. The ethereal extract was washed with water, dried over anhydrous sodium sulphate and evaporated in a weighed platinum dish, leaving 0.375 gm. of solid melting at 120–121°C. After recrystallization from water this compound melted at 122°C. and was identified as benzoic acid. The yield of pure substance was 0.330 gm. or 94% if it is assumed that two moles of benzoic acid were produced from one mole of the material melting at 101.5°C.

Acknowledgment

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SYNTHESIS OF C^{14} CARBOXYL-LABELED PHENYLALANINE[1]

BY G. O. HENNEBERRY, W. F. OLIVER AND B. E. BAKER

Abstract

C^{14} carboxyl-labeled phenylalanine has been synthesized by a modified Strecker reaction. A yield of 27.6% based on sodium carbonate (C^{14}) has been obtained and the distribution of the remainder of the activity in the by-products determined.

Introduction

With a view to using carboxyl-labeled phenylalanine in metabolic studies the literature was surveyed for a feasible method of synthesizing this compound. Gurin and Delluva (2) reported a method for preparing doubly labeled phenylalanine. Kendall and MacKenzie (5) prepared alanine by a modified Strecker reaction which involved the coupling of acetaldehyde with ammonium chloride and sodium cyanide followed by hydrolysis. This seemed to be a method of making phenylalanine which could be adapted easily to the preparation of this compound labeled only in the carboxyl group.

Experimental

I. Preliminary Experiments with Nonactive Materials

Several attempts were made to prepare phenylalanine from phenylacetaldehyde by the application of the procedure of Kendall and MacKenzie, but no phenylalanine was obtained. However, a small yield (6–7%) was obtained by following the directions given by Hickinbottom (4) for the preparation of phenylaminoacetic acid. In this procedure methanol was used as solvent so that the reactants were in a single phase. The yield was increased to 28–30% based on sodium cyanide by using an excess of phenylacetaldehyde freshly prepared by hydrolyzing 1,1-dimethoxy-2-phenylethane and by liberating the amino acid from the hydrochloride with silver oxide instead of with lead oxide.

II. Experiments with Radioactive Carbon

(*a*) *Preparation of Barium Carbonate* (C^{14})

The apparatus illustrated in the figure was constructed to facilitate the transfer of active materials and to eliminate possible contamination by atmos-

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pheric carbon dioxide. It consisted of a wide mouthed, 500 ml. extraction flask with a side arm, *c*, for the admission of nitrogen; three 16 mm. Pyrex test tubes, *a*, were attached to the bottom of the flask by means of 22/40 ground glass joints. The small desiccator, *b*, was held in place by a 29/42 joint, and a fritted glass filter, *f*, was attached to a glass sleeve with DeKhotinsky cement.

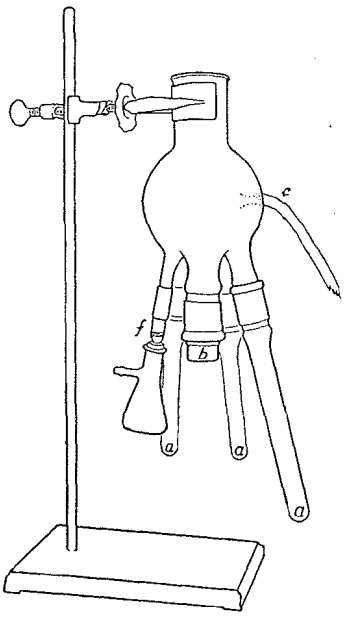

FIG. 1. *Apparatus for processing active carbonates.*

The small vial containing the stock solution of sodium carbonate (C^{14}) was attached to the desiccator opening by means of rubber bands and 1 ml. (0.02 mc.) transferred to each of two 16 ml. test tubes, *a*, with a pipette. To each of these tubes was then added 1 ml. of 0.4% ammonium chloride solution followed by 2 ml. of saturated barium hydroxide. In addition, 3 mgm. of C^{12} in the form of sodium carbonate solution was added to each sample to act as a carrier for the barium carbonate (C^{14}). The volume of liquid in each tube at this stage was approximately 7 ml. The barium carbonate precipitate was digested on a steam bath for one hour, cooled slowly, and separated from the mother liquor (Sample (A)) by means of the sintered glass filter, *f*. It was washed with water, then with acetone, and finally suspended in acetone and transferred to the desiccator, *b*. The acetone (B) was removed by evaporation under reduced pressure. A yield of 141.1 mgm. of dry, very friable barium carbonate was obtained.

(*b*) *Preparation of Sodium Cyanide* (C^{14})

The active carbonate was transferred to one of the reaction tubes, *a*, by means of the acetone (B) which was then evaporated and collected in a "Dry Ice" trap. The carbonate was ground in the tube to a fine powder with a

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snugly fitting glass pestle; 1.450 gm. of sodium azide was then added and mixed thoroughly with the carbonate. The mixture was decomposed at 375°C. and then fused at 630°C. for 20 min. by a method reported previously (3) by two of the authors. The cyanide was distilled as hydrogen cyanide from the reaction mixture (Residue (C)) and trapped in about 10 ml. of water containing 43.2 mgm. of sodium hydroxide. A total volume of 40 ml. was obtained. After concentrating (Distillate (D)) the cyanide solution to approximately 1 ml. *in vacuo*, the volume was made up to 25 ml. with methanol and a 0.01 ml. aliquot (E) withdrawn for radioactive assay. The methanol solution was then reduced to 15 ml. by distillation under reduced pressure (Distillate (F)).

(*c*) *Preparation of Phenylalanine* (C^{14})

The phenylacetaldehyde used in this synthesis was freshly prepared by refluxing 10 gm. of 1,1-dimethoxy-2-phenylethane with 7 ml. of acidic 50% methanol for 10 min. After removing the solvents by distillation under reduced pressure the crude phenylacetaldehyde was added to a solution of 0.5575 gm. of ammonium chloride in 1.7 ml. of water and cooled to 0°C. This was immediately followed by the methanolic solution of labeled sodium cyanide (15 ml.). An additional quantity of nonactive sodium cyanide (0.5375 gm.) dissolved in 6 ml. of 50% methanol was added very slowly to the reaction mixture, which was then allowed to stand at room temperature for 18 hr.

One milliliter of 50% sodium hydroxide solution was added to the reactants and the alcohol removed by distillation *in vacuo* (Distillate (G)). The oily layer was separated from the aqueous solution of inorganic salts (H) by extraction with ether. The ethereal solution was acidified with 10 ml. of 30% (by volume) hydrochloric acid and distilled into a solution of sodium hydroxide (Distillate (I)). The gummy residue was heated with three 10 ml. portions of 3*N* hydrochloric acid at the boiling point to extract the phenylalanine from the gummy mass. After combining the extracts the solution was evaporated to dryness under reduced pressure (Distillate (J)). It was found necessary to treat the crude phenylalanine with fuming hydrochloric acid at room temperature in order to remove the last traces of gummy impurities (K). The phenylalanine solution was reduced to 2 ml. in volume; 5 ml. of ethanol was added and the pH adjusted to 5.96 with alcoholic ammonia. On cooling, phenylalanine separated out; this was then filtered off. The mother liquor was treated with 0.1 gm. of Norite A and the volume reduced to 0.5 ml. An additional amount of phenylalanine was obtained by adding 1.5 ml. of ethanol and cooling to 0°C. The combined crops of phenylalanine were recrystallized from alcohol, and a yield of 304.7 mgm. was obtained. The mother liquor and washings (L) were collected for radioactive assay.

(*d*) *Radioactive Assay of Samples*

All samples were monitored and only those showing activity were assayed. Aliquots of the samples were oxidized following the procedure of Lindenbaum

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et al (6). However, it was found necessary to use a stronger combustion mixture than was recommended. It consisted of 11 gm. of chromic acid, 67 ml. of fuming sulphuric acid (30% sulphur trioxide), and 33 ml. of syrupy orthophosphoric acid (sp. gr. 1.710). Each sample was treated with 17 ml. of this mixture. To the barium carbonate suspension from each combustion, 1 gm. of ammonium chloride was added and the precipitate digested at 100°C. for one hour, then centrifuged.

The barium carbonate plates were prepared for counting as directed by Armstrong and Schubert (1). The foregoing authors suggested drying the precipitate in a stream of air. It was found in the course of the present work that drying *in vacuo* produced more uniform precipitates.

Two counters were used in the assay—a commercial bell-counter with a 2.01 mgm. per sq. cm. mica window, and a bell-counter constructed in our own laboratory. For the latter, India ruby mica, supplied through the courtesy of the Mica Company of Canada, was used. It was found that this mica could be split under water to any desired thickness with the dexterous use of a very fine tungsten needle.

The results of the assays are given in the table. The first row designates the samples as described in the text, the second row gives the percentage distribution of total activity as between the various samples. Corrections have been made for background, variations in counter efficiency, and self-absorption. Samples D, E, F contained cyanide. Accordingly these samples were precipitated with silver nitrate because chromic acid does not oxidize cyanide efficiently. The error introduced by assuming that the self-absorption of silver cyanide is the same as that of barium carbonate will be very small, as less than 2% of the total activity is involved.

	Distribution of C^{14} in the products of the phenylalanine synthesis												
Sample	A	B	C	D*	E*	F*	G	H	I	J	K	L	Phenylalanine
Distribution, %	0	0.1	0	1.8	0.05	0.5	0.2	53.8	1.2	0.2	10.9	3.7	27.6

* *Samples D, E, F (cyanide).*

Acknowledgments

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THE MERCURY PHOTOSENSITIZED REACTIONS OF BENZENE AT HIGH TEMPERATURES[1]

By E. J. Y. Scott[2] and E. W. R. Steacie

Abstract

An investigation has been made of the mercury photosensitized decomposition of benzene at high temperatures. Practically no reaction occurs at room temperature. At higher temperatures the main product is diphenyl although even at 400°C. the maximum value of ϕ_{diphenyl} is 0.1. E_{diphenyl} has been found to be 13 kcal. mole^{-1}. There is evidence that an activated molecule mechanism occurs. The secondary reactions are complex and it is not possible to arrive at a detailed mechanism, but the probable main reaction steps have been pointed out.

Introduction

The work of Bates and Taylor (1) provided the first indication that benzene might undergo a photosensitized reaction with mercury $^3P_1$ atoms. When a mixture of mercury and benzene vapors was exposed to radiation from a mercury vapor lamp, small but definite amounts of hydrogen and methane were formed in addition to a tarry residue possessing an odor of diphenyl. Forbes and Cline (6) later produced evidence that $^1P_1$ rather than $^3P_1$ atoms were responsible for the reaction. This was demonstrated by interposing a sodium nitrate filter (opaque to 1849 Å but not to 2537 Å radiation) between the cell and the lamp. Under these conditions no reaction could be detected although a rapid decrease in over-all pressure was observed when the filter was removed.

The results described in the present paper show that although photosensitization by 2537 Å produces only small conversions at room temperature, appreciable reaction occurs at high temperatures.

Experimental

Two static systems were employed depending on (*a*) the type of cell used, and (*b*) the position of the lamp relative to the cell.

System I comprised the conventional static type of arrangement in which radiation from a mercury-neon low pressure arc was condensed by a lens onto the face of a cylindrical quartz cell (10 cm. long) situated in an aluminum block furnace.

Considerably higher conversions were obtainable using an annular lamp-cell of the type shown in Fig. 1 (System II). The internal walls were constructed of thin quartz with a view to transmitting as much of the resonance lines as

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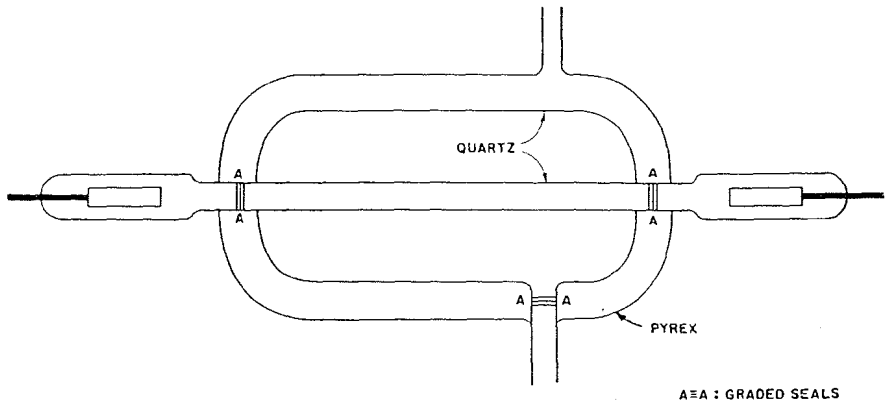

FIG. 1. *Lamp-reaction vessel system.*

possible. The jacket intermediate between the lamp wall and the cell served either as a filter compartment or as the cell proper. In order to ensure that the mercury vapor pressure was constant, a few drops of mercury were allowed to settle in or near the cell depending on whether the reaction occurred at or above 25°C.

The circulatory system III was for the most part of the conventional type. The gases were circulated by a Puddington pump (10) through a two liter ballast volume, a heated mercury saturator, desaturator (at 25°C.) and cell. The volume of the system was 2930 cc. but when the ballast volume was not included in the circuit, the volume became 870 cc. The cell, consisting of a cylindrical quartz tube of 130 cc. capacity, 30 cm. long and 25 mm. diameter, was fixed in juxtaposition to a U-shaped mercury-neon low pressure arc lamp (11 in. long). An apparatus of this type would be expected to give a high intensity of resonance radiation with the minimum proportion of 1849 Å. The latter was reduced by constructing the lamp and cell of 2 mm. thick quartz and by ensuring a 1 cm. air gap in the light path. The lamp reaction system was enclosed in an electric furnace with the electrodes projecting from the furnace. Temperatures were measured by a chromel-alumel thermocouple attached to the back face of the cell.

Mercury cutoffs served to isolate the reaction system from the analytical, storage, and evacuation parts of the apparatus. Pressures could be measured by a manometer or by a McLeod gauge depending on their magnitude.

Analysis

At the conclusion of an experiment, a trap in the system was cooled with liquid nitrogen and circulation continued for 30 min. In this way, methane and hydrogen were separated from the rest of the products. Hydrogen was preferentially combusted on copper oxide heated to 280°C., while the remaining methane was analyzed, if necessary, on a Blacet-Leighton apparatus (2). In

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experiments where a large excess of hydrogen was used, most of the hydrogen was removed by condensing in a silica gel trap at −196°C. and pumping for 30 min.

The C_2–C_5 fraction was then separated by a Ward–Boomer type of still (8) into C_2, C_3, C_4, and C_5 fractions. The carbon and hydrogen numbers and degree of unsaturation of each of these fractions could be found using the Blacet–Leighton apparatus. In point of fact, the amounts of these fractions were so small that this latter procedure was not often adopted.

In some cases the amount of benzene consumed during the reaction was measured by condensing the C_6 + fraction into a standard volume before and after the experiment.

At high temperatures diphenyl was observed as a white sublimate a few inches from the entrance to the furnace. This was sublimed into a trap and sealed off. The diphenyl was then dissolved in a standard volume of ethanol and estimated quantitatively by means of a Beckman Spectrophotometer using 1 cm. cells and 2475 Å radiation. In view of the high extinction coefficient of the diphenyl band at this wave length ($\epsilon = 16750$) small amounts of benzene would not invalidate these results. A sample of the white solid product was obtained by sublimation and found to melt at 68–69°C. On mixing with pure diphenyl, no lowering of the melting point could be detected. Microanalysis gave: C, 93.47; H, 6.52 (Theoretical: C, 93.5; H, 6.52).

In addition a small amount of yellow liquid was isolated, which gave an absorption spectrum similar to that which might be expected from a hydrogenated diphenyl, say $C_{12}H_{12}$. Assuming an ϵ of about 10,000, an approximate estimate of the importance of this compound could be obtained (see Table I).

The residue in the cell would not distil at 500°C. For the purpose of obtaining an approximate carbon balance, this was combusted by passing in oxygen at 550°C. for two hours and the carbon dioxide formed was collected in a trap at −180°C. Carbon dioxide could not be detected when a control experiment under identical conditions was run with no residue in the cell. Although the amount of carbon dioxide was only measured under one set of conditions, it was necessary to clean the cell by oxidizing the polymer in this fashion at the completion of every run. After re-evacuation, the cell was flushed with benzene and evacuated overnight.

Materials

Merck reagent benzene, stored over sodium wire, was used throughout and further purification was effected by bulb to bulb distillation. Hydrogen was taken from a commercial cylinder and purified by diffusion through a palladium tube. The propane, employed in the actinometric experiments, was obtained in cylinders from Ohio Chemical and Manufacturing Company and was also subjected to bulb to bulb distillation.

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Results

Preliminary runs were designed to verify the experimental results already reported in the literature. Using static system I, after 20 hr. exposure at 25°C. with a benzene pressure of 50 mm., only 4 cu. mm. of permanent gas could be detected. When the temperature was raised to 400°C., after five hours' illumination 48 cu. mm. were formed. Under the same conditions without illumination the yield of noncondensables was reduced to zero. It seemed safe to assume that under these conditions, only 2537 Å radiation reached the cell. This was checked by placing a Corning filter No. 791 opaque to 1849 Å but transmitting 50% 2537 Å between the cell and the lamp. The rate of production of the permanent gas was approximately halved.

Since benzene itself absorbed appreciably between 2200 and 2650 Å, the relative importance of direct photolysis was checked by replacing the resonance lamp by a Hanovia S–500 lamp. This lamp emitted a reversed 2537 line but its intensity in the above spectral region was approximately 20 times that of the resonance lamp. The yield of noncondensables was found to be reduced by almost 90%. This afforded satisfactory evidence that the extent of photolysis was negligible compared with the photosensitized reaction.

By using static system II, the experimental conditions could be altered to conform more closely to those used by Forbes and Cline. After 33 hr. at 25°C., the pressure dropped from 51 mm. to 41 mm. and a yellow residue could be observed on the inner wall of the annular cell. 10 cu. mm. of permanent gas was formed at the same time.

In view of the above experiments it seemed certain that 2537 radiation could affect a photosensitized reaction at least at high temperatures. All further experiments were made with the circulatory system III, already described.

Several control runs on the thermal reaction were made. At 400°C. the percentage of diphenyl formed thermally was found to be less than 1% of that formed photochemically. Similarly noncondensable gas has been measured up to 500°C. The effect of the thermal reaction was again found to be less than 1% of the photochemical.

The relative importance of the various products formed in the photosensitized reaction is shown in Table I. This is a typical circulatory run although in general much smaller conversions were used. In order to obtain an estimate of the amount of benzene consumed, the conversion in this case was large (62%). The reaction produces mainly diphenyl which accounts for 55% of the benzene decomposed. The combustible residue in the cell accounts for 20%, hydrocarbons C_1–C_5 for 8%, other diphenyl derivatives for 5%, while 12% remain unaccounted for. The C_2 fraction contains 50% C_2H_6, 30% C_2H_4, and 20% C_2H_2 while the C_3 fraction comprises 85% C_3H_8 and 15% C_3H_6.

Although the amounts of hydrocarbons of low molecular weight are small, the significant quantities of hydrogen present in these compounds indicate that

TABLE I

PRODUCTS OF THE PHOTOSENSITIZED REACTION

Volume of system, 2930 cc. Reaction temp. 400°C.
Volume of reaction vessel, 130 cc. Hg pressure $\sim 2 \times 10^{-3}$ mm.
Circulation rate, 175 cc./min. Exposure, 4 hr.
Initial amount of benzene, 299 micromoles.

	H_2	CH_4	C_2	C_3	C_4	$C_{12}H_{10}$	$C_{12}H_{12}$ (?)	CO_2 from residue	C_6H_6
Cc. formed at N.T.P.	0.17	0.38	0.39	0.16	0.09	—	—	5.02	- 4.18
Micromoles formed	7.7	17.1	17.4	7.1	4.0	51.2	5.0	224	-190.5
Equivalent amount of C_6H_6 (micromoles) calculated from carbon blance	—	2.9	5.8	3.6	2.7	102.4	10.0	37.3	-190.5

a considerable amount of hydrogen must be formed during the polymerization process. The residue is thus highly unsaturated.

The amount of C_1 to C_5 products may be markedly increased by the addition of hydrogen to the reaction as will be seen by comparison of runs 141 and 121 in Table II.

The quenching effects of hydrogen and benzene are of the same order of magnitude so that it can be assumed that in run 141 hydrogen quenches about 90% of the radiation. These results parallel closely those of Schiff and Steacie (11), who found that H atoms produced by a discharge reacted with benzene at room temperature yielding low molecular weight hydrocarbons.

The products found by Forbes and Cline (6) from the mercury photosensitized reaction of hydrogen–benzene mixtures at room temperature were mainly cyclohexadiene and hydrogenated diphenyls. It seems likely by comparison of runs 140, 121, and 126 that the small amounts of hydrogen and gaseous hydrocarbons formed at high temperature are caused by the thermal decomposition of these unsaturated compounds.

TABLE II

PRODUCTS OF THE PHOTOSENSITIZED REACTION OF HYDROGEN-BENZENE MIXTURES AT 400°

Exposure: 30 min.; other conditions as in Table I

Run number	Pressure of benzene (mm.)	P_{H_2} mm.	Products, cc. at N.T.P.					
			H_2	C_1	C_2	C_3	C_4	C_5
141	5.5	53	—	2.47	0.81	0.65	0.19	0.448
121	5.0	0	0.068	0.043	0.039	0.024	—	—
140*	7.0	42	0.090	0.022	0.023	0.010	—	—
126	27.0	0	0.118	0.024	0.022	0.034	—	—

* *The values in this run were obtained by carrying out the reaction at 25°C. for 150 min., pumping off any gas formed, and heating the cell at the conclusion of the run to 400°C.*

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The investigation of the effect of pressure on the formation of diphenyl was limited by the vapor pressure of benzene at the trapping temperature for diphenyl (0°C.). Thus, only pressures between 1 and 25 mm. could be used. The results of these experiments are shown in Table III and Fig. 2.

TABLE III

EFFECT OF PRESSURE ON DIPHENYL FORMATION AT 400°C.

Volume of system, 870 cc. Other conditions as in Table I.

Run number	Benzene press. (mm.)	Time (min.)	$C_{12}H_{10}$ (micromoles)	Run number	Benzene press. (mm.)	Time (min.)	$C_{12}H_{10}$ (micromoles)
219	2	90	13.0	225	18	60	19.8
220	5	30	12.0	211	20	30	8.8
222	5	60	27.3	214	20	60	19.5
224	10	60	28.3	229	20	90	34.0
210	15	30	11.8	226	22.5	60	17.5
223	15	60	27.3	228	25	60	18.0
227	15	90	37.7				

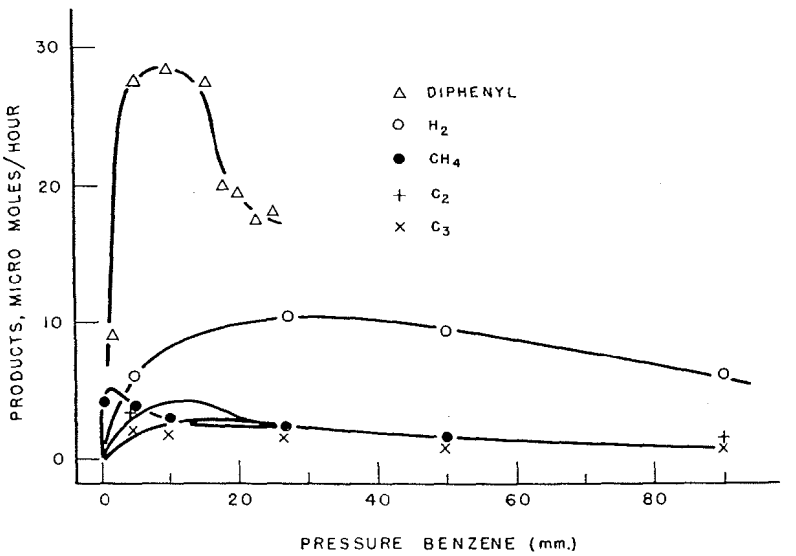

FIG. 2. *Effect of benzene pressure on reaction products.*
Diphenyl values taken from 60 min. runs in Table III.
Other values from 30 min. runs in Table IV.

Table IV and Fig. 2 show the effect of benzene pressure on other products.

The falling off in rates at lower pressures is presumably due to incomplete quenching of resonance radiation. The decrease in rates of all these products at high pressures strongly suggests that some sort of deactivation process is occurring. It is of interest to note that the maximum in the curve of diphenyl occurs at the same pressure (10 mm.) as the corresponding curve in the ethylene photosensitized reaction (7), ethylene possessing a quenching effect similar to that of benzene.

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TABLE IV

EFFECT OF PRESSURE ON THE PRODUCTION OF GASEOUS PRODUCTS

Experimental conditions as in Table I

Run number	Pressure of benzene (mm.)	Time (min.)	(Micromoles)			
			H_2	CH_4	C_2	C_3
109	0.07	30	0.31	0.62	0.45	0.18
124	0.50	15	0.27	0.98	0.36	0.18
122	0.50	30	0.67	2.14	0.62	0.62
123	0.50	60	0.67	3.92	0.80	0.71
121	5.0	30	3.06	1.92	1.74	1.07
120	10.0	30	4.00	1.43	2.05	0.89
88	27.0	15	2.85	0.49	0.80	—
96	27.0	30	5.12	1.25	1.20	0.98
126	27.0	30	5.26	1.07	0.89	1.52
97	27.0	60	11.70	2.05	3.03	3.35
100	27.0	90	13.80	2.94	3.35	2.54
115	50.0	30	4.65	0.85	0.45	0.40
114	94.0	30	3.12	0.45	0.54	0.36

It will be noticed that at low pressure, methane is produced in increasing amounts. This phenomenon has been noted before in mercury photosensitized reactions (5) and it has been customary to associate this effect with atomic cracking reactions. The rate of methane production in the present case is independent of exposure time.

Tables V and VI give the effect of temperature on the rate of disappearance of benzene and on the rate of formation of diphenyl. Arrhenius plots of the data give activation energies of 11.5 and 13 kcal. respectively. The conversions were lower for the diphenyl values, and the results are therefore more reliable.

TABLE V

EFFECT OF TEMPERATURE ON THE RATE OF DISAPPEARANCE OF BENZENE

Experimental conditions—as in Table I
Pressure of benzene—2 mm.

Run number	Temp. °C.	Time (min.)	Benzene reacted (micromoles)	$C_{12}H_{10}$ micromoles	$K_{benzene}$ micromoles/hr.
185	200	240	22.1	3.30	5.5
189	300	30	—	3.57	
179	300	60	18.7	5.65	
177	300	60	15.6	6.89	17
173	300	120	34.3	9.30	
172	300	240	68.7	16.25	
181	325	30	12.5	4.80	25
184	350	30	19.0	5.96	38
182	375	30	22.1	6.52	44
175	400	30	34.3	10.10	
176	400	30	50.0	9.54	
183	400	30	37.9	7.14	79
187	400	30	44.2	10.09	
174	400	60	87.4	14.95	
190	400	60	71.4	15.60	

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TABLE VI

EFFECT OF TEMPERATURE ON THE FORMATION OF DIPHENYL

Pressure of benzene—10 mm.
Experimental conditions—as in Table I.

Run number	T, °C.	Time (min.)	Diphenyl (micromoles per hr.)	$K_{diph.}$	Run number	T, °C.	Time (min.)	Diphenyl (micromoles per hr.)	$K_{diph.}$
171	200	60	1.5	1.5	163	300	360	23.7	4.0
170	200	120	2.6	1.3	162	300	480	31.1	3.9
168	200	240	3.4	0.9	192	350	30	6.3	12.6
169	200	420	4.6	0.7	165	400	10	4.1	24.6
191	300	60	6.7	6.7	166	400	20	8.8	26.4
155	300	60	5.0	5.0	164	400	30	14.3	28.6
160	300	120	9.4	4.7	188	400	30	13.0	26.0
157	300	240	18.8	4.7	167	400	40	17.2	25.8

The effect of temperature on the formation of hydrogen and gaseous hydrocarbons was examined at higher pressure (27 mm.) and temperatures (350 to 500°C.). In this way the amounts of gas obtainable were increased while maintaining small percentage conversions. The activation energies obtained from these results are unexpectedly high: $E_{H_2} = 24.5$ and $E_{CH_4} = 23.5$ kcal. per mole but in view of the relatively small amounts of these products and the complexity of the processes forming them, they are probably not of much significance.

TABLE VII

EFFECT OF TEMPERATURE ON THE PRODUCTION OF HYDROGEN AND HYDROCARBONS

Pressure of benzene—27 mm.
Other conditions—as in Table I.

Run number	Temp., °C.	Exposure time, min.	Micromoles				
			H_2	CH_4	C_2	C_3	C_4
91	350	120	0.38	0.11	0.05	—	—
101	350	180	0.44	0.09	0.10	0.10	—
88	400	15	0.29	0.05	0.08	—	—
87	400	30	0.59	0.10	0.22	—	—
96	400	30	0.51	0.13	0.12	0.10	0.10
97	400	60	1.17	0.21	0.30	0.35	0.14
100	400	90	1.38	0.29	0.35	0.25	0.04
90	450	15	1.03	0.21	0.12	0.08	—
89	450	30	1.85	0.29	0.29	0.25	—
99	450	60	3.29	0.64	0.70	0.43	0.08
92	500	5	0.97	0.13	—	—	—
98	500	10	2.14	0.30	0.24	0.10	0.003
94	500	15	3.73	0.32	0.06	0.05	—
103	500	20	3.82	0.74	0.83	0.34	0.09

Quantum Efficiency

Since most of the experiments were carried out in the region of 400°C. actinometric experiments were made at that temperature. The quantum yield of hydrogen formation in the mercury photosensitized reaction of propane has been found by Bywater and Steacie (4) to be 1.4 at 140 mm. pressure and

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400°C. Using their value, the intensity of radiation was found to be 2.8×10^{-4} Einstein per hr. corresponding to a ϕ_{diphenyl} of 0.1 at 10 mm. pressure. The quantum yield of benzene disappearance is therefore of the order of 0.2.

These values are only to be considered approximate but they show that, even under the optimum conditions, the reaction has a low quantum yield. This supports the view that some kind of deactivating process occurs.

Discussion

The diverse nature of the products indicates that the mercury photosensitized reaction of benzene is extremely complex. However, many of the products, such as hydrogen, C_1 to C_4 hydrocarbons, and probably the cell residue, may be presumed to be the result of secondary reactions at the high temperatures employed. If diphenyl is considered to be the most significant product, as seems to be the case at least at low pressures, then two significant facts must be explained; first, the lack of reaction at room temperature and second, the activation energy of approximately 13 kcal. for diphenyl formation and benzene disappearance.

The effect of pressure on the reaction is quite definite. Increase of pressure causes a decrease in yield of all the reaction products provided quenching is complete. Apparently in the initial step an activated molecule is produced,

$$Hg(^3P_1) + C_6H_6 = Hg(^1S_0) + C_6H_6^*, \quad (1)$$

which is deactivated at higher pressures by (2).

$$C_6H_6^* + M = C_6H_6 + M. \quad (2)$$

Since diphenyl is the main reaction product it is probably formed by an initial rupture of the C–H bond followed by mutual combination of the phenyl radicals generated.

$$C_6H_6^* = C_6H_5 + H \quad (3)$$
$$2C_6H_5 = C_{12}H_{10}. \quad (4)$$

The above steps account for the effect of pressure on the formation of diphenyl but are not sufficient to explain the lack of reaction at room temperature.

It seems most unlikely that Reactions (1), (2), or (3) should have an appreciable activation energy. It, therefore, seems certain that the lack of reaction at room temperature must be due to a re-formation of benzene from C_6H_5 and H. It is known from a variety of evidence that H-atoms react rapidly with benzene (3, 6, 9, 11). The mechanism of re-formation of benzene might therefore be the reverse of Reaction (3), or

$$H + C_6H_6 = C_6H_7 \quad (5)$$
$$C_6H_7 + C_6H_5 = 2C_6H_6. \quad (6)$$

This is, in effect, equivalent to asserting that benzene is an unusually efficient third body for phenyl radical and hydrogen atom recombination.

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In order to account for the activation energy of benzene disappearance and diphenyl formation it seems essential to assume that alternative radical reactions occur which compete with the recombination steps at high temperatures. The most likely reaction of this sort seems to be

$$H + C_6H_6 = C_6H_5 + H_2 \qquad (7)$$

which would be expected to have an activation energy of the order of magnitude of 13 kcal.

Another alternative reaction which cannot be excluded is an attack of a phenyl radical on a benzene molecule by (8).

$$C_6H_5 + C_6H_6 = C_{12}H_{10} + H\ . \qquad (8)$$

This reaction violates the Rice–Teller principle, but seems to occur readily in solution (12).

The above mechanism is by no means complete or established. It seems plausible, however, and there is no point in further speculation on the basis of existing data.

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SOUND VELOCITY AND SOUND ABSORPTION IN THE CRITICAL TEMPERATURE REGION[1]

By W. G. Schneider

Abstract

The velocity and absorption of ultrasound (600 kc.) has been measured throughout the critical temperature region of sulphur hexafluoride. Measurements were carried out for the coexisting liquid phase and vapor phase below T_c, and for the supercritical gas, and simultaneously, observations of the meniscus behavior in the neighborhood of T_c were made. The sound velocity for both liquid and vapor phases below T_c decreased with increasing temperature and became equal at T_c, the velocity at this point being 121.5 m. per sec. In the temperature range from 0.6° below T_c to T_c the velocity in the vapor was greater than that in the liquid. A very high absorption of sound was observed, having a maximum value at T_c and extending over a temperature range of approximately 1°. In the temperature range from T_c to 0.6° below T_c, the absorption in the liquid phase was greater than that in the vapor.

Introduction

An anomalous and very high absorption of ultrasound in the critical temperature region of sulphur hexafluoride has been previously reported (2). A more detailed series of measurements for both the coexisting liquid and vapor phase has now been completed. In these measurements the sound velocity and sound absorption were measured alternately in the liquid phase and vapor phase as the system was heated from a temperature a few degrees below the critical to a temperature several degrees above the critical temperature. The measurements were made with an acoustic interferometer built into a heavy-walled glass tube permitting observations of the meniscus and of the position of the quartz crystals of the interferometer. Sulphur hexafluoride was used in these experiments both because its molecules are nonpolar and spherically symmetric and because it has very convenient critical properties (T_c = 45.55°C., P_c = 36 atm.).

Experimental

Description of the Acoustic Interferometer

The acoustic interferometer, schematically shown in Fig. 1, was of the double crystal type, and was in many respects similar to the interferometer previously described (3). The acoustic chamber consisted of a heavy-walled cylindrical glass tube A, 3 in. long and 15/16 in. internal diameter. Pressure tight seals were obtained on the squared ends of the tube by means of lead washers compressed on the glass cylinder from both ends by plunger C. This plunger also houses the keyed piston P, on which the quartz crystal is mounted, and the metric screw drive. In order to assure perfect alignment of the

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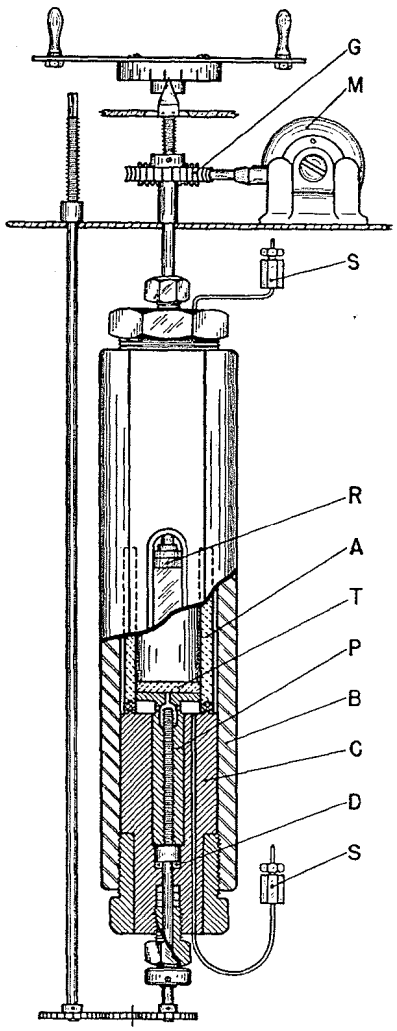

FIG. 1. *Schematic diagram of the acoustic interferometer.*

crystals, the plunger C is machined to a snug fit in the outer cylinder B. The transmitting crystal T is mounted on the lower piston and the receiving crystal on the upper piston. The crystal leads were brought out through capillary tubes and through the pressures seals S. To the upper pressure seal a steel capillary tube was joined for evacuating and filling the interferometer.

By means of a gear arrangement both crystals could be moved into the liquid phase or into the vapor phase. The receiver crystal could also be moved at a slow and uniform rate by the motor M, simply by inserting a tapered pin into the gear drive. The auxiliary apparatus and the procedure for the velocity of sound measurements were exactly as described previously (3). By means of a window slotted into the chamber B, the whole length of the acoustic

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chamber was visible and the position of the crystals as well as the position and behavior of the meniscus could be observed at all times.

All measurements were made at a frequency of 600 kc.

Procedure

Before assembly all parts of the interferometer were thoroughly cleaned. After mounting in a thermostat, capable of maintaining the temperature constant to within 0.002°C., the interferometer was thoroughly evacuated and flushed with pure sulphur hexafluoride. To fill the interferometer to a density close to the critical density, the thermostat was held at a temperature approximately 0.5° below the critical temperature, and gas was admitted slowly from a storage bomb and allowed to condense in the interferometer until the liquid level was exactly halfway up the glass tube A. That the filling obtained in this manner was close to the critical density was evidenced by the fact that, on slowly raising the temperature, the meniscus disappeared without perceptible motion up or down in the tube. All measurements reported in this paper were made on a single filling of the interferometer. It is perhaps also worth emphasizing that the system was not stirred mechanically at any time (apart from the gentle mixing caused by movement of the crystals), and the critical temperature, T_c, was taken as that temperature at which the meniscus was observed to disappear. For the relationships between the critical temperature so defined, and the critical temperature which has been defined for a stirred system, see reference (1).

Readings of the sound velocity were obtained in the following manner. Both crystals were moved into the phase to be measured and positioned about 1 cm. apart. The thermostat was adjusted to the desired temperature and the system was then allowed to thermostat for 12 hr., after which a reading was taken by moving the receiver crystal, by means of motor M, towards or away from the transmitter crystal and recording the resonance peaks. The 12 hr. thermostating period was found to be necessary to obtain reproducible results; readings taken at two hour and also four hour intervals were found to be erratic, but after 12 hr. an apparently stable equilibrium had been reached, the measurements remaining unaltered 24 or 36 hr. later. For the vapor the velocity readings were taken in a region approximately 1 cm. below the top of the interferometer, and for the liquid approximately 1 cm. above the bottom (or approximately 3 cm. below the meniscus level).

Results

Sound Velocity

The velocity of sound measurements through the critical temperature region are summarized in Table I and plotted as a function of temperature in Figs. 2 and 3 for the vapor and liquid phases respectively. To obtain the vapor (or liquid) data, readings were commenced several degrees below the critical temperature and the temperature was raised in steps to several degrees above

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the critical temperature. As stated earlier, each reading was taken only after thermostating at a given temperature for 12 hr. Then to check the reversibility of the system, after the highest temperature was reached, the temperature was lowered in steps back through the critical temperature to the starting temperature, as shown by the black circles on the velocity curve of Fig. 2. A similar reversibility had previously been observed for the liquid phase (2).

TABLE I

SUMMARY OF SOUND VELOCITY AND SOUND ABSORPTION MEASUREMENTS

Temp., °C.	Sound velocity, m./sec.	Absorption coefficient	Remarks*
Vapor phase			
41.917	151.20	0.050	↑
42.003	150.7	0.063	↓
42.732	148.8	0.055	↓
42.742	148.8	0.048	↑
43.605	146.4	0.056	↑
43.757	145.5	0.058	↓
44.280	143.5	0.074	↑
44.626	—	0.097	↓
44.681	141.4	0.099	↓
44.952	—	0.111	↓
45.189	136.8	0.132	↓
45.388	133.7	0.169	↓
45.394	133.2	0.161	↑
45.478	131.2	0.195	↑
45.489	130.7	0.198	↓
45.502	130.7	0.208	↑
45.553	128.2	0.271	↑ Faint opalescence
45.572	128.2	0.292	↓ Opalescence more intense
45.617	125.2	0.374	↑ Opalescence more intense
45.647	124.9	0.410	↓ Heavy opal.—meniscus visib.
45.669	121.6	0.518	↑ Very heavy brownish opal. Meniscus no longer visible
45.688	122.2	0.528	↓ Meniscus no longer visible
45.724	122.1	0.454	↑ Opalescence less intense
45.766	123.4	0.410	↓ Opalescence less intense
45.773	123.3	0.382	↑ Opalescence fainter
45.839	123.9	0.330	↑ Faint opalescence
45.861	123.7	0.328	↓ Faint opalescence
45.936	124.7	0.266	↑ Very faint opalescence
46.084	127.0	0.199	↑ Very faint opalescence
46.178	127.9	0.184	↓ Very faint opalescence
46.329	129.9	0.143	↑
46.340	—	0.157	↓
46.854	134.1	0.065	↑
47.438	137.4	0.043	↓
47.924	139.9	0.044	↑
48.479	142.0	0.041	↓
49.013	144.4	0.041	↑

* ↑ *Indicates measurements were taken during series with rising temperature.*
↓ *Indicates measurements were taken during series with decreasing temperature.*

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TABLE I (*Cont'd.*)

Temp., °C.	Sound velocity, m./sec.	Absorption coefficient	Remarks*
Liquid phase			
42.003	194.8	0.060	↑
43.035	179.0	0.064	↑
43.882	163.6	0.072	↑
44.698	146.7	0.089	↑
45.152	134.7	0.173	↑
45.379	129.2	0.260	↑
45.487	125.5	0.360	↑ No visible opalescence
45.535	124.3	0.395	↑ Very faint opalescence
45.590	122.5	0.456	↑ Faint opalescence
45.639	121.4	0.546	↑ Heavy opalescence—meniscus distinguishable
45.691	121.8	0.540	↑ Very heavy opalescence—no meniscus
45.739	122.6	0.466	↑ Heavy opalescence
45.785	123.3	0.404	↑ Opalescence less intense
45.847	124.2	0.342	↑ Opalescence fainter
45.930	125.2	0.280	↑ Opalescence faint
46.053	126.4	0.221	↑ Opalescence very faint
46.239	128.4	0.177	↑ Opalescence very faint
46.687	133.1	0.120	↑
47.482	137.8	0.049	↑
48.531	142.5	0.048	↑
49.149	145.3	0.049	↑

* ↑ *Indicates measurements were taken during series with rising temperature.*

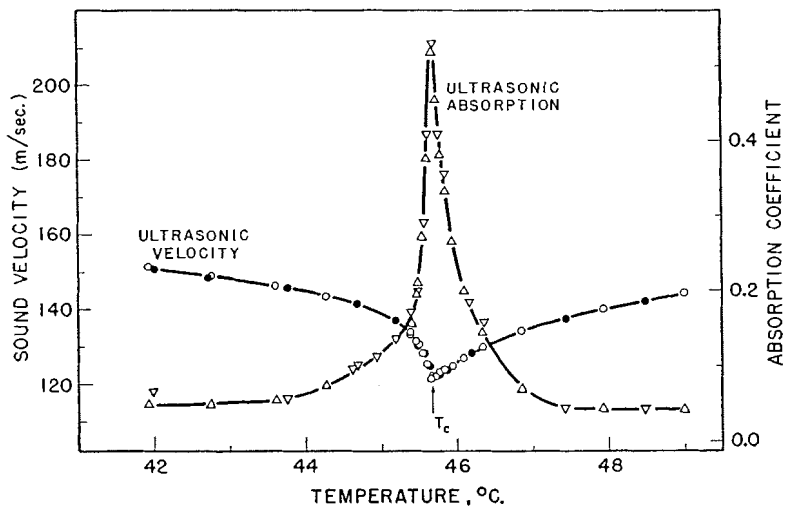

FIG. 2. *Plot of the sound velocity and sound absorption in the vapor phase vs. temperature.*

—○—
—△— } measurements taken with rising temperature.

—●—
—▽— } measurements taken with decreasing temperature.

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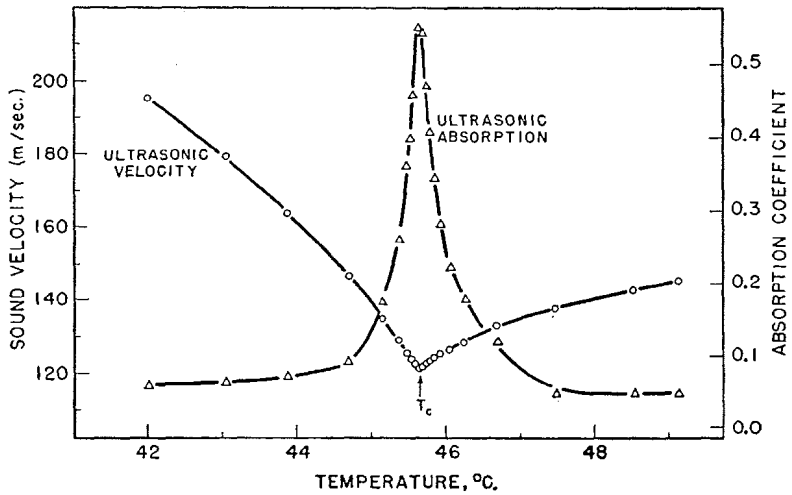

FIG. 3. *Plot of the sound velocity and sound absorption in the liquid phase vs. temperature.*

For comparison the velocity curves of Figs. 2 and 3, which were measured separately for the vapor and liquid phases, are shown plotted together in Fig. 4. In this plot the full curve represents the "liquid" curve, the individual points on the curve having been omitted for the sake of clarity. The circles and the dotted curve represent the vapor measurements. It should be pointed out that the branch of the velocity curve above T_c for the liquid curve shown in Figs. 3 and 4 is actually for a supercritical gas, but differs from the corresponding branch (i.e., above T_c) of Fig. 2 in that for the "liquid" curve the measurements were made throughout at a point approximately 1 cm. above the bottom of the interferometer; for the vapor curve the corresponding readings were taken at the top of the interferometer.

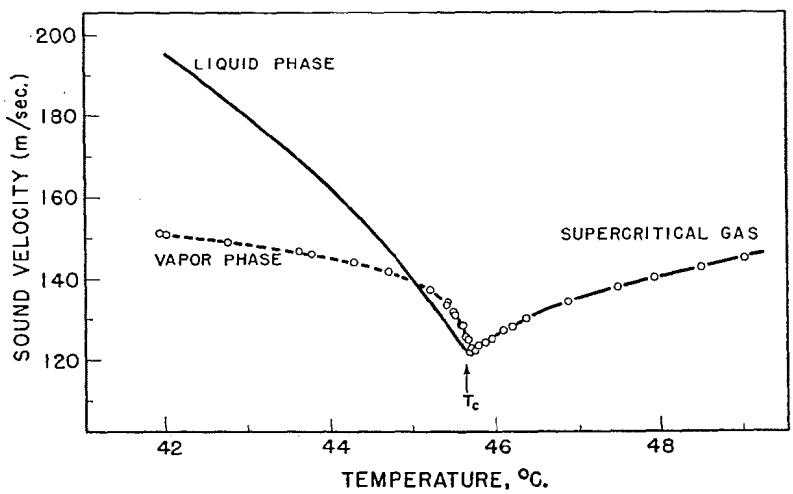

FIG. 4. *Superposition of sound velocity data for the liquid and the vapor phase; the full curve is for the liquid phase, the circles and dotted curve for the vapor phase.*

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As shown in Fig. 4, the velocity curves for liquid and vapor cross at a temperature approximately 0.6° below T_c, and from this temperature up to the critical temperature the sound velocity is higher in the vapor than in the liquid. This difference, which is at present inexplicable, is well outside the limits of experimental error and must be assumed to be real; the excellent superposition of the two curves above T_c lends further support to this conclusion.

Both the liquid and vapor curves exhibit a pronounced minimum in the velocity at T_c, the temperature of meniscus disappearance, which was observed to be 45.65° ± 0.01°C. The minimum in the vapor curve occurs at 45.669°C., and that for the liquid curve at 45.639°C. However, since in this region the temperature was varied in steps of approximately 0.05°, the minima of the two curves can, within this limit, be considered coincident. The sound velocity at this point is 121.5 m. per sec.

The sound velocity can be expressed by the relation:

$$c = \left[-v^2 \gamma \left(\frac{\partial P}{\partial v} \right)_T \right]^{\frac{1}{2}}, \tag{1}$$

where c = sound velocity,
v = volume,
P = pressure,
and $\gamma = c_P/c_v$.

At first sight it would appear that since $\left(\frac{\partial P}{\partial v} \right)_T$ tends to zero at the critical point, the sound velocity should tend to zero. However γ simultaneously tends to infinity and hence c can remain finite. The combination of the two effects gives rise to the characteristic minimum at the critical point.

Sound Absorption

The sound absorption was measured at each temperature simultaneously with the velocity measurements, and was observed to become very large in the immediate neighborhood of the critical point. In Table I, and Figs. 2 and 3, the absorption coefficient is shown as a function of temperature. For the present purpose we have arbitrarily defined the absorption coefficient α by the relation:

$$A = A_0 e^{-\alpha/\lambda x}, \tag{2}$$

where A_0 is the initial amplitude of the sound wave, A the amplitude at distance x, and λ is the wave length. The absorption coefficient α is hence the absorption coefficient per wave length, and was measured directly from the recorded resonance peaks. An example of a recording of the resonance peaks obtained at a temperature close to T_c is shown in Fig. 5. To measure α, a smooth curve was drawn through the crests of the resonance peaks, and a base line was drawn through the troughs; the amplitudes A and A_0 were then

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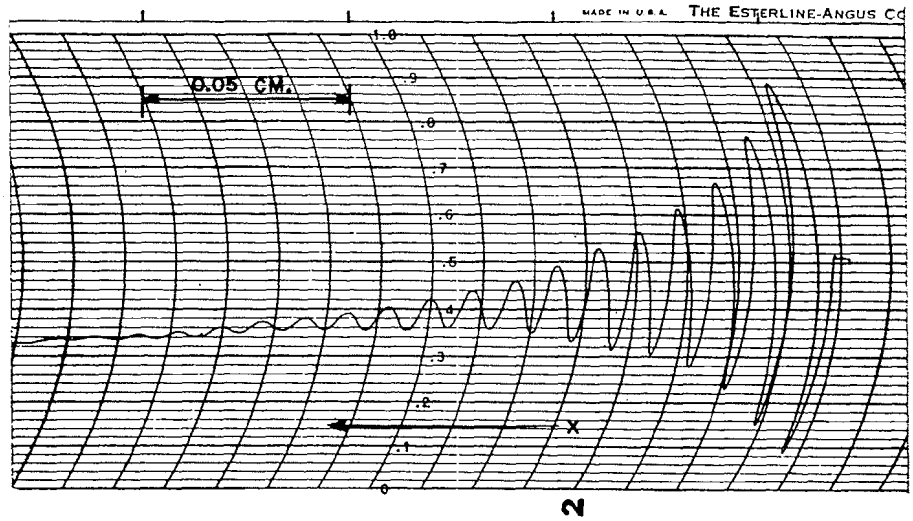

FIG. 5. *Reproduction of a typical recorder tracing obtained at a temperature close to T_c showing a rapid falling-off in amplitude of the resonance peak.*

read off relative to the base line. Thus if A_0 is the amplitude of the first peak obtained in this manner, and A_{10} the amplitude of the 20th peak (since the peak separation is $\lambda/2$), we have from Equation (2):

$$\alpha = \frac{1}{10} \ln \frac{A_0}{A_{10}} . \tag{3}$$

The α obtained in this way is not the true absorption coefficient, and, since a double crystal interferometer was used in this work, it is not clear what relation it bears to the absorption coefficient as ordinarily defined. In the present work, however, we are concerned only with relative values of α as a function of temperature, and an exact analysis is not required.

As shown by the curves in Figs. 2 and 3, the absorption coefficient increases rapidly just below the critical temperature and attains a maximum value at T_c, the point at which the meniscus disappears and the sound velocity attains a minimum value. Above this temperature the absorption again diminishes to a low value. The absorption measurements could be accurately reproduced with either a stepwise increase or decrease in the temperature (and with a 12 hr. period of equilibration before each measurement) (see Fig. 2), and hence the resulting absorption curve is to be regarded as a characteristic property of a system in the critical temperature region. It is noteworthy, in this connection, that the temperature range over which high sound absorption occurs is approximately 1°, and extends over a range both below and above the critical point.

Fig. 6 shows a superposition of the absorption curves which were measured separately for the liquid and vapor phases. As was the case with the sound velocity curve, the branches of the absorption curve above T_c superimpose to

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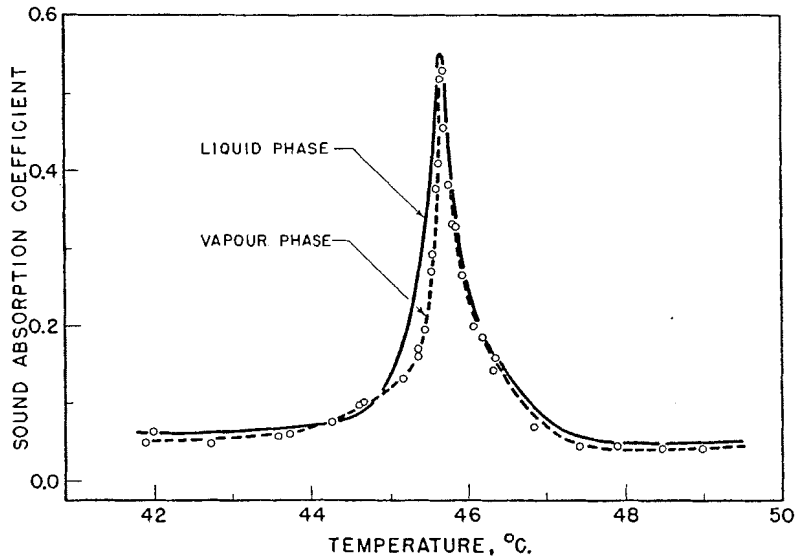

FIG. 6. *Superposition of the sound absorption data for the liquid and the vapor phase; the full curve is for the liquid phase, the circles and the dotted curve for the vapor phase.*

within the experimental error. Over a temperature interval extending to approximately 0.6° below T_c, the absorption curve for the liquid is considerably higher. We noted earlier that in this temperature region the sound velocity curves for the two phases crossed, the vapor exhibiting the higher velocity.

To explain the high sound absorption in the critical region two alternative explanations suggest themselves. The first of these is based on a simple diffraction of the sound beam, the second on the behavior of a relaxation phenomenon which is characteristic of the system in this region.

To consider the first of these two alternatives we may regard the sound beam as undergoing a "scattering", similar to the scattering of light in the critical region. The latter is due to the characteristic critical opalescence, and it is noteworthy that the opalescence is most intense in the temperature region where the absorption curve exhibits a maximum. (See Table I.) In order to obtain scattering, the scattering "centers" must be of the order of magnitude of the wave length, which in our experiments near T_c was approximately 0.2 mm. To realize scattering centers of this magnitude, one must assume the existence of fairly large droplets in the vapor phase, and gas bubbles in the liquid phase. Under the influence of a gravitational field it is difficult to see why such a system should be stable over long periods of time.

According to our second model we postulate the existence of a configurational relaxation effect. If the spatial configuration of the system is different before and after passage of the sound wave, an entropy change takes place which leads to an excess absorption of sound energy. Alternatively, if molecular

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clustering is assumed, the clusters may be partially disrupted during the rarefaction phase of the sound wave, and during the ensuing compression do not have sufficient time to re-form, or else they are re-formed with a different configuration. In other words the "structural" changes taking place in the system follow a time dependence which causes them to be out of phase with the sound field.

Acknowledgment

I am greatly indebted to Mr. A. Dubois and Mr. W. A. Stevenson for the construction of the acoustic interferometer and other apparatus used in the present work.

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COMPOSITIONAL HETEROGENEITY OF BUTADIENE–ACRYLONITRILE COPOLYMERS PREPARED IN EMULSION AT 5°C.[1]

By W. H. Embree, J. M. Mitchell, and H. Leverne Williams

Abstract

The copolymerization of butadiene and acrylonitrile is very similar to the copolymerization of butadiene and styrene. Polymers predominantly butadiene may be studied by conventional solution techniques but the study of polymers rich in acrylonitrile requires improved solvents for these materials. Polymerization rates are greatest for monomer ratios approximating equal proportions. The mercaptan modifier disappears much more slowly than in the butadiene–styrene system, the regulating index approximating unity. The number average molecular weights calculated from the mercaptan disappearance curves indicate uniform polymer molecular weights to relatively high conversions after which there is a decrease. The viscosity data indicate a rise in viscosity with conversion, which effect is overcome for charges rich in acrylonitrile by the lessening of branching, the more rapid disappearance of mercaptan at high conversion, and the tendency of polymers containing over 50% acrylonitrile to show very low dilute solution viscosities in the solvents tested. Viscosity molecular weights have been calculated and estimates of the molecular weight distribution made. These distributions appear to be quite narrow and the usual broadening at higher conversions is prevented by the increased modifier consumption and increased vinyl content of the polymer prepared with 50 parts acrylonitrile in the charge. The bound acrylonitrile has been determined at various conversions and the reactivity ratios have been found to be $r_1 = 0.28$ and $r_2 = 0.02$ for emulsions and $r_1 = 0.18$ and $r_2 = 0.03$ for oil phase portion only. Q is 0.74 and e is 1.47 as calculated by the Alfrey–Price equations.

Introduction

Many acrylonitrile polymers and copolymers have been studied but the data published on the emulsion copolymerization of butadiene and acrylonitrile are scarce. The most directly useful results are those of Wall (23, 24) and of Semon (19, 20). Some data obtained during the copolymerization of other monomers with acrylonitrile (4, 5, 6, 9, 15) may be used to calculate the approximate behavior of the butadiene–acrylonitrile system. The purpose of this work is to co-ordinate the data and to fill in the gaps in the published information.

The butadiene–acrylonitrile system is complicated by two factors. The polymer is insoluble in butadiene which may make the oil phase portion of the system heterogeneous. Acrylonitrile is appreciably soluble in water and is extremely reactive towards many common materials such as mercaptan, peroxides, amines, etc. Thus the distribution of acrylonitrile between the oil and water phases and its interaction with polymerization recipe ingredients must be considered.

[1] *Manuscript received in original form September 13, 1950, and, as revised, November 28, 1950.*

Presented at the High Polymer Forum, Chemical Institute of Canada, Ottawa, June 15, 1950. Contribution from the Research and Development Division, Polymer Corporation Limited, Sarnia, Ontario, Canada.

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Two series of experiments were conducted some years apart. In the first a recipe similar to one used for butadiene–styrene studies was used (see (13)). When interest became centered around low temperature polymerizations to yield better and more uniform butadiene-styrene copolymers, the activated recipes (see (12, 22)) were applied successfully to the butadiene–acrylonitrile system.

Techniques

The polymerization technique was that generally used in the rubber industry (3, 12, 13, 16, 22). Modifier disappearance curves and intrinsic vistex viscosities were determined conventionally (16). Bound acrylonitrile was estimated by Kjeldahl nitrogen determinations. The fractionation curves were prepared from the usual solvent–nonsolvent precipitation procedure (see (14)). Gel (3, 13) was considered as all insoluble material in the particular solvent, and the swelling index (3, 13) as the ratio of the weight of swollen gel to weight of polymer in the gel. The dilute solution viscosity (3, 13) was measured on the soluble portion of the dry polymer. Monomer charge ratios are weight to weight, which with butadiene and acrylonitrile are very nearly mole to mole.

Experimental

Dilute Solution Viscosity and Gel of Polymers Prepared at 30°C.

The effect of degree of conversion on the solution properties of polymers is shown in Table I. The gel and swelling index remain relatively constant but

TABLE I

EFFECT OF CONVERSION ON THE GEL, SWELLING INDEX, AND DILUTE SOLUTION VISCOSITY

Time (hr.)	% Conversion	% Gel	Swelling index in chlorobenzene solution	Dilute solution viscosity in chlorobenzene solution
71.5/28.5 charge ratio butadiene to acrylonitrile				
4	37.1	49	65	2.88
6	46.2	46	50	2.74
8	57.3	44	82	2.64
11	68.2	70	67	3.49
15	80.1	46	53	1.92
20	86.7	41	52	0.84
60/40 charge ratio butadiene to acrylonitrile				
3	22	12	19	1.95
5	56.6	25	41	2.84
7	77.7	49	49	1.73
10	93.7	72	38	0.91
14	96.2	94	31	0.86
19	96.8	94	26	0.82

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the dilute solution viscosity of the soluble portion rises to a maximum and then decreases. Somewhat similar results are obtained for the dilute solution viscosity of a 60–40 butadiene–acrylonitrile charge. There tends to be an increase in the amount of gel with conversion more in keeping with the lower dilute solution viscosity. The latter may also be due to the higher acrylonitrile content of the polymer or reduced effectiveness of the modifier which was unchanged from the previous experiment, i.e., 0.45 part of dodecyl mercaptan per 100 parts monomers.

Fractional Precipitation of Polymers Prepared at 30°C.

Three of the polymers were submitted to fractional precipitation from chlorobenzene–methanol solvent–nonsolvent system. The data for the samples are shown in Table II. The gel content of the second sample appears high

TABLE II

SAMPLES FOR FRACTIONATION

Sample	Charge ratio	% Conversion	% Gel	Dilute solution viscosity
T-551-1*	75/25	74.5	—	—
AM-4, 16-5-4	71.5/28.5	68.2	70	3.49
AM-4, 21-6-3	60/40	77.7	49	1.73

* *A sample prepared in the Pilot Plant 5-gallon glass lined autoclave.*

in view of the high dilute solution viscosity. The integral and differential distribution curves are in Fig. 1. T–551–1 starts to precipitate with 45 volume % methanol content. There is a peak at 45.6 volume % and most of the polymer has precipitated when 46 volume % has been reached. AM–4, 16–5–4 begins to precipitate with 44 volume % methanol, reaches a slightly higher peak at 45 volume % and is largely precipitated with 46 volume %. AM–4,21–6–3 being of lower viscosity does not start to precipitate until 46 volume % methanol has been reached, a short peak is formed at 47 volume % and the polymer has largely precipitated by 48.5 volume % methanol. Thus the behavior of the polymers was qualitatively similar to that observed in the butadiene–styrene system but the precipitation becomes evident only at high methanol contents of the mixed solvent-nonsolvent, and the molecular weight distribution appears very narrow.

A thorough study of sol–gel equilibrium, swelling index, viscosity, and fractionation curves is required since considerable evidence in the above work was found for strong dependence of some of these variables on solvent to polymer ratio.

Effect of Charge Ratio on the Rate of Conversion at 5°C.

The effect of variation of the butadiene–acrylonitrile charge ratio on the rate of conversion was studied. The data are in Table III and show clearly that 63/37 and 50/50 charge ratios polymerize at the fastest rates. The cause for this optimal rate of conversion will be discussed later.

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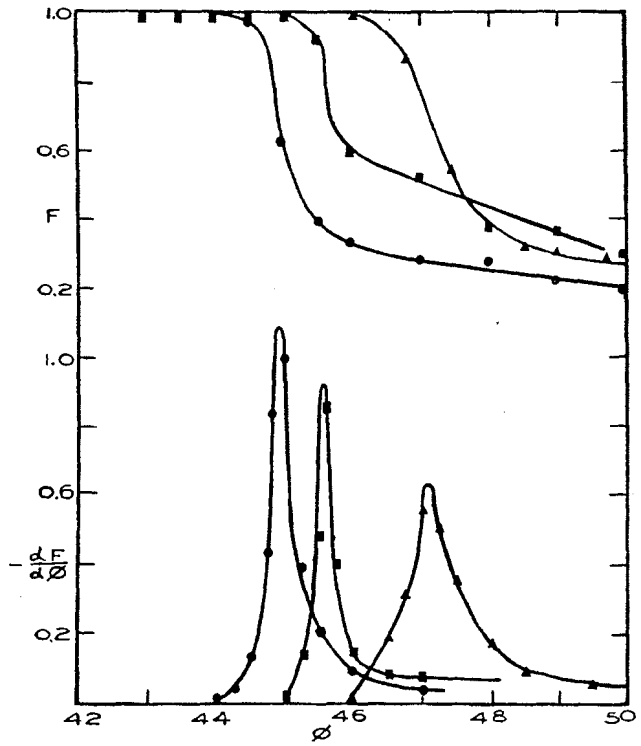

FIG. 1. *Fraction of polymer in solution (F) as a function of volume per cent of methanol (ϕ) in chlorobenzene-methanol mixture and differential curves ($-dF/d\phi$) for sample AM-4, 16-5-4 (●), T-551-1 (■) and AM-4, 21-6-3 (▲).*

TABLE III

EFFECT OF CHARGE RATIO ON THE RATE OF CONVERSION AT 5°C.

Charge ratio—butadiene/acrylonitrile	% conversion in 17 hr.
75/25	75.8
63/37	96.7
50/50	93.8
25/75	79.0
0/100	0.0

Modifier Disappearance Curves at 5°C.

Some measure of the molecular weight heterogeneity of the polymer may be obtained by measuring the modifier disappearance curves. Titration of the mercaptan was impossible in the normal charge; even without polymerization there appeared to be no residual mercaptan. This was caused by a reaction between the acrylonitrile and the mercaptan (1), whereby the mercaptan was no longer titratable although it still functioned as a modifier or chain transfer agent. This reaction is:

$$RSH + CH_2 = CHCN \rightarrow RSCH_2 - CH_2CN$$

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However, this difficulty could be overcome by adding the mercaptan, 0.7 part MTM* per 100 parts monomer, after the acrylonitrile had become diluted with the butadiene and distributed between the two phases. The most convenient method was to add it by syringe and needle to the completed charge optionally in the form of an alcoholic solution. This technique proved adequate to obtain the modifier disappearance data shown in Fig. 2.

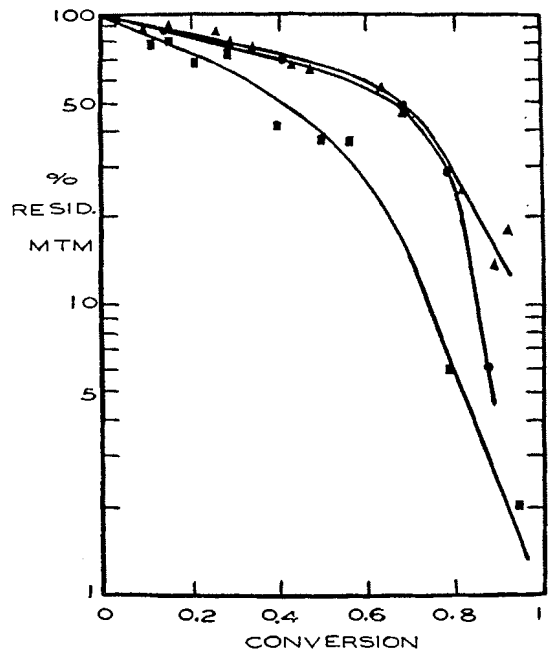

FIG. 2. *Modifier disappearance data for mixed tertiary mercaptan blend MTM for 90/10 butadiene/acrylonitrile charge ratio (■), 66/34 charge ratio (●), and 50/50 charge ratio (▲).*

It is evident that the rate of disappearance is considerably slower than in butadiene–styrene system (3, 13) and that the rate diminishes with increasing acrylonitrile in the charge. Thus must be interpreted tentatively in terms of a low reactivity of the acrylonitrylyl radical for mercaptan hydrogen. A more comprehensive study of the action of mercaptans as modifiers in this system is to be published (7).

The regulating index, defined as

$$r = \frac{-d \ln R}{dP},$$

where R is the per cent residual mercaptan at fractional conversion P, was calculated for each charge ratio. The results were 1.38 for 90/10, 0.83 for 66/34, and 0.71 for 50/50 charge ratio. These offer a means of numerical comparison with similar calculations in the GR–S and Buna S–3 system (3, 13). There was no waste factor evident in any of the results.

* *Phillips Petroleum Co. blend of 60% tertiary C-12, 20% tertiary C-14, and 20% tertiary C-16 mercaptans.*

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Number Average Molecular Weights

Assuming an average molecular weight for the mercaptan of 220 and that one mercaptan molecule is consumed per molecule of polymer formed, the number average molecular weights based on the data in Fig. 2 were calculated. The results are in Table IV. At low conversions where branching is small and the termination by other than mercaptan is minimal, the results should be reasonably representative.

TABLE IV

NUMBER AVERAGE MOLECULAR WEIGHTS CALCULATED FROM MODIFIER DISAPPEARANCE DATA

% Conv.	90/10 charge ratio		66/34 charge ratio		50/50 charge ratio	
	Mercaptan consumed, %	Molecular weight calc.	Mercaptan consumed, %	Molecular weight calc.	Mercaptan consumed, %	Molecular weight calc.
10	14	2.2×10^4	8	3.9×10^4	8	3.9×10^4
20	25	2.5	14	4.5	14	4.5
30	35	2.7	21	4.5	21	4.5
40	47	2.7	27	4.7	27	4.7
50	61	2.6	33	4.8	37	4.8
60	72	2.6	41	4.6	41	4.6
70	82	2.7	54	4.1	54	4.1
80	94	2.7	74	3.4	71	3.5
90	98	2.9	—	—	84	3.4

These calculations show that the molecular weights of the 90/10 charge ratio polymers are relatively uniform at all conversions and that the molecular weights of 66/34 and 50/50 charge ratio polymers are relatively constant to high conversions at which time the new polymers are of lower molecular weights so that the average is lower. This is shown more clearly by calculating the increment number average molecular weights, Table V, in the same manner. The increment molecular weights for the 90/10 charge ratio remain constant but those for the 66/34 and 50/50 charge ratios decrease above 60% conversion after passing through a broad maximum.

TABLE V

CALCULATED INCREMENT NUMBER AVERAGE MOLECULAR WEIGHTS FROM MODIFIER DISAPPEARANCE DATA

Conversion range	Increment number average molecular weight		
	90/10 charge ratio	66/34 charge ratio	50/50 charge ratio
0–10%	2.2×10^4	3.9×10^4	3.9×10^4
10–20	2.9	5.2	5.2
20–30	3.1	4.5	4.5
30–40	2.6	5.2	5.2
40–50	2.2	5.2	5.2
50–60	2.9	3.9	3.9
60–70	3.1	2.4	2.4
70–80	2.6	1.6	1.8
80–90	7.8	—	2.4

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Dilute Solution Viscosity of Polymers Prepared at 5°C.

Another means of measuring molecular weight heterogeneity is by following the dilute solution viscosity of the polymer at various conversions. The viscosity changes with 75/25 and 66/34 charge ratios are shown in Fig. 3. It will be noted that with fresh latex the viscosity increases regularly with conversion but after the latex is aged the viscosity of the initial polymer has increased and that of the higher conversion samples has remained constant. The absence of a maximum as shown in Table I may be attributed to the larger amount of mercaptan present or to the lower polymerization temperature. Previous work (23) appears to have been done on aged latex. Similar data were collected for 50/50 and 25/75 butadiene to acrylonitrile charge ratio and are in Fig. 4. The viscosity increases to a maximum and then decreases for the 50/50 charge ratio. The decrease may be due to the increased rate of mercaptan disappearance at higher conversion together with the reduced tendency for branching of the substantially vinyl polymer. It seems that the dimethylformamide solvent consistently yields lower results than dichlorobenzene–isopropanol mixture. Again the viscosity of the aged latex has changed in the lower conversion ranges but has not increased above that of unaged latex in the higher conversion ranges. The few data with the 25/75 charge ratio indicate a regular decrease in viscosity which might be expected from the increasing acrylonitrile content of the polymer in addition to changes in the modifier disappearance curve and the reduced chances of branching.

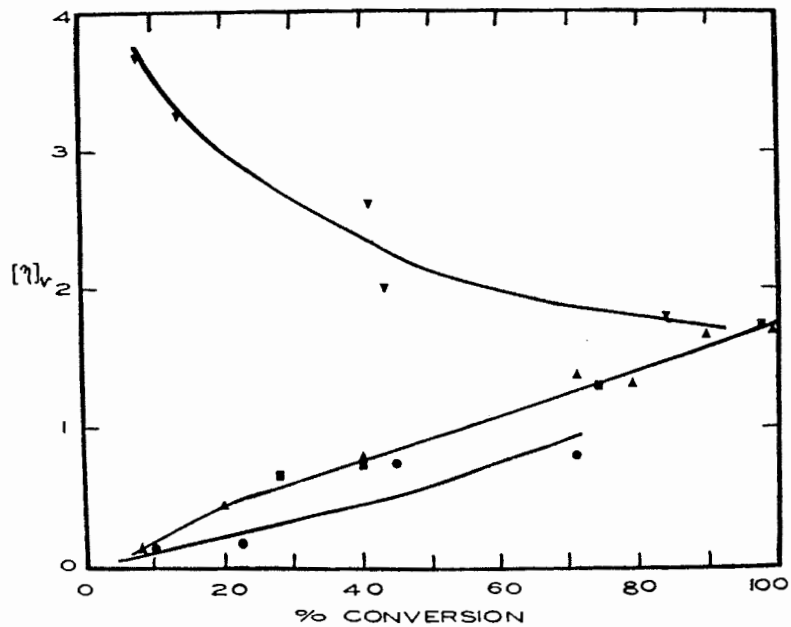

FIG. 3. *Viscosity conversion curves. 75/25 butadiene/acrylonitrile charge ratio in benzene-isopropanol* (●); *66/34 same* (■); *66/34 in o-dichlorobenzene-isopropanol* (▲), *same after two months* (▼).

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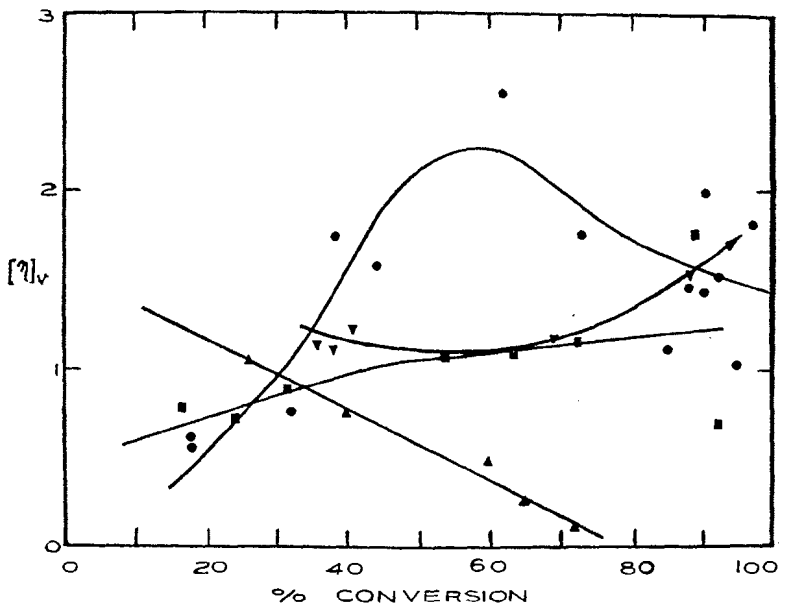

FIG. 4. *Viscosity conversion curves. 50/50 butadiene/acrylonitrile charge ratio in dichlorobenzene-isopropanol (•); same in dimethylformamide (■); same after two months (▼); 25/75 charge ratio in same (▲).*

The increment viscosity may be calculated from the viscosity conversion data. The increment viscosity is that which will change the viscosity of the whole polymer from the value at the beginning of the range to the value at the end of the range. The data are in Table VI. The increment viscosity for the 75/25 and 66/34 ratios increases regularly, for the 50/50 charge ratio rapidly and then diminishes, and for the 25/75 ratio diminishes regularly.

Viscosity Molecular Weights

Conversion of the viscosity data into molecular weights can be made by using a Staudinger type equation. Almost any arbitrary equation would

TABLE VI

CALCULATED INCREMENT VISCOSITY FROM VISCOSITY–CONVERSION DATA

Conversion range	75/25 charge ratio	66/34	50/50	25/75
	Increment viscosity			
10–20%	0.32	0.68	—	—
20–30	0.68	0.95	1.83	0.55
30–40	0.68	1.28	3.31	0.15
40–50	1.05	1.57	4.54	−ve
50–60	1.57	1.92	2.50	−ve
60–70	2.14	2.18	0.80	−ve
70–80	—	2.61	0	—
80–90	—	2.82	0	—
90–100	—	3.33	0	—

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suffice for relative values. One applicable in this work has been published (18). The difference between the data for benzene and toluene solution is not sufficient to exclude the use of the equation for toluene solution when benzene or dichlorobenzene is the solvent. The intrinsic viscosities in all these solvents appear to be nearly identical in practice as shown in part of Fig. 3. The equation is $\eta = 4.9 \times 10^4 . M^{0.64}$. This was used to calculate the molecular weight versus conversion, Table VII. The increment viscosity molecular weights were calculated likewise and are in Table VIII.

TABLE VII

CALCULATED VISCOSITY AVERAGE MOLECULAR WEIGHTS

% Conversion	75/25 charge ratio	66/34 charge ratio	50/50 charge ratio	25/75 charge ratio
10	$<1 \times 10^4$	$<1 \times 10^4$	—	—
20	1.5	4.5	6.9×10^4	24.0×10^4
30	3.0	8.0	18.5	18.5
40	4.9	12.5	34.0	12.5
50	7.8	17.8	45.0	6.9
60	12.0	21.8	48.0	3.1
70	17.5	24.5	43.0	<1
80	—	29.5	38.0	—
90	—	34.5	34.5	—
100	—	37.5	29.5	—

TABLE VIII

CALCULATED INCREMENT VISCOSITY MOLECULAR WEIGHTS

Conversion range	75/25 charge ratio	66/34 charge ratio	50/50 charge ratio	25/75 charge ratio
10–20	2.8×10^4	7.8×10^4	—	—
20–30	7.8	18	3.9×10^4	7.2×10^4
30–40	7.8	27	66	21
40–50	21	34	84	−ve
50–60	34	40	53	−ve
60–70	46	46	14	−ve
70–80	—	58	0	—
80–90	—	58	0	—
90–100	—	66	0	—

Heterogeneity of Polymers

Having both the number average molecular weights and the viscosity average molecular weights it is possible to estimate the heterogeneity of the polymer (8, 16). From the relationships and the viscosity molecular weight equation it can be derived (following the suggestion of Meehan*) that

$$\beta = 2.37 \sqrt{\log R} \text{ and } M_0 = \overline{M}_n R^{-0.610},$$

where R is $\overline{M}_v/\overline{M}_n$. Using the above values, β and M_0 were calculated for

* *Private communication to participants in The Rubber Reserve research program.*

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the 66/34 and 50/50 charge ratios. The data are in Table IX. For both ratios the heterogeneity increases with conversion, and the peak of the distribution curve shifts to lower molecular weights.

TABLE IX

CALCULATION OF THE HETEROGENEITY AND PROBABLE MAXIMUM IN THE DISTRIBUTION CURVE OF MOLECULAR WEIGHTS

% Conversion	66/34 charge ratio		50/50 charge ratio	
	β	M_0	β	M_0
10	−ve	9.4×10^4	—	—
20	0	4.5	0.47	3.4×10^4
30	0.59	3.2	1.46	1.9
40	1.12	2.4	2.04	1.4
50	1.35	2.2	2.30	1.2
60	1.60	2.0	2.41	1.1
70	1.84	1.4	2.42	1.0
80	2.22	0.9	2.46	0.8
90	—	—	2.38	0.8

In a similar manner the heterogeneity and the peak of the distribution curve for the increment polymer can be calculated, and the data are in Table X. The form of the curves is similar although the heterogeneity of the 50/50 ratio copolymer seems to be diminishing with increasing conversion. This again occurs when polymer of lower molecular weight is formed.

From these calculated curves the usual derived data can be obtained. These include the percentage of polymer having various characteristics, etc. In general the values of β and M_0 are sufficient to visualize the approximate molecular weight distribution of the polymers, and the data show that the system behaves much like GR-S or Buna S-3 (3) except as will be shown later when polymer rich in acrylonitrile is formed.

Bound Acrylonitrile versus Conversion

In addition to molecular weight heterogeneity there is chemical heterogeneity along the chain. One aspect of this problem which can be studied is

TABLE X

CALCULATION OF HETEROGENEITY AND PROBABLE MAXIMUM IN THE DISTRIBUTION CURVE OF MOLECULAR WEIGHTS FOR THE INCREMENT POLYMER

Conversion range	66/34 charge ratio		50/50 charge ratio	
	β	M_0	β	M_0
10–20	1.0	4.1×10^4	—	—
20–30	1.8	1.9	2.2	1.3×10^4
30–40	2.0	1.9	3.9	1.1
40–50	2.1	1.6	2.6	1.0
50–60	2.4	0.9	2.4	1.0
60–70	2.7	0.4	1.8	1.1
70–80	2.9	0.2	—	—

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the variation of bound acrylonitrile with conversion. The results for the 75/25 butadiene/acrylonitrile charge ratio are in Fig. 5. The bound acrylonitrile values were determined experimentally and used to calculate the increment acrylonitrile. This is the acrylonitrile content of the polymer being produced over a narrow range near the conversion indicated. Also the bound acrylonitrile was used to calculate the charge ratio of the residual monomers which would be expected to be related to the increment acrylonitrile through the reactivity ratios of the respective monomers. It is evident that the bound acrylonitrile is higher in the initial polymer than it is in the charge ratio and that polymer increasingly rich in butadiene is formed during the reaction to bring the final average polymer to a bound acrylonitrile equivalent to the charge ratio. During the reaction also the percentage of butadiene in the residual monomers increases.

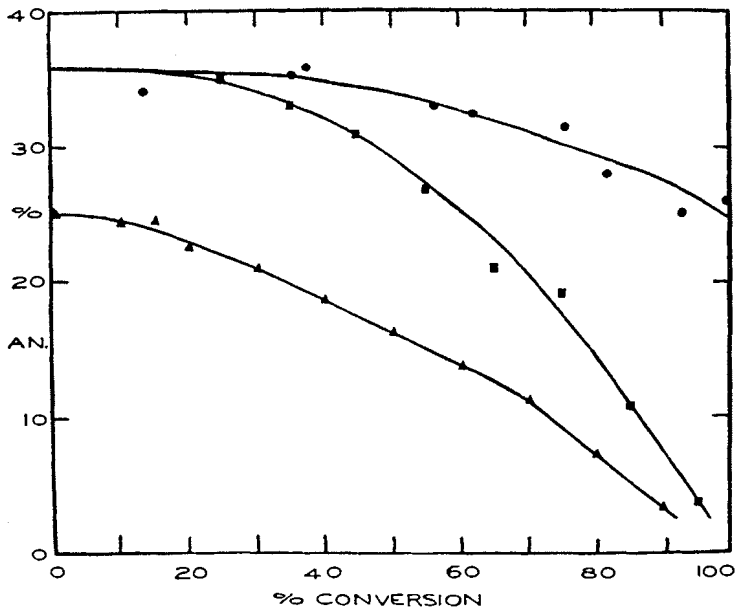

FIG. 5. *Acrylonitrile versus conversion for 75/25 butadiene/acrylonitrile charge ratio.* (●) *in polymer,* (■) *in increment polymer,* (▲) *in residual monomer.*

A different picture is observed when the 50/50 butadiene/acrylonitrile charge ratio is used, Fig. 6. These data show that the polymer formed is remarkably uniform chemically to 90% conversion after which there is a short period in which acrylonitrile content in the polymer formed rises steeply. The residual charge ratio increases slowly at first and then more rapidly until it appears as if all the butadiene is exhausted near the end of the reaction.

Still a different picture is evident from the 25/75 butadiene/acrylonitrile charge ratio, Fig. 7. In this case the bound acrylonitrile starts at a value much lower than the charge ratio and increases slowly at first and then rapidly until the final average is equivalent to the charge ratio. The increment

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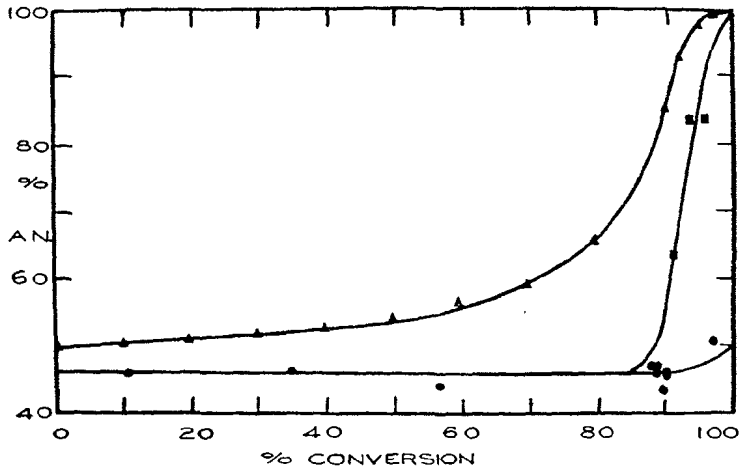

FIG. 6. *Acrylonitrile versus conversion for 50/50 butadiene/acrylonitrile charge ratio.* (•) *in polymer,* (■) *in increment polymer,* (▲) *in residual monomer.*

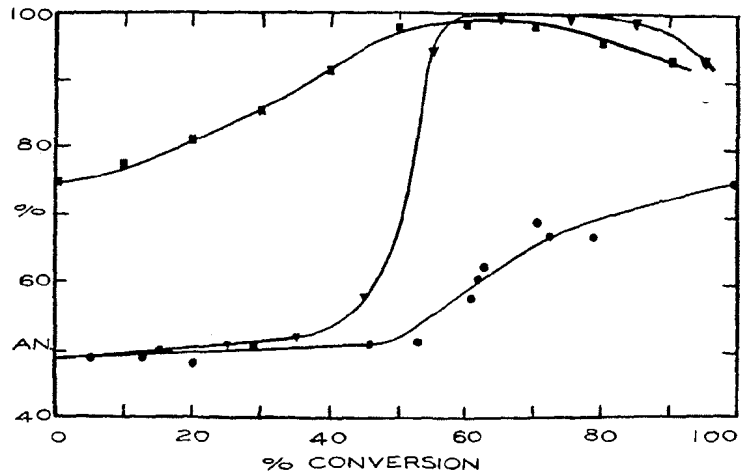

FIG. 7. *Acrylonitrile versus conversion for 25/75 butadiene/acrylonitrile charge ratio.* (•) *in polymer,* (▼) *in increment polymer,* (■) *in residual monomer.*

acrylonitrile likewise increases slowly at first and then rapidly. It attains the impossible values of slightly over 100%, which indicates that the slope of the bound acrylonitrile curve is changing too rapidly probably through an analytical error. Not only are bound acrylonitrile analyses difficult in this region but also the latex suddenly forms a suspengel which must be sampled by breaking the bottle and chipping off a portion of the spongy mass. This is an uncertain way of obtaining a representative sample. Also the mechanism of formation of this suspengel may be such that abnormal bound acrylonitrile values would result. This same error appears naturally in the residual charge ratio which indicates the disappearance of butadiene and its later reappearance. Both anomalies can be removed by slight changes in the original bound acrylo-

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nitrile curves. Similar anomalies were observed in systems rich in styrene (13) although the deviations were less pronounced and were definitely due to analytical errors in the region investigated.

Reactivity Ratios of the Monomers, Q and e

By extrapolating the bound acrylonitrile versus conversion curve to zero conversion an estimate of the reactivity ratio r_1 and r_2 (where r_1 is the ratio of the rate of reaction of butadienyl radical with butadiene to the rate of reaction of butadienyl radical with acrylonitrile and r_2 is the ratio of the rate of reaction of acrylonitrylyl radical with acrylonitrile to the rate of reaction of acrylonitrylyl radical with butadiene) may be made by the linear method (2). The results are $r_1 = 0.29$ and $r_2 = 0.02$. The value of r_1 is lower than the previously tabulated results (24) owing to the wider molar ratios used and possibly to the method of calculation which eliminates the undue weighting of the results obtained with small amounts of acrylonitrile in the charge. The value of r_2 reported earlier (24) was -0.1, which was meaningless. The present value of $r_2 = 0.02$ seems to fit the experimental results satisfactorily.

It is interesting to plot the per cent acrylonitrile in the charge against the per cent acrylonitrile in the initial polymer formed. In this way an S-shaped curve is obtained, Fig. 8, in which the points are from Figs. 5, 6, and 7, and the curve is the theoretical for $r_1 = 0.29$ and $r_2 = 0.02$ in the equation

$$\frac{dB}{dA} = \left(\frac{B}{A}\right)\left(\frac{r_1\left(\frac{B}{A}\right) + 1}{\left(\frac{B}{A}\right) + r_2}\right),$$

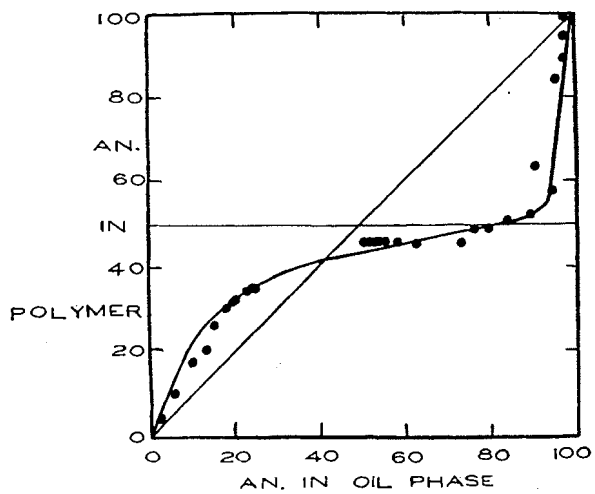

FIG. 8. *Acrylonitrile in polymer versus acrylonitrile in charge.* (•) *data from Figs. 5, 6, and 7. Curve theoretical for* $r_1 = 0.29$ *and* $r_2 = 0.02$.

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in which $\frac{B}{A}$ is the molar ratio of butadiene to acrylonitrile in the monomers and $\frac{dB}{dA}$ is the molar ratio of butadiene to acrylonitrile in the polymer being formed. For convenience these were calculated in terms of per cent acrylonitrile. The closeness of the agreement is satisfactory except for the charges very low in acrylonitrile. Were the copolymerization random, the result would be a straight line connecting zero and 100%. With butadiene and acrylonitrile, the polymer formed when less than 44% acrylonitrile is in the charge is richer in acrylonitrile than is the charge ratio, whereas if the acrylonitrile in the charge is greater than 44% the acrylonitrile in the polymer is less than in the charge ratio. This illustrates the strong tendency for butadiene and acrylonitrile to alternate in the chain, an effect which will be discussed later in more detail.

The data of Smith (21) may be used to calculate the distribution of acrylonitrile between an oil phase and water, assuming that the oil phase behaves similarly to styrene. This may not be true but until a satisfactory study* of the partition of acrylonitrile between butadiene and water is available the data (21) are at least an approximation. The calculated values used in the study are in Table XI.

TABLE XI

CALCULATION PERCENTAGE OF THE ACRYLONITRILE IN THE OIL PHASE

Butadiene/acrylonitrile charge ratio	Acrylonitrile % in oil phase
90/10	56
80/20	62
70/30	65
60/40	69
50/50	71
40/60	72
30/70	73
20/80	74
10/90	75
0/100	76

Recalculating the results in Figs. 5, 6, and 7 on this basis yields values of $r_1 = 0.18$ and $r_2 = 0.03$. Plotting the data in Fig. 9 shows that now the experimental results are close to the theoretical curve for $r_1 = 0.18$ and $r_2 = 0.03$ all along the line. At least a satisfactory approximation has been achieved.

* *A preliminary study of the distribution of acrylonitrile between butadiene and water suggests that under the experimental conditions used in this paper 87%, 92%, and 94% of the acrylonitrile is in the oil phase for 75/25, 50/50, and 25/75 butadiene/acrylonitrile charge ratio respectively. These results applied to Figs. 5, 6, and 7 yield $r_1 = 0.24$ and $r_2 = 0.03$. Such data would yield points and a theoretical curve similar to but intermediate between those of Figs. 8 and 9.*

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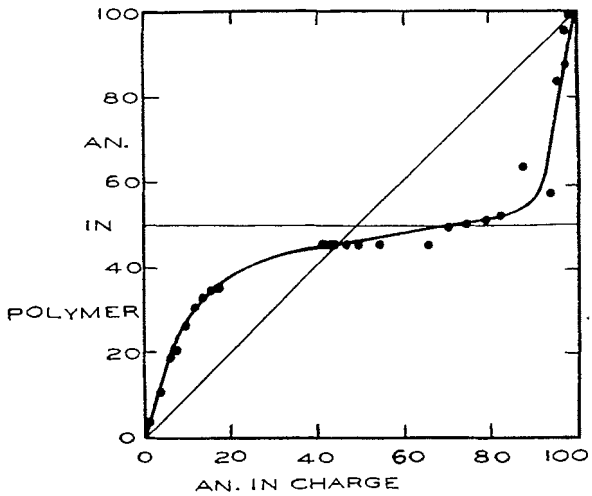

FIG. 9. *Acrylonitrile in polymer versus acrylonitrile in oil phase of charge.* (•) *data from Figs. 5, 6, and 7 as changed by Table XI. Curve theoretical for* $r_1 = 0.18$ *and* $r_2 = 0.03$.

Discussion

A general comparison of interest is the increment acrylonitrile curves. A series has been published by Semon (19, 20). His results showed that 62.6/37.4 mole ratio of butadiene to acrylonitrile was azeotropic, i.e., the polymer was of constant composition throughout. Also his data showed that when the charge ratio varied from 56/44 to 77/23 the initial polymer formed varied from 1.5/1 to 2/1 mole ratio of butadiene to acrylonitrile. The experimental data above are qualitatively similar but suggest an azeotropic mixture containing a higher acrylonitrile proportion. The exact value would seem to be a fortuitous balance between reactivity ratio, distribution of monomers between phases, and perhaps other factors, and it would be surprising if these could be balanced exactly to 100% conversion. Also the data above suggest that the initial polymer produced at 5°C. is richer in acrylonitrile than for the corresponding charge ratio at higher temperatures since the mole ratio of the initial polymer when the charge ratio is varied from 25/75 to 75/25 varies from 1/1 to 1.75/1 mole ratio butadiene to acrylonitrile, i.e., lower than at the higher polymerization temperature. This may be due to lower solubility of acrylonitrile in water at the lower temperatures. The azeotropic charge ratio from Fig. 9 would appear to be 54/46 butadiene/acrylonitrile for bulk phase polymerization. Comparison with similar curves for the styrene–acrylonitrile system (21) shows the more flattened central portion of the curve and the shift upwards of the azeotropic concentration of the above data.

The dilute solution viscosity indicates that the molecular weight increases usually regularly but in the case of the 50/50 ratio to a maximum and then decreases and in the case of the 25/75 ratio polymer decreases regularly. In the former the changed direction of the trend coincides with the formation of

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low molecular weight polymer owing to increased rate of disappearance of the mercaptan, and in the latter to this effect and the formation of polymer richer than 50% in bound acrylonitrile. The high acrylonitrile polymer seems to behave in a different fashion from the less rich copolymer in the same solvent, perhaps in a manner similar to a polyelectrolyte but under the influence of those forces associated with the oil resistance of this type of polymer.

The relationship between viscosity and molecular weight is sufficiently close to be of suitable use for calculation of approximate viscometric molecular weights. These compared with the number average molecular weights yield some indication of the probable maximum of the molecular weight distribution and the heterogeneity of the various polymers. Since a number of effects have to be considered negligible the results can be in considerable percentage error but probably little relative error. In general as the conversion increases the heterogeneity becomes greater and the probable maximum in the distribution curve occurs at lower molecular weights. However, when the viscosity curve reverses direction with the formation of low molecular weight polymer the relationships again do not follow the expected pattern, i.e., the heterogeneity passes through a maximum and the peak of the distribution curve remains relatively constant. The data obtained when polymer containing over 50% acrylonitrile is formed are difficult to interpret as yet.

It will be noted that in copolymerizations with butadiene or styrene with acrylonitrile (11) there is a greater tendency for these monomers to form a radical more reactive towards acrylonitrile than to themselves, whereas acrylonitrile also forms a radical and more reactive towards butadiene or styrene than to acrylonitrile. Such a situation would cause the polymer chain to tend to alternate between acrylonitrile and butadiene or styrene. Thus the rate of polymerization is greatest for approximately equal molar ratios. This also leads to a small value of the $r_1 . r_2$ product (10) which is considered a measure of the alternating tendency. Price (17) has used such data also to compute a value Q and a value e, the former to represent the average reactivity of the double bond and the latter to represent a measure of the polarity of the complex. The Q and e for acrylonitrile in the butadiene–acrylonitrile system appear to be 0.74 and 1.47 respectively. The values are appreciably higher than those recorded (see (11)) owing to the greater tendency of butadiene and acrylonitrile to alternate under the conditions of these experiments. This has been observed for the butadiene–styrene system (16). Further investigation under more varied conditions is needed to ascertain whether such effects are real.

Acknowledgments

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THE COMPOSITIONAL HETEROGENEITY OF BUTADIENE–STYRENE COPOLYMERS SYNTHESIZED AT −18°C. IN EMULSION[1]

By R. J. Orr and H. Leverne Williams

Abstract

A study has been made of butadiene–styrene copolymers formed at −18°C. From analyses for bound styrene in the product for various conversions and initial butadiene–styrene ratios the reactivity ratios were calculated to be $r_1 = 1.37$ and $r_2 = 0.38$ compared with 1.8 and 0.6 at 45°C. Q and e for butadiene were 1.38 and 0.008 relative to styrene at 1 and −0.8. Increment bound styrene curves calculated for each stage of the reaction indicated that the polymers were remarkably homogeneous at low conversions. The chain transfer reaction using mixed tertiary mercaptans as the modifier was studied. Regulating indices were found to have decreased with polymerization temperature. Number average ($\overline{M}_n$) and viscosity average ($\overline{M}_v$) molecular weights were calculated from mercaptan disappearance and vistex intrinsic viscosity data respectively. The molecular weight heterogeneity increased with increasing conversion and initial mercaptan content. The increment number average molecular weights were found to diminish with conversions, whereas the increment viscosity average increased at higher conversions as conversion increased.

Introduction

While general purpose chemical rubbers are products containing about 23% bound styrene it is possible to copolymerize butadiene and styrene in all ratios to copolymers which show a continuous variation in their properties between those of polybutadiene and polystyrene. Recently it has been shown that polymerization temperatures much lower than formerly used yielded a superior product when butadiene was present as a major component of the monomer blend (31, 32). Among reasons for this improvement have been advanced (3, 4, 8, 13, 14, 20, 25, 33) the suggestions of greater regularity of the chain and the formation of a more linear polymer chain structure.

The preparation of copolymers using the present techniques gives rise to products showing chemical and physical heterogeneity. The chemical heterogeneity results from variations in the proportions of the two copolymerized species along the polymer chain. This is a result of the difference in activity of the two monomers which governs the relative rates with which the two monomers enter the copolymer. The physical heterogeneity is a result of the presence of a range of molecular weights in the product. The distribution of the molecular weight is for the most part a function of the types of chain transfer agents present and their mode of disappearance. While all these factors are well known for the butadiene–styrene copolymerizations at 50°C., it has become most desirable to know how they change with temperature.

[1] *Manuscript received in original form September 26, 1950, and, as revised, November 28, 1950.*

Contribution from the Research and Development Division, Polymer Corporation Limited, Sarnia, Ontario. Presented in part before the Chemical Engineering Subject Division, Chemical Institute of Canada, Toronto, June, 1950.

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Techniques

The polymerizations were carried out in 8 oz. peroxide bottles with punctured metal screw caps (10) in which the fiber gasket was replaced by a double rubber gasket consisting of an outer oil resistant Koroseal* sheet and an inner self sealing Butyl** gasket prepared from undercured unpigmented sheets.

The recipe used in the synthesis of the polymer is shown in Table I. The development of this recipe was reviewed earlier and the techniques outlined in detail (28).

TABLE I

CHARGE RECIPE FOR −18°C. POLYMERIZATION

Monomers	100
Potassium fatty acid S.F. soap flakes (Swift Co.)	5.1 pt./100 monomers
Daxad 11***	0.1
Methanol	46
Water, distilled	157
MTM****	As stated
$FeSO_4 . 7H_2O$	0.20
As_2O_3	0.034
Sequestrene AA*****	0.12
$K_4P_2O_7$	0.056
Diisopropylbenzene monohydroperoxide (Hercules)	0.15
Ditertiary butyl hydroquinone	0.2

* *A product of B.F. Goodrich Chemical Co.*
** *A product of Polymer Corporation Ltd.*
*** *Trade name of a dispersing agent, Dewey and Almy Chemical Co.*
**** *A mixed tertiary mercaptan consisting of 60% C_{12}, 20% C_{14}, 20% C_{16}, average molecular weight 220, Phillips Petroleum Co.*
***** *Ethylene dinitrilo tetraacetic acid, Alrose Chemical Co.*

After the reaction was stopped the degree of conversion of monomer to polymer was determined (12) and the unreacted monomers were removed from the latex by low pressure steam. The latex was filtered through glass wool to remove precoagulum and coagulated in isopropanol. The polymer was washed with water, dried, and milled or pressed to a thin sheet suitable for determination of refractive indices. The refractive index of this sheet was determined at 60°C. (26) and the styrene content of the polymer calculated. No correction was made for density changes of the polymer due to its more regular structure when produced at lower temperatures (25). The mercaptan in the latex was determined by amperometric titration (15, 16). The intrinsic viscosities of the polymers formed were measured at 29.9°C. by dissolving the latex directly in a 80:20 benzene–isopropanol solution. Dilutions were made with pure benzene so that intrinsic viscosities in benzene could then be calculated (7, 11, 26).

Experimental

Bound Styrene versus Conversion

The per cent styrene in the polymer was measured for various initial ratios of butadiene to styrene in the charge and for various conversions. The data are in Fig. 1. In general there is an appreciable conversion range over which

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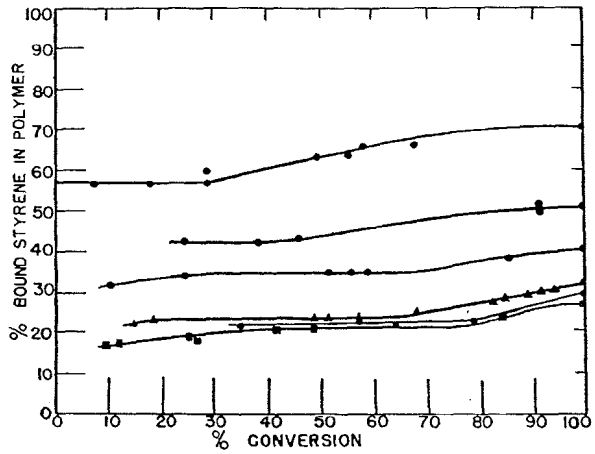

FIG. 1. *Bound styrene versus conversion. The charge ratios top to bottom are 30/70, 50/50, 60/40, 70/30, 72/28, and 75/25 butadiene to styrene.*

the bound styrene does not change much before it rises to correspond to the charge ratio. The length of this plateau also tends to decrease with increasing styrene content in the charge. Somewhat similar results have been reported elsewhere for single charge ratios at 5°C. and −20°C. (25, 33). Additional data obtained in a comparable study at a single charge ratio (X–435 recipe) at 5°C. are in Table II. Comparison of these values with those obtained at

TABLE II

BOUND STYRENE VERSUS CONVERSION AT 5°C. FOR 72/28 CHARGE RATIO (27)

Conversion, %	% Styrene in polymer
5.6	20.7
14.1	20.0
24.3	20.1
28.8	21.1
34.3	20.5
39.8	20.7
49.6	21.7
49.8	21.3
52.6	21.7
62.6	21.2

higher temperatures (21, 22, 24, 25) shows that the tendency towards constant bound styrene at low conversions is characteristic of low temperature polymerizations. However, there is a comparatively small change in the chemical heterogeneity with temperature.

Extrapolation of the curves in Figure 1 to zero conversion yields the data in Table III.

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TABLE III

BOUND STYRENE AT ZERO CONVERSION BY EXTRAPOLATION OF THE DATA IN FIG. 1

Charge ratio	% bound styrene
30/70	57.0
50/50	41.0
60/40	30.8
70/30	22.8
72/28	21.2
75/25	18.1

Monomer Reactivity Ratios, Q and e

Use of the linear method for calculating reactivity ratios (6) yielded $r_1 = 1.37$ and $r_2 = 0.38$, where r_1 is the ratio of the rate of reaction of butadienyl radical with butadiene to the rate of reaction of butadienyl radical with styrene, and r_2 is the ratio of the rate of reaction of styryl radical with styrene to the rate of reaction of styryl radical with butadiene. Alfrey and Price (2) describe the behavior of monomers in terms of two factors, Q the average reactivity and e, the polar properties of the monomers. For this treatment styrene was taken as the reference monomer having a Q of 1 and an e of -0.8. If the reactivity ratios did not change appreciably with temperature, butadiene would possess the same Q and e values in relation to styrene as it did at 50°C., i.e., 1.33 and -0.8 (29). The values obtained at -18°C. are 1.38 and 0.008 respectively. While Q has remained unchanged e has changed greatly. e appears very sensitive to changes in r_1 or r_2. In the consideration of a large number of monomer reactivity ratios, Lewis, Mayo, and Hulse (18) pointed out that $r_1 \times r_2$ equals unity if the monomers are entering the polymer chain completely at random. In the present system $r_1 \times r_2$ is 0.52 which indicates a slight tendency to alternation in the butadiene–styrene copolymer.

Increment Bound Styrene, Residual Unreacted Styrene

The increment bound styrene is the average composition of the polymer formed over an increment in conversion. In Table IV are the increment bound styrenes for the various charge ratios. It may be seen that for 30/70 charge ratio the increments are quite constant to 30–40% conversion and for the remaining charge ratios the increments are quite constant up to about 50–60% conversion. After this period the polymer increases in styrene content as the conversion proceeds usually rapidly at first and then more slowly. It is evident from Table II that similar results were obtained at 5°C. (27).

The residual styrene in the monomers may be calculated at various conversions. The data are in Table V. The residual styrene in the charge rises with conversion in a manner very similar to the bound styrene of the increment polymer (Table IV). The two values should be related through the reactivity

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TABLE IV

INCREMENT BOUND STYRENE CALCULATED FROM FIG. 1

Conversion range, %	% bound styrene in increment polymer for					
	30/70 charge ratio	50/50 charge ratio	60/40 charge ratio	70/30 charge ratio	72/28 charge ratio	75/25 charge ratio
0–10	57.6	41.6	31.0	22.9	21.3	18.6
10–20	59.0	42.8	31.8	23.1	21.7	19.8
20–30	60.4	44.0	32.3	23.6	21.8	20.7
30–40	64.6	45.2	32.9	23.6	22.0	21.7
40–50	73.6	46.4	33.0	23.8	22.2	22.7
50–60	75.8	57.2	32.6	24.6	27.0	23.1
60–70	73.0	60.2	45.2	32.0	23.4	24.6
70–80	76.0	59.4	52.8	37.6	25.4	26.4
80–90	78.4	53.2	57.4	39.9	37.0	33.0
90–100	80.8	50.0	49.0	48.9	61.8	39.0

TABLE V

RESIDUAL STYRENE IN CHARGE VERSUS CONVERSION

Conversion, %	% Residual styrene in charge for					
	30/70 charge ratio	50/50 charge ratio	60/40 charge ratio	70/30 charge ratio	72/28 charge ratio	75/25 charge ratio
0	70	50	40	30	28	25
10	71	51	41	31	28	26
20	73	52	42	32	36	26
30	75	53	43	33	31	27
40	76	54	45	34	32	29
50	77	56	48	37	34	29
60	77	56	51	39	37	31
70	78	54	53	42	42	33
80	79	52	53	44	49	36
90	81	50	49	49	62	39

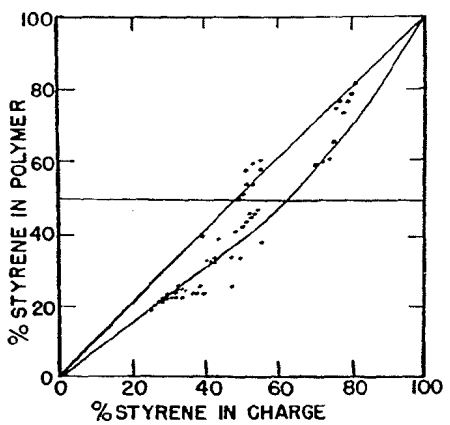

FIG. 2. *Per cent styrene in polymer versus per cent styrene in monomer blend.* (•) *calculated from experimental data. The curve is for* $r_1 = 1.37$ *and* $r_2 = 0.38$.

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ratios r_1 and r_2. When the residual styrene in the charge is plotted against the styrene content of the increment polymer the points in Fig. 2 are obtained.

The line is the theoretical for $r_1 = 1.37$ and $r_2 = 0.38$ using the relationship

$$\frac{dB}{dS} = \frac{B}{S}\left(\frac{r_1\left(\frac{B}{S}\right) + 1}{\left(\frac{B}{S}\right) + r_2}\right),$$

where S is the concentration of styrene and B is the concentration of butadiene. In order to make the information of more practical use the calculations were done using the per cent styrene in the increment polymer and in the residual monomers rather than mole ratios. Although the agreement may at first sight appear poor, the results are actually good. The values of r_1 and r_2 were calculated from low conversion data, and the points obtained at low conversion lie on the theoretical curve. Points obtained at high conversion lie below the line for high butadiene charges and above the line for high styrene charges, that is, r_1 and r_2 both increase with conversion. The data attained with the 50/50 charge ratio were off the curves both as used to calculate r_1 and r_2 and in Fig. 2. The cause for this anomaly is not known.

Modifier Disappearance Curves

Another form of heterogeneity is that of molecular weight. The method of investigation of this phase of the problem was by a study of the chain transfer mechanism at this temperature together with the measurement of viscosity average molecular weights. Three different initial mercaptan charges were used with a 70/30 charge ratio and two other charge ratios were investigated similarly with one modifier content. The data on mercaptan disappearance are in Fig. 3. It is evident that the mercaptan disappears slowly and is not markedly affected by concentration of mercaptan or of monomer charge ratio.

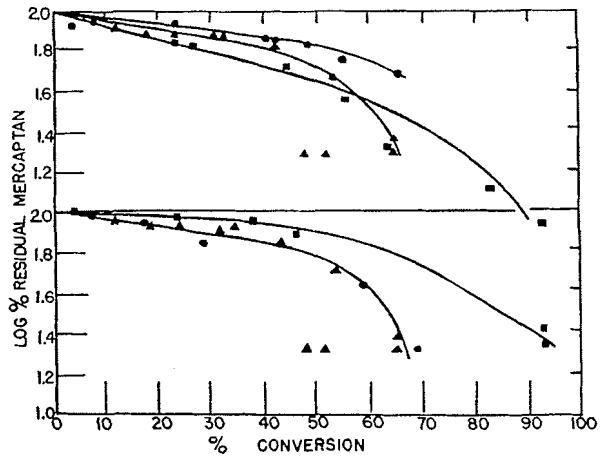

FIG. 3. *Modifier disappearance curves. The charge ratios butadiene to styrene and parts mercaptan are upper (top to bottom) 70/30 and 0.12, 70/30 and 0.24, 70/30 and 0.48; and lower (top to bottom) 50/50 and 0.24 (■), 70/30 and 0.24 (▲), and 30/70 and 0.24 (●).*

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If the natural logarithm of the residual mercaptan is plotted against the per cent conversion, it is found that a linear relationship exists at low conversions. The slope of the linear portion has been adopted as a measure of the relative rates of the chain transfer reaction and conversion of monomer to polymer. These slopes were determined from Fig. 3 and the results are given in Table VI. The accuracy of the method is not great so that the results are not considered exact.

TABLE VI

REGULATING INDICES OF MTM AT −18°C.

Charge ratio	Initial RSH content parts/100 monomers	Regulating index
70/30 butadiene/styrene	0.12	0.5
70/30 "	0.24	0.7
70/30 "	0.48	1.4
50/50 "	0.24	0.5
30/70 "	0.24	0.6
72/28 " (27)	0.20–0.60	7.8

It may be seen from this that the regulating index under all conditions is quite small. There appears to be a trend toward larger regulating indices at higher initial mercaptan concentrations. Comparison with higher temperature (7, 26) fatty acid soap systems where values in the range of 1.5 to 2.5 were obtained (compared with 7.8 at 5°C. (27) using a rosin acid soap) indicates that the chain transfer reaction slows down more with temperature than does the rate of propagation. The effect of the methanol antifreeze used at −18°C. on the modifier disappearance curves has yet to be determined.

Number Average Molecular Weights

Assuming that for each molecule of mercaptan consumed there was one polymer molecule formed, number average molecular weights can be calculated by the formula:

$$\text{Number average molecular weight } (\overline{M}_n) = \frac{\text{Total weight of polymer.}}{\text{Number of moles of polymer}}$$

The results are in Table VII. The assumption is valid at least until branching or cross linking begins (see below). Termination reactions by other than mercaptans tend to decrease the number average molecular weights. Thus the values calculated for low conversions are subject to minimal error.

The results show that the number average molecular weight decreases with increasing modifier in the charge and with increasing conversion. The latter effect is due to the increased rate of consumption of mercaptan at the higher conversion, Fig. 3. At 5°C. (27) the reverse is true initially since the rate of modifier disappearance diminishes with increasing conversion then increases; the number average molecular weight increases with conversion. These

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TABLE VII

CALCULATED NUMBER AVERAGE MOLECULAR WEIGHTS

Conversion, %	70/30 charge ratio			50/50 charge ratio, 0.24 part MTM	30/70 charge ratio, 0.24 part MTM	72/28 charge ratio at 5°C., 0.40 part MTM (27)
	0.12 part MTM	0.24 part MTM	0.48 part MTM			
10	37×10^4	13×10^4	3.5×10^4	18×10^4	18×10^4	1.1×10^4
20	37	14	4.0	18	15	1.6
30	39	14	3.9	18	13	2.2
40	31	13	3.8	15	11	2.8
50	25	9.5	3.9	13	9.8	3.6
60	22	8.1	4.1	13	8.9	6.1
70	20	7.5	4.2	11	8.2	—
80	—	—	4.4	11	—	—
90	—	—	4.6	11	—	—

results are illustrated more clearly by the increment number average molecular weight. These are the molecular weights of the polymers formed over the conversion range indicated. The data are in Table VIII.

Intrinsic Viscosity versus Conversion

The intrinsic viscosity versus conversion curves are in Fig. 4. Inspection of the intrinsic viscosity data indicates that the viscosity–conversion curve is quite flat until relatively high conversions are reached. No gel-point was apparent. This indicates that at these lower temperatures gel formation and hence the cross-linking reaction is greatly suppressed, leading to formation of a greater predominance of long linear polymers. The intrinsic viscosity did show a rise at higher conversions. Both this rise and the plateau preceding it were functions of the initial mercaptan content in the manner shown in Table IX.

TABLE VIII

CALCULATED INCREMENT NUMBER AVERAGE MOLECULAR WEIGHTS

Conversion range, %	70/30 charge ratio			50/50 charge ratio, 0.24 part MTM	30/70 charge ratio, 0.24 part MTM	72/28 charge ratio at 5°C. (27), 0.40 part MTM
	0.12 part MTM	0.24 part MTM	0.48 part MTM			
0–10	3.7×10^4	1.3×10^4	0.35×10^4	1.8×10^4	1.8×10^4	1.1×10^4
10–20	3.7	1.5	0.46	1.8	1.3	3.0
20–30	3.7	1.5	0.38	1.8	0.92	6.5
30–40	2.0	0.92	0.35	0.92	0.83	12.2
40–50	1.5	0.48	0.42	0.83	0.65	11.0
50–60	1.3	0.46	0.51	0.83	0.61	9.2
60–70	1.2	0.54	0.57	1.0	0.59	—
70–80	—	—	0.61	0.92	—	—
80–90	—	—	0.64	0.97	—	—

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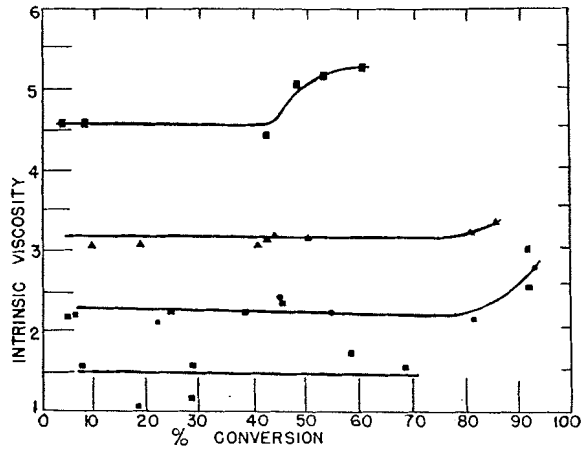

FIG. 4. *Viscosity conversion curves. The charge ratios butadiene to styrene and parts mercaptan (top to bottom) are 70/30 and 0.12, 70/30 and 0.24, 50/50 and 0.24 (•), and 70/30 and 0.48 (■), and 30/70 and 0.24.*

TABLE IX

INFLUENCE OF INITIAL MERCAPTAN CONTENT ON CHARACTERISTICS OF INTRINSIC VISCOSITY CONVERSION CURVES FOR 70/30 CHARGE RATIO

Initial mercaptan content	Conv. % before showing vistex rise	Height of viscosity plat.
0.12 parts (0.00054 mole)	45	$[\eta] = 4.5$
0.24 parts (0.00108 mole)	80	3.1
0.48 parts (0.00216 mole)	90	2.2–2.3

As the styrene content of the polymer is raised, the vistex viscosity decreases perhaps owing to the role of styrene as a chain transfer agent or to a change in the viscosity–molecular weight relationship.

The viscosity conversion curves appear to be more similar to those obtained in the high styrene range at higher polymerization temperatures than to those obtained in the low styrene range (26). Somewhat intermediate results are obtained at 5°C. For example (27) the conversion and corresponding intrinsic vistex viscosity for 72–28 charge ratio and 0.40 part MTM modifier are 25.2%, 0.49; 35.8%, 1.06; 47.8%, 1.18; 60.0%, 1.47; and 67.0%, 2.05. At 5°C., variation in the amount of modifier changes the form of viscosity–conversion curves in the usual manner, i.e., more modifier lowers and flattens the curve, less raises and humps the curve. At −18°C. this effect, if present, is minimized.

Viscosity Molecular Weight

It is possible from intrinsic viscosity data to calculate viscosity—average molecular weights by means of the well known equation $\eta = KM^a$, where η is the intrinsic viscosity,

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M is the viscosity average molecular weight, and

K and α are constants characteristic of the polymer, solvent, and temperature at which η was measured.

Almost any reasonable arbitrary curve would suffice for relative values but it was of interest to estimate a most probable one. At 65% conversion, K and α of polybutadiene in toluene at 30°C. show the following dependence on polymerization temperature (13).

Polymerization temperature (°C.)	K	α
50	72.5×10^4	0.45
5	26.4×10^4	0.55
−20	10.6×10^4	0.63

For polystyrene polymerized at 60°C. K is 1.6 and α is 0.69 in toluene at 30°C. (1). This was assumed not to change for polymer prepared at still lower polymerization temperatures. For GR–S in toluene at 30°C. K is 5.25 and α is 0.667 (30). Inspection of the data on butadiene indicates a nearly linear relation between α and T, whereas K and T are only approximately linear. Assuming linearity then the plot K or α versus temperature for polybutadiene and polystyrene intersect or if they do not in fact intersect they approach very close for polymers prepared at very low polymerization temperatures. At that polymerization temperature at which K and α for polybutadiene are equal to or approach K and α for polystyrene, all copolymers of these monomers should have a K and α equal to or approaching that of polybutadiene and polystyrene. This polymerization temperature is of the order of −28°C. at which $K = 1.6$ and $\alpha = 0.69$ in toluene at 30°C. for polybutadiene, polystyrene and copolymers. Drawing a line from K and for GR–S to this intersection it is possible to estimate K and α for polymer of the GR–S type prepared at −18°C. The equation is $\eta = 2.0 \times 10^4 M^{0.69}$ at 30°C. in toluene. Some calculated data are in Table X using this equation. It is also evident from the data above that at a polymerization temperature of 50°C., introduction of a

TABLE X

CALCULATED VISCOSITY AVERAGE MOLECULAR WEIGHTS

Conversion, %	70/30 charge ratio, 0.12 part MTM	70/30 charge ratio, 0.24 part MTM	70/30 charge ratio, 0.48 part MTM	50/50 charge ratio, 0.24 part MTM	30/70 charge ratio, 0.24 part MTM	72/28 charge ratio at 5°C. (27), 0.40 part MTM*
10	21×10^5	12×10^5	7.7×10^5	7.8×10^5	3.8×10^5	0.62×10^5
20	21	12	7.7	7.8	3.8	1.08
30	21	12	7.7	7.8	3.8	1.30
40	21	12	7.7	7.8	3.8	1.30
50	24	12	7.7	7.8	3.8	1.50
60	29	13	7.7	7.9	3.8	1.98
70	—	13	7.7	8.2	3.8	4.0
80	—	14	7.8	9.0	3.8	—
90	—	15	8.2	10.0	—	—

* *Assuming* $K = 3.0 \times 10^4$.

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relatively large amount of butadiene into the polymer causes only a very small change in K and α. At $-20°C.$ the separation between K and α for polystyrene and polybutadiene is much less. Thus it seems evident that K and α derived above should show little dependence on the bound styrene content of the polymer. In general the value cannot be sufficiently in error to invalidate the results for the purpose of this paper.

Similarly the increment viscosity average molecular weight may be calculated. The data are in Table XI.

TABLE XI

CALCULATED INCREMENT VISCOSITY AVERAGE MOLECULAR WEIGHTS

Conversion range, %	70/30 charge ratio			50/50 charge ratio, 0.24 part MTM	30/70 charge ratio, 0.24 part MTM	72/28 charge ratio at 5°C. (27), 0.40 part MTM*
	0.12 part MTM	0.24 part MTM	0.48 part MTM			
0–10	2.1×10^5	12×10^5	7.7×10^5	7.8×10^5	3.8×10^5	0.62×10^5
10–20	2.1	12	7.7	7.8	3.8	1.60
20–30	2.1	12	7.7	7.8	3.8	1.75
30–40	2.1	12	7.7	7.8	3.8	1.30
40–50	3.8	13	7.7	7.8	3.8	2.5
50–60	5.7	15	7.7	8.4	3.8	4.8
60–70	—	19	8.80	10.3	3.8	2.3
70–80	—	21	7.7	14.5	3.8	—
80–90	—	24	13.5	17.0	—	—

* *Assuming* $K = 3.0 \times 10^4$.

Discussion

Of considerable interest is the change in the copolymerization constants with temperature. The values of r_1 equal to 1.37 and r_2 equal to 0.38 are quite definitely lower than the previous values for butadiene and styrene in emulsion measured at 45°C. (24, 26), i.e., r_1 equal to 1.8 and r_2 equal to 0.6. The decrease is in the same direction as other investigators have found (9, 19, 23) and may mean that the energy of activation of homo-propagation is slightly more than for heteropolymerization. A similar conclusion was reached in a concurrent study (5) of the butadiene–acrylonitrile system. Calculation of r_1 and r_2 by the method of Mayo and Lewis (*cf.* 23) yielded the values r_1 equal to 1.66 and r_2 equal to 0.42. Since these values were obtained in the range of 10–25% conversion the somewhat higher values are in the right direction but the increase is rather surprising. The results do not change the conclusions reached in this paper since the product of r_1 and r_2 is changed only to 0.70. Calculation of the Q and e values corresponding to $r_1 = 1.37$ and $r_2 = 0.38$ yields the interesting data that Q remains unchanged with polymerization temperature but e becomes markedly less negative. This is relative to styrene with the same values as are used at higher temperatures. Thus the question arises as to a suitable standard for e at various temperatures. It is interesting to note that the change in e appears greater than that predicted (24), i.e., that e

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should vary as the reciprocal of the square root of the absolute temperature. A similar conclusion was reached in a concurrent study (5) of the butadiene–acrylonitrile system. This may mean that the radius of the intermediate complex has changed also with temperature since it is not considered likely that the dielectric constant has altered substantially under these conditions. The effect of any methanol in the oil phase would appear to be negligible also (19).

An approximation to the molecular weight distribution (17) may be determined from the viscosity average molecular weight ($\overline{M}_v$) and the number average molecular weight ($\overline{M}_n$) by the logarithmic number distribution Maxwellian type with unlimited range toward infinite molecular weight, i.e.,

$$dn = \frac{Ne^{-y^2}\,dy}{\sqrt{\pi}},$$

where $y = 1/\beta \ln \frac{M}{M_0}$

dn = number of molecules in the interval y to $y + dy$,
N = total number of molecules,
β = degree of heterogeneity and is zero for a homogeneous polymer, and
M_0 = molecular weight at which peak occurs in the distribution curve.

From the above relationships it may derived for butadiene–styrene copolymers (following the suggestion of E. J. Meehan) that:

$$\beta = 2.35\sqrt{\log R}, \text{ and } M_0 = \overline{M}_n R^{0.598}, \text{ where } R = \frac{\overline{M}_v}{\overline{M}_n}.$$

Also, if $y = 1/\ln M/M_0$, it may be shown that F_m, the weight fraction of the polymer having less than the molecular weight M is equal to

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{z} e^{-z^2}\,dz, \text{ where } z = y - \tfrac{1}{2}.$$

This is the familiar probability integral for which values have been tabulated. When F_m is plotted against M it gives the integral molecular weight distribution of the polymer. Some data are in Table XII.

Comparison with β determined at higher temperatures (7, 6th polymer Table XII) reveals that GR–S at 20% conversion had a β of 1.30 when 0.5 part of dodecyl mercaptan is used as regulator. With 0.48 part (0.00216 mole) MTM and at 20% conversion β had a value of 2.65. This larger value of β may be due to decreasing polymerization temperature. This difference is much greater than any error introduced by the estimated viscosity molecular weight relationship.

The values of β are probably maximal since errors in the choice of K tend to decrease β. The large values of β reflect the very large ratio of $\overline{M}_v$ to $\overline{M}_n$ as calculated from the experimental data and may be a measure of the structural changes in the polymer formed at −18°C. relative to that formed at 50°C. It may also be related to the statistical assumptions which may no longer be valid when the chain transfer reaction is reduced.

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TABLE XII

RATIO OF VISCOSITY TO NUMBER AVERAGE MOLECULAR WEIGHT, DEGREE OF HETEROGENEITY, AND MOLECULAR WEIGHT AT WHICH THE PEAK IN THE DISTRIBUTION CURVE OCCURS

Conv., %	70/30 charge ratio 0.12 part MTM			70/30 charge ratio 0.24 part MTM			70/30 charge ratio 0.48 part MTM		
	R	β	M_0	R	β	M_0	R	β	M_0
10	5.68	2.04	1.3×10^5	9.25	2.31	0.34×10^5	22.0	2.73	5.5×10^3
20	5.68	2.04	1.3	8.60	2.10	0.38	19.24	2.67	6.8
30	5.48	2.02	1.4	8.60	2.10	0.38	19.74	2.68	6.5
40	6.77	2.14	0.98	9.25	2.31	0.34	20.5	2.69	6.2
50	9.61	2.33	0.64	12.65	2.35	0.21	19.74	2.68	6.4
60	13.18	2.58	0.46	16.05	2.58	0.15	18.76	2.65	7.1
70				17.35	2.62	0.14	18.34	2.64	7.3
80							17.72	2.62	7.9
90							17.83	2.63	8.2
	50/50 charge ratio, 0.24 part MTM			30/70 charge ratio, 0.24 part MTM			72/28 charge ratio at 5°C. (27), 0.40 part MTM		
10	4.33	1.87	7.5×10^4	2.12	1.34	11.5×10^4	5.62	2.04	3.9×10^3
20	4.33	1.87	7.5	2.53	1.49	8.6	6.34	2.10	5.6
30	4.33	1.87	7.5	2.92	1.60	6.8	5.65	2.04	8.2
40	5.20	1.99	5.6	3.45	1.72	5.3	7.22	2.00	8.5
50	6.00	2.07	5.0	3.87	1.80	4.4	4.05	1.83	16.0
60	6.08	2.08	4.4	4.27	1.87	3.7	3.25	1.68	30.0
70	7.36	2.19	3.3	4.65	1.92	3.3			
80	8.08	2.24	3.2						
90	9.00	2.29	3.0						

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THE CALCULATION OF THE CHANGE IN VIBRATIONAL FREQUENCY DUE TO CHANGES IN MASS, GEOMETRY, AND POTENTIAL CONSTANTS OF A MOLECULE[1]

By H. J. Bernstein

Abstract

An expression for the change in vibrational frequency in terms of changes in the kinetic and potential energy of a molecule has been derived.

For numerical calculations approximations are given. The change in frequency due to configurational changes has also been estimated in a qualitative manner. Finally, an approximate relation between the frequencies observed for a certain symmetry type and those calculated by means of force constants derived from some other symmetry type is given as an aid in assigning vibrational spectra.

Introduction

A change in mass, in geometry, or a change in the constants of the potential function of a molecule is usually accompanied by a lowering of the molecular symmetry. This complicates the direct calculation of the frequency resulting from the above changes by making it necessary to solve determinantal equations of higher order than for the unchanged molecule. Since calculation of the new frequency is so laborious, it is useful to have a simpler method of estimating the effect on the frequency of the above mentioned changes. Such a method was developed by Lord Rayleigh (4) who devised a perturbation theory of vibrating systems to cover such problems.

If the kinetic and potential energies are expressed in terms of the normal co-ordinates ϕ, viz:

$$2T = a_1\dot{\phi}_1^2 + a_2\dot{\phi}_2^2 + a_3\dot{\phi}_3^2 +$$
$$2V = c_1\phi_1^2 + c_2\phi_2^2 + c_3\phi_3^2 + ,$$

Lord Rayleigh showed that for changes in a_1 and c_1 corresponding to da_1 and dc_1

$$\frac{d\lambda_1}{\lambda_1} = -\frac{da_1}{a_1} + \frac{dc_1}{c_1}, \tag{1}$$

where $\lambda_1 = 4\pi^2\,\nu_1^2 = 4\pi^2\,c^2\,\bar{\nu}_1^2$ for $\bar{\nu}$ in cm^{-1}. We may note here that

$$\frac{d\bar{\nu}}{\bar{\nu}} = \tfrac{1}{2}\frac{d\lambda}{\lambda}.$$

A good many years later in a discussion on the frequency shift due to isotopic substitution Teller (7) arrived at the result

$$\frac{d\lambda_k}{\lambda_k} = -\frac{\sum dT_i}{T_k}, \tag{2}$$

where dT_i is the change in kinetic energy associated with substitution of atom i in the k^{th} vibration, and T_k is the kinetic energy during the vibration.

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By considering the effect of isotopic substitution (when $\frac{\Delta m}{m}$ is small) as a perturbation of the kinetic energy Wilson (8) also derived Equation (2). Then by treating the problem as a perturbation of the potential energy Wilson (10, 11) derived an explicit relation between the shift in frequency $\Delta\nu$, the coefficients of the perturbing potential, and the coefficients of transformation to the normal co-ordinates. In particular, it was shown (9) for $\Delta m/m$ small, substitution of one isotope B^i for B in AB_4 shifts the totally symmetrical vibration by an amount

$$\frac{\Delta\lambda}{\lambda} = -\tfrac{1}{4}\frac{\Delta m}{m}. \tag{3}$$

This result had been obtained by Salant and Rosenthal (5, 6) by direct calculation of a complex and tedious nature.

The normal co-ordinates of the system are required to calculate frequency shifts by the above mentioned methods of Rayleigh and Wilson. Since it is not always convenient to obtain these, the method outlined below is given for any set of convenient co-ordinates. The relation (2) of Teller will be derived as a special case.

Change in Frequency Due to Change in Mass (Isotopic Shift)

Let q_i be the displacement of the i^{th} nucleus from the equilibrium position, then

$$2T = a_1\dot{q}_1^2 + a_2\dot{q}_2^2 + 2a_{12}\dot{q}_1\dot{q}_2 + + + \tag{4}$$
$$2V = b_1q_1^2 + b_2q_2^2 + 2b_{12}q_1q_2 + + + \ . \tag{5}$$

The solutions for simple harmonic motion are of the form

$$q_i = A_{ik}\cos\sqrt{\lambda_k}t\ , \tag{6}$$

where A_{ik} is the amplitude associated with the i^{th} particle during the k^{th} vibration.

The Lagrange equations of motion are then:

$$(b_1 - a_1\lambda_k)A_{1k} + (b_{12} - a_{12}\lambda_k)A_{2k} + + = 0 \tag{7}$$
$$(b_{12} - a_{12}\lambda_k)A_{1k} + (b_2 - a_2\lambda_k)A_{2k} + + = 0\ , \text{etc.} \tag{8}$$

Multiplying (7) by A_{1k} and (8) by A_{2k}, etc., and adding it is found that

$$\lambda_k = \frac{b_1A_{1k}^2 + b_2A_{2k}^2 + 2b_{12}A_{1k}A_{2k} + + +}{a_1A_{1k}^2 + a_2A_{2k}^2 + 2a_{12}A_{1k}A_{2k} + + +} \tag{9}$$

$$= \frac{V(A_{ik}A_{jk})}{T(A_{ik}A_{jk})} = \frac{v}{\tau}\ (\text{say})\ . \tag{10}$$

It is possible to expand λ as a function of the amplitudes, b's and a's:—

$$\lambda(A_{ik} + \Delta A_{ik}, a_i + \Delta a_i, b_i + \Delta b_i) - \lambda(A_{ik}, a_i, b_i) = \sum\Delta A_{ik}\left(\frac{\partial\lambda_k}{\partial A_{ik}}\right) + \sum\Delta a_i\left(\frac{\partial\lambda_k}{\partial a_i}\right) + \sum\Delta b_i\left(\frac{\partial\lambda_k}{\partial b_i}\right) + \sum\frac{\Delta A^2{}_{ik}}{2!}\left(\frac{\partial^2\lambda_k}{\partial A_{ik}^2}\right)\ . \tag{11}$$

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In all problems which are considered here Δa_1 and Δb_1 are small so that higher powers may be neglected. In some cases however there are large changes of the amplitudes to be considered; as a result the second order term has been included in the expansion. Now

$$\frac{\partial \lambda_k}{\partial A_{ik}} = \frac{1}{\tau}\left(\frac{\partial v}{\partial A_{ik}} - \lambda_k \frac{\partial \tau}{\partial A_{ik}}\right) = \frac{1}{\tau} \times \text{the } i^{th} \text{ Lagrange equation} = 0$$

and $\dfrac{\partial^2 \lambda_k}{\partial A_{ik}^2} = b_k - a_k \lambda_k$. It is apparent, that for normal co-ordinates, λ is independent of the values of A_{ik},* and for generalized co-ordinates is independent of A_{ik} to the first order of small quantities, and for large changes in A_{ik} depends on the value of $b_k - a_k \lambda_k$. For the k^{th} vibration the following approximations are valid:—

$$\tau \sim a_k A_{kk}^2$$
$$v \sim b_k A_{kk}^2$$

so that $b_k - a_k \lambda_k \sim 0$ from (10). Thus, for generalized co-ordinates λ is very insensitive to changes in amplitudes.

Equation (11) now becomes

$$\Delta\lambda = \sum_i \left(\frac{\partial \lambda_k}{\partial a_i}\right) \Delta a_i + \sum_i \left(\frac{\partial \lambda_k}{\partial b_i}\right) \Delta b_i \,. \tag{11a}$$

For small changes in a_i and b_i, substituting for the differentials evaluated from (10) into (11a) gives

$$\frac{d\lambda}{\lambda} = -\frac{\sum d\tau_i}{\tau_k} + \frac{\sum dv_i}{v_k}$$
$$= -\frac{\sum dT_i}{T_k} + \frac{\sum dV_i}{V_k} \,. \tag{12}$$

This equation reduces to the one (Equation (2)) derived by Teller and Wilson when there is no change in the constants of the potential function, i.e., isotopic substitution. Equation (12) may be used also to calculate the shift $\Delta\lambda/\lambda$ when the energy is expressed in generalized co-ordinates.

To estimate isotopic shifts it is convenient to adopt the displacement co-ordinates r_1, r_2, r_3, etc., and express the kinetic energy in the form:

$$2T = n_1 m_1 \dot{r}_1^2 + n_2 m_2 \dot{r}_2^2 + n_3 m_3 \dot{r}_3^2 + \ldots\ldots\ldots,$$

where there are n_1, n_2, n_3 . . . . . equivalent atoms of mass m_1, m_2, m_3 . . . . . , etc. The potential energy may be expressed then as

$$2V = c_1 r_1^2 + c_2 r_2^2 + 2c_{12} r_1 r_2 + \,.$$

For simple harmonic motion $r_i = B_{ik} \cos (\lambda_k)^{\frac{1}{2}} t$. From Equation (10)

$$\lambda_k = v_k/\tau_k = v_k/n_1 m_1 B_{1k}^2 + n_2 m_2 B_{2k}^2 + n_3 m_3 B_{3k}^2 + \,, \tag{13}$$

where
$$\tau_k = n_1 m_1 B_{1k}^2 + n_2 m_2 B_{2k}^2 + n_3 m_3 B_{3k}^2 + \,, \tag{14}$$

so
$$d\tau_k = n_1 B_{1k}^2 dm_1 + n_2 B_{2k}^2 dm_2 + \,. \tag{15}$$

* *Rayleigh's (op. cit. p. 110) discussion of the stationary property of normal modes suggested the above treatment of this problem.*

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These expressions are valid when all n_1, n_2, n_3, etc., atoms have been substituted by the isotopes m_1^i, m_2^i, m_3^i, etc. If N_1 atoms of m_1 have been substituted and N_2 atoms of m_2 and N_3 atoms of m_3, etc., then

$$d\tau_k = N_1 B_{1k}^2 dm_1 + N_2 B_{2k}^2 dm_2 + N_3 B_{3k}^2 dm_3 + . \qquad (16)$$

Actual calculation of $\Delta\lambda/\lambda$ falls into the following classes:—

(i) For τ_k a function of m_1 only, i.e., a stretching vibration,

(ii) For τ_k a function of m_1 and m_2 only, i.e., stretching and deformation vibrations,

(iii) When τ_k is a function of all the masses, i.e., m_1, m_2, m_3, etc.

(i) *When τ_k is a function of m_1 only*

$$\frac{d\tau}{\tau} = N_1 B_{1k}^2 dm_1 / n_1 B_{1k}^2 m_1 = \frac{N_1}{n_1} \cdot \frac{dm_1}{m_1},$$

so

$$\frac{d\lambda}{\lambda} = -\frac{N_1}{n_1} \cdot \frac{dm_1}{m_1} \qquad (17)$$

for $\frac{dm_1}{m_1}$ small.

This is the result obtained by Wilson for the effect of isotopic substitution on the totally symmetrical vibration of AB_4.

Some examples and applications of Equation (17) are given in Tables I–VII inclusive for CCl_4, BCl_3, NCCl, C_2H_4, C_2H_2, HCN, C_6H_6. The deuterated benzenes, ethylenes, and acetylene may be considered as examples since the CH group is considered as a whole and thus $\Delta m/m$ is small for substitution of a deuterium atom.

TABLE I

ISOTOPE EFFECT IN CCl_4

		CCl_4^{35}	$CCl_3^{35}Cl^{37}$	$CCl_2^{35}Cl_2^{37}$	$CCl^{35}Cl_3^{37}$	CCl_4^{37}
$\nu_1(A_1)$	(Obs)[1]	461.5	458.4	455.1		
	(Calc)[2]	461.5	458.2	455.0	451.8	448.4
	(Calc)[4]	461.5	458.2	455.0	451.8	448.4
$\nu_{23}(E)$	(Obs)[1]	219.0	216.8			
	(Calc)[2]	219.0	217.4	215.8	214.2	212.6
	(Calc)[4]	219.0	217.5	216.0	214.5	213.0
$\nu_{456}(F_2)$	(Obs)[1]	315.5	312.6			
	(Calc)[3]	315.5	313.9	312.3	310.9	308.9
	(Calc)[4]	315.5	314.4	313.3	312.2	311.1

[1] *A. Langseth, Z. Physik, 72: 350. 1931.*
[2] *Calculated from Equation (17).*
[3] *Calculated from Equation (18).*
[4] *Calculated by C. K. Wu and G. B. B. M. Sutherland (J. Chem. Phys. 6: 111. 1936.) from the equations of Rosenthal, Urey, and Bradley.*

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TABLE II

ISOTOPE EFFECT IN BCl_3

		$B^{11}Cl_3^{35}$	$B^{10}Cl_3^{35}$	$B^{11}Cl_2^{35}Cl^{37}$	$B^{11}Cl^{35}Cl_2^{37}$	$B^{10}Cl_2^{35}Cl^{37}$
$\nu_1(A_1')$	(Obs)[1]	473.6	473.6	469.3	464.0	469.3
	(Calc)[3]	473.6	473.6	469.1	464.6	469.1
$\nu_4(E')$	(Obs)[1]	936.7	971.0			
	(Calc)[2]	934.8	971.0			

[1] *B. Bak, J. Jorgensen and Co., Copenhagen (1943).*
[2] *Calculated from Equation (18).*
[3] *Calculated from Equation (17).*

TABLE III

ISOTOPE EFFECT IN NCCl

		$N^{14}C^{12}Cl^{35}$	$N^{14}C^{12}Cl^{37}$	$N^{14}C^{13}Cl^{35}$	$N^{14}C^{13}Cl^{37}$
ν_1	(Obs)[1]	2206.6		2171.0	
	(Calc)[2]	2206.6	2206.6	2157.0	2157.0
ν_2	(Obs)[1]	728.9	720.8		
	(Calc)[2]	728.9	723.6	706.3	701.3

[1] *B. Bak, J. Jorgensen and Co., Copenhagen (1943).*
[2] *Calculated from Equation (18).*

TABLE IV

ISOTOPE EFFECT IN ETHYLENE

		C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_2D_4
ν_1	(Obs)[1]	1623	1599	1572[4]	1545	1515
	(Calc)[2]	1623	1594	1565	1536	1507
	(Calc)[3]	1623	1596	1569	1542	1515

[1] *G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., N.Y. (1945).*
[2] *Calculated from Equation (18) taking CH_2 as a group.*
[3] *Linear interpolation between C_2H_4 and C_2D_4.*
[4] *Average of cis, trans, and asymmetric frequencies.*

TABLE V

ISOTOPE EFFECT IN ACETYLENE

		C_2H_2	C_2HD	C_2D_2
ν_1	(Obs)[1]	1974	1851	1762
	(Calc)[2]	1974	1868	1762
	(Calc)[3]	1974	1933	1882

[1] *G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., N.Y. (1945).*
[2] *Linear interpolation between C_2H_2 and C_2D_2.*
[3] *Calculated from Equation (18) taking CH as a group.*

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TABLE VI

ISOTOPE EFFECT IN HYDROGEN CYANIDE

		$HC^{12}N^{14}$	$HC^{13}N^{14}$	$DC^{13}N^{14}$	$DC^{12}N^{14}$
ν_1	(Obs)[1]	2095	2063		1926
	(Calc)[2]	2095	2048	2003	2048

[1] *B. Bak, J. Jorgensen and Co., Copenhagen (1943).*
[2] *Calculated from Equation (18) and taking CH as a group.*

TABLE VII

ISOTOPE EFFECT IN BENZENE

		C_6H_6	C_6H_5D	$C_6H_4D_2$	$C_6H_3D_3$	$C_6H_2D_4$	C_6HD_5	C_6D_6
				o m p	*sym vic unsym*	*o m p*		
$\nu_1(A_{1g})$	(Obs)[1]	992.5	980.9	975.0	962.6	957.9	950.9	945.2
	(Calc)[2]	992.5	984.6	976.7	968.8	960.9	953.0	945.2
	(Calc)[3]	992.5	985.6	978.7	971.8	964.9	958.0	951.1
$\nu_{12}(B_{1u})$	(Obs)[1]	1010	1008.6	1000	994	980	977	962
	(Calc)[2]	1010	1002	994	986	978	971	962
	(Calc)[3]	1010	1003	996	989	982	975	968
$\nu_6(E_g)$	(Obs)[1]	606.4	599	597	593	587	585	579
	(Calc)[2]	606.4	602	597	593	588	584	579
	(Calc)[4]	606.4	602.4	598.2	594.1	589.9	585.7	581.5

[1] *A. Langseth and R. C. Lord, Kgl. Danske Videnskab. Selskab., XVI; (6) 1. 1938.*
[2] *Linear interpolation between C_6H_6 and C_6D_6.*
[3] *Calculated from Equation (17) taking CH as a group.*
[4] *Calculated from Equation (18) taking CH as a group.*

(ii) *When τ_k is a function of m_1 and m_2*, one atom of m_1 and one of m_2 are involved in a stretching vibration since these are the terminal atoms of the bond. For a diatomic molecule the amplitude is inversely proportional to the mass and for a bond in a polyatomic molecule this relation will be approximately true, thus

$$\frac{d\tau}{\tau} \sim \frac{N_1}{n_1} \cdot \frac{dm_1}{m_1} \cdot \frac{m_2}{m_1 + m_2}$$

and so

$$\frac{d\lambda}{\lambda} \sim -\frac{N_1}{n_1} \cdot \frac{dm_1}{m_1} \cdot \frac{m_2}{m_1 + m_2}. \qquad (18)$$

For deformation vibrations the masses involved are

$$2m_1 \cos^2 \phi \text{ and } m_2 \text{ (apex atom)}$$

so again the actual masses involved are m_1 and m_2 since for most molecules $2 \cos^2 \phi \sim 1$.

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For bending vibrations then

$$\frac{d\lambda}{\lambda} \sim -\frac{N_1}{n_1} \cdot \frac{dm_1}{m_1} \cdot \frac{m_2}{m_1 + m_2} . \tag{19}$$

where m_2 is the apex atom and isotopic substitution is made for m_1 only.

Examples of this may be seen in the tables (I–VII).

(iii) *For τ_k a function of m_1, m_2, m_3, etc.*, large changes in m_3 will have a small effect on λ_k when the vibration considered is the one not associated with mass m_3. From (13) we see that

$$\lambda_k \sim \frac{\text{const.}}{\text{const.} + \text{const.} \times m_3} .$$

Thus $\lambda_k \sim a - bm_3$, (20)

where a, b are constants, gives the effect on λ_k of substitution for m_3 which is not a particle primarily associated with the k^{th} vibration.

The figure shows the dependence of the (frequency)^2 of the nonstretching hydrogen vibrations on the mass $\frac{X+Y}{2}$ in the compounds XCH_2Y. The data are taken from Kohlrausch's book (3). It has been assumed that the

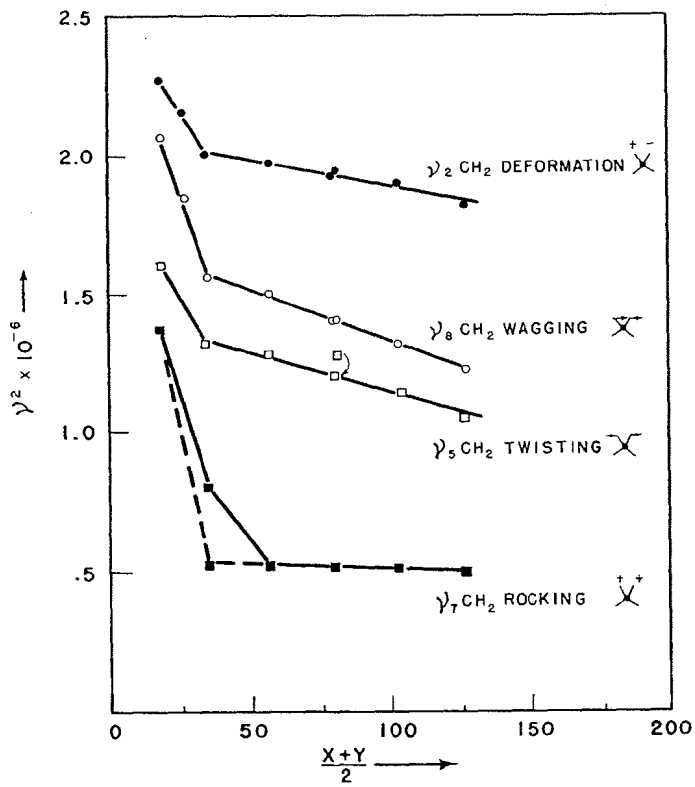

FIG. 1. *Effect of substitution for X and Y in the series $X{\cdot}CH_2{\cdot}Y$ on the nonstretching hydrogen vibrations.*

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potential function for the molecules XCH_2Y has remained unaltered for X, Y substitution. From the figure it is seen that the assumptions have been justified for the Cl, Br, and I substitution but that for fluorine containing compounds a straight line of different slope is obtained.

Another case of isotopic substitution to be considered is that of deuterium for hydrogen,

then $\lambda_k^{\mathrm{H}} = \frac{\nu_k^{\mathrm{H}}}{\tau_k^{\mathrm{H}}}$ and $\lambda_k^{\mathrm{D}} = \frac{\nu_k^{\mathrm{D}}}{\tau_k^{\mathrm{D}}}$;

but since λ is quite insensitive to amplitude changes,

$$\frac{\lambda^{\mathrm{H}}}{\lambda^{\mathrm{D}}} \sim \frac{\tau^{\mathrm{D}}}{\tau^{\mathrm{H}}} \sim \frac{m_{\mathrm{D}}}{m_{\mathrm{H}}}\left\{1 - \left(\frac{\mathrm{B}_{2k}}{\mathrm{B}_{1k}}\right)^2 \cdot \frac{m_{\mathrm{D}} - m_{\mathrm{H}}}{m_{\mathrm{D}} m_{\mathrm{H}}} \cdot m_2\right\}$$

$$\sim \frac{m_{\mathrm{D}}}{m_{\mathrm{H}}} \quad . \tag{21}$$

When T is a function of m_1 only

$$\frac{\lambda^{\mathrm{H}}}{\lambda^{\mathrm{D}}} = \frac{m_{\mathrm{D}}}{m_{\mathrm{H}}} \, .$$

Equation (21) is illustrated in Table VIII where the shift in frequency for substitution of one D remains practically constant when additional D's are added.

TABLE VIII

LARGE ISOTOPE EFFECT, $\nu_7(B_1)$*

Molecule		Observed	Average	Deviation from mean
C_6H_6		3048		
C_6H_5D		2270	2270	6
$C_6H_4D_2$	*o*	2281		
	m	2284	2281	5
	p	2279		
$C_3H_3D_3$	*sym*	2272		
	vic	2288	2281	5
	asym	2284		
$C_6H_2D_4$	*o*	2290		
	m	2272	2276	0
	p	2265		
C_6HD_5		2268	2268	8
C_6D_6		2266	2266	10
			2276	4

* *Data and assignment from A. Langseth and R. C. Lord, Kgl. Danske Videnskab. Selskab, XVI: (6) 1. (1938).*

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Change in Frequency Due to Configurational Changes

To compare the frequencies of corresponding modes of vibration for the totally symmetrical vibrations of *cis* and *trans* dichloroethylene, Equation (10) may be of considerable use. The potential function for *cis* may be written $2V = 2K_{CH}\Delta R_{CH}^2 + 2K_{CCl}\Delta R_{CCl}^2 + K_{CC}\Delta R_{CC}^2 + 2\delta_{HCC}\Delta\theta_{HCC}^2 + 2\delta_{ClCC}\Delta\theta_{ClCC}^2$ and the kinetic energy is

$$2T = 2m_H(\dot{x}_H^2 + \dot{y}_H^2) + 2m_{Cl}(\dot{x}_{Cl}^2 + \dot{y}_{Cl}^2) + 2m_C(\dot{x}_C^2 + \dot{y}_C^2)$$

The kinetic energy for the *trans* molecule has the same expression as that for the *cis* molecule. For the totally symmetrical vibrations the potential energy for the *trans* molecule has the same form as that for the *cis* but includes a term (absent in *cis*) which is the contribution to the potential energy due to the relative motion of the carbon atoms*. If one may assume that interactions between nonbonded atoms are small enough to neglect, and that the amplitudes of the atoms and force constants in *cis* and *trans* molecules are approximately equal then

$$\frac{\lambda_{trans}}{\lambda_{cis}} = \frac{\nu_{cis} + \text{contribution due to relative CC motion}}{\nu_{cis}} \geq 1 \qquad (22)$$

since the contribution due to the CC motion is $+^{ive}$. The frequency of the totally symmetrical mode of vibration in the *trans* molecule is thus greater than the frequency in the corresponding totally symmetrical mode for the *cis* molecule. See Table IX.

TABLE IX

CHANGE IN FREQUENCY DUE TO CONFIGURATION*

cis $C_2H_2Cl_2$		*trans* $C_2H_2Cl_2$		C_2 $C_2H_4Cl_2$	C_{2h} $C_2H_4Cl_2$	
3077		3071		2844	2965	
1587		1576		1445	1437	
1179	A_1	1270	A_g	1207	1298	A_g
711		844		943	990	
173		349		654	748	
				265	303	
3072		3080				
1294	B_1	1200	B_u			
848		817				
571		265				

* *Data from H. J. Bernstein and D. A. Ramsay (J. Chem. Phys. 17: 556. 1949.) for the dichloroethylenes and H. J. Bernstein (unpublished results) for the dichloroethanes.*

For the antisymmetrical planar vibrations of *cis* and *trans* dichloroethylene, there is relative CC motion for *cis* but none for *trans*,

thus $$\frac{\lambda_{trans}}{\lambda_{cis}} = \frac{\nu_{trans}}{\nu_{trans} + \text{contribution due to relative CC motion}} \leq 1 \qquad (23)$$

* *See F. Lechner, Sitzber. Akad. Wiss. Wien (IIa), 141: 633. 1932, for example.*

See Table IX for examples. In the case of deformation vibrations where the contribution due to relative CC motion is felt most one would expect these relations to be valid. For other vibrations however the assumptions may break down sufficiently to upset this order (see Table IX for examples).

A Relation Between the Frequencies Observed for a Particular Symmetry Type and the Frequencies Calculated for this Type from Force Constants Derived from Some Other Type

Generally the only symmetry type to which observed frequencies (obtained from Raman and infrared spectra) can be assigned unambiguously is the totally symmetrical type. The depolarization data from the Raman spectrum make this assignment possible. For a molecule of rather high symmetry then, there remain usually several more symmetry types to which assignments cannot be made from considerations of the spectra only. Usually it is necessary to invoke calculations of frequencies based on the force constants calculated from the observed totally symmetrical type frequencies. Since there are the same number of frequencies as principal force constants in any symmetry type, it is necessary to use the simple potential function (i.e., no cross-terms). These force constants will in general be first approximations to the true force constants which would be obtained if the complete quadratic potential function (using all interaction constants) were used. So that using these constants to calculate the frequencies belonging to a different symmetry type will at best be only a first approximation. Although the numerical agreement between the observed and calculated frequencies under these conditions cannot be expected to be good, yet there is a very definite relation between the observed and calculated frequencies which is of great help in making final assignments.

From the general relation (10, 11)

$$\Pi = GF , \tag{24}$$

where $\Pi = \lambda_1 \lambda_2 \lambda_3 \ldots\ldots\ldots \lambda_i$,

G = the G matrix which is a function of masses and geometry only,

F = the F matrix which is a function of force constants only, we see that

$$\frac{d\Pi}{\Pi} = \frac{dG}{G} + \frac{dF}{F} ,$$

$$= \frac{dF}{F} \tag{25}$$

for no mass changes or changes in geometry.

In the case outlined above where only the principal force constants K_1, K_2, $\ldots\ldots K_i$ are used

$$F = K_1 K_2 K_3 \ldots\ldots K_i .$$

Thus
$$\frac{dF}{F} = \frac{1}{F}\left\{\frac{\partial F}{\partial K_1} dK_1 + \frac{\partial F}{\partial K_2} dK_2 + + \right\} .$$

$$= \frac{dK_1}{K_1} + \frac{dK_2}{K_2} + + \quad .$$

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Hence $$\frac{d\Pi}{\Pi} = \frac{d\lambda_1}{\lambda_1} + \frac{d\lambda_2}{\lambda_2} + \qquad = \frac{dK_1}{K_1} + \frac{dK_2}{K_2} + \quad . \qquad (26)$$

If the force constants K_1 and K_2 are calculated from the frequencies observed for the totally symmetrical type which has two modes in it, say, then these constants used in the secular equation of a different type possessing two modes will yield calculated frequencies considerably different from those observed. The observed frequencies would correspond to the true force constants which may be represented by $K_1 + \Delta K_1$ and $K_2 + \Delta K_2$. Equation (26) relates the per cent difference between the observed and calculated frequencies in terms of the per cent difference between the true force constants and those used. Since the true force constants are obtained when the interaction constants are introduced in the potential function it is evident that upon introduction of a small interaction constant the value of $d\Pi$ will be zero. This is readily seen by evaluating λ_1, λ_2, from Equations (7), (8) for a symmetry type in which there are two modes only, viz.:

$$\lambda^2 - \frac{(a_1b_2 + b_1a_2 - 2b_{12}a_{12})\,\lambda}{a_1a_2 - a_{12}^2} + \frac{b_1b_2 - b_{12}^2}{a_1a_2 - a_{12}^2} = 0 \,. \qquad (27)$$

Thus introduction of an interaction constant b_{12}, say, will appear to the second power in the product of the frequencies. To the first order of small quantities $d\Pi = 0$ and Equation (26) becomes

$$0 = \frac{d\lambda_1}{\lambda_1} + \frac{d\lambda_2}{\lambda_2} = \frac{dK_1}{K_1} + \frac{dK_2}{K_2} \,.$$

The calculated and observed frequencies for this new type will be related in a manner such that the per cent increase in one frequency is equal to the per cent decrease in the other frequency or vice versa. Also the true force constants are related to those used by the same sort of relation

$$\frac{dK_1}{K_1} = -\frac{dK_2}{K_2} \,.$$

The problem of three vibrations of a symmetry type for which

$$0 = \frac{d\lambda_1}{\lambda_1} + \frac{d\lambda_2}{\lambda_2} + \frac{d\lambda_3}{\lambda_3} = \frac{dK_1}{K_1} + \frac{dK_2}{K_2} + \frac{dK_3}{K_3}$$

reduces to the two vibration case if one of the calculated frequencies agrees very closely with the value observed (i.e., $d\lambda = 0$).

This criterion has been applied (1) with success in the case of the vibrational assignment of the S_8 molecule which has the symmetry of the D_{4d} point-group. From force constants derived from the totally symmetrical class, Bhagavantam and Venkatarayudu (2) calculated the frequencies of the type E vibrations to be 452, 243, and 122 cm^{-1}. Lines at 434, 241, 185, and 152 cm^{-1} are observed in the Raman spectrum. Since these authors employed the criterion of closest arithmetical agreement between observed and calculated frequencies their assignment for the type E vibrations was 434, 241, and 151 cm^{-1}. However, since there is no ambiguity about the line calculated at 452 cm^{-1} and if as an

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approximation it is considered to be very close to the observed value at 434 cm^{-1} the problem reduces to estimating the remaining two frequencies by the method outlined above. This criterion indicates that two calculated frequencies must be chosen such that

$$\frac{d\lambda_1}{\lambda_1} = -\frac{d\lambda_2}{\lambda_2}.$$

Of the calculated frequencies 243, 122 and the observed frequencies 241, 185, and 152, only 243 and 185, and 122 and 152 satisfy approximately this relation. Thus the assignment indicated by this criterion is 434, 185, 152 with 241 belonging to some other symmetry type. By using this assignment it was possible (1) to interpret all of the 35 Raman and infrared bands of S_8, whereas with the previous assignment of Bhagavantam and Venkatarayudu about eight bands remain unassigned.

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THE PAPILIONACEOUS ALKALOIDS

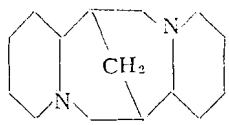
XI. IDENTITY OF GENISTEINE WITH *l*-α-ISOSPARTEINE[1]

BY LÉO MARION AND NELSON J. LEONARD

Abstract

Genisteine has been shown to be identical with *l*-α-isosparteine by means of a direct comparison of the physical properties of the alkaloids and their corresponding derivatives.

The analytical data upon which the formula, $C_{16}H_{28}N_2$, for the lupin alkaloid genisteine, from *Cytisus scoparius* L. (3, 4), was assigned are neither very satisfactory nor extensive. Also, the properties of genisteine and *l*-α-isosparteine, $C_{15}H_{26}N_2$ (I) (5), and their respective derivatives show many striking



I

similarities. These facts strongly suggested the probable identity of genisteine with *l*-α-isosparteine, and we have been able to establish this identity by direct comparison.

Valeur (3) reported no analyses for genisteine but showed the absence of an N-methyl group. The molecular formula assigned to genisteine, $C_{16}H_{28}N_2$, was based upon two sets of analytical figures in the work of Winterfeld and Nitzsche (4). The figures reported for loss of water from genisteine hydrate, m.p. 117°C., are satisfactory for *either* $C_{16}H_{28}N_2$ or $C_{15}H_{26}N_2$ (found: H_2O, 6.90, 6.81%; calc. for $C_{16}H_{28}N_2 \cdot H_2O$: H_2O, 6.77%; calc. for $C_{15}H_{26}N_2 \cdot H_2O$: 7.13%), while those reported for the water-free, freshly distilled base are satisfactory for *neither* $C_{16}H_{28}N_2$ nor $C_{15}H_{26}N_2$ (found: C, 77.20; H, 13.77%; calc. for $C_{16}H_{28}N_2$: C, 77.42; H, 11.42%; calc. for $C_{15}H_{26}N_2$: C, 76.86; H, 11.18%). The work of Winterfeld and Nitzsche confirmed the specific rotation of genisteine hydrate ($[\alpha]_D$ −52.3° in ethanol) and the melting point of genisteine picrate (215°C.) given by Valeur, who also described genisteine aurichloride (m.p. 188°C., with decomposition) and platinichloride (darkening point 235°C.).

[1] *Manuscript received December 12, 1950.*
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The ready formation of a solid monohydrate by genisteine was reminiscent of the behavior of *l*-α-isosparteine (2, 5), and the specific rotation of genisteine hydrate was close to that observed (2) for *l*-α-isosparteine monohydrate ($[\alpha]_D^{30} -55.8°$ in methanol). The melting point of genisteine picrate was likewise similar to that recorded (2) for *l*-α-isosparteine dipicrate (221°C., with decomposition). These points of similarity were strongly suggestive, and added indication of the identity of genisteine with *l*-α-isosparteine was found in the preparation of the previously unreported aurichloride (m.p. 193.5–194.5°C.) and platinichloride (m.p. 271–273°C., with decomposition) derivatives of *l*-α-isosparteine.

Final confirmation of the identity was possible when an authentic sample of genisteine became available for direct comparison with *l*-α-isosparteine. The melting points of genisteine hydrate and *l*-α-isosparteine hydrate were found to be identical and undepressed on admixture. The infrared absorption spectra of the two hydrates were also found to be identical.[2] The melting points of the diperchlorate, dipicrate, aurichloride, and platinichloride of genisteine were identical with the corresponding derivatives of *l*-α-isosparteine, and in each case admixture caused no depression. Thus, there is no doubt that genisteine and *l*-α-isosparteine are one and the same alkaloid. The latter name is favored for the designation of the alkaloid since it indicates the isomeric relation with the more common lupin alkaloid sparteine (2).

Experimental[3]

Genisteine

A sample of genisteine (4) was kindly supplied to us by Prof. Karl Winterfeld. The base was sublimed *in vacuo* (50–60°C. at 0.2 mm.) and recrystallized from 66% ethanol from which the hydrate separated as colorless elongated plates, m.p. 96–117°C. The melting point was undepressed by admixture with *l*-α-isosparteine hydrate. $[\alpha]_D^{23} -58.0°$ (*c*, 1.775 in methanol). *l*-α-Isosparteine hydrate has $[\alpha]_D^{30} -55.8°$ (*c*, 7.216 in methanol (2). Found: C, 71.55; H, 11.14; N, 11.29%. Calc. for $C_{15}H_{26}N_2 \cdot H_2O$: C, 71.38; H, 11.18; N, 11.10%. The infrared absorption curves of the two hydrates were superposable (see Curve 4, Fig. 2, in reference (2)).

Genisteine diperchlorate

A small quantity of genisteine hydrate was dissolved in methanol and the solution made just acid to Congo red by the addition of three drops of 65% perchloric acid. The resulting solution was diluted with ether to incipient turbidity and was cooled in the refrigerator. The salt crystallized in arborescent aggregates, m.p. 252–255°C. (uncorr.) either alone or in admixture with *l*-α-isosparteine diperchlorate (1).

[2]*Both spectra, as determined in chloroform solution, are expressed by Curve 4, Fig. 2, in reference 2. The authors are indebted to Miss Elizabeth M. Petersen for determination of the infrared absorption spectra under conditions identical with those previously employed (2).*

[3]*All melting points are corrected unless otherwise indicated.*

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Genisteine dipicrate

Genisteine hydrate (12.2 mgm.) was dissolved in ethanol (2 cc.) and added to a solution of picric acid (22.2 mgm.) in ethanol (2 cc.), 0.2 cc. of ethanol being used to rinse the flask. The mixture was heated on the steam bath, allowed to cool, and kept in the refrigerator for a few hours. The picrate was recrystallized from ethanol–water from which it separated as small, yellow prisms, m.p. 222°C., either alone or after admixture with *l*-α-isosparteine dipicrate (1, 2).

Genisteine aurichloride

The collected mother liquors from which the diperchlorate and the dipicrate had crystallized were combined, evaporated to dryness, and the residue was dissolved in water. Hydrochloric acid was added and the solution was extracted with ether to remove the liberated picric acid. The aqueous solution was subsequently alkalized with sodium hydroxide and extracted repeatedly with ether. The combined ethereal extract was dried over sodium hydroxide pellets and evaporated to dryness. On standing, the residue crystallized.

About half of this recovered genisteine hydrate was dissolved in ethanol (1 cc.) and to the solution were added three drops of concentrated hydrochloric acid and five drops of a 5% gold chloride solution. The salt separated immediately but redissolved on heating. After 10 min. on the steam bath, the solution was allowed to cool and the crystalline aurichloride that separated was recrystallized from 1 cc. of ethanol containing two drops of concentrated hydrochloric acid. It consisted of yellow elongated prisms, m.p. 199°C. (dec.). In admixture with a sample of *l*-α-isosparteine aurichloride (m.p. 193.5–194.5°C.) it melted at 198.5°C. (dec.).

Genisteine platinichloride

The remainder of the recovered genisteine hydrate was dissolved in ethanol (2 cc.) and three drops of concentrated hydrochloric acid were added together with platinic chloride (15 mgm.), and the mixture was heated on the steam bath for 30 min. The platinichloride separated as orange colored needles. It was filtered and boiled with ethanol (3 cc.) containing four drops of hydrochloric acid. The salt did not dissolve and was filtered. It melted at 276–278° (dec.) and in admixture with a sample of *l*-α-isosparteine platinichloride (m.p. 271–273°C.) melted at 273.5–275.5°C. (dec.).

Acknowledgment

The authors express their gratitude to Prof. Karl Winterfeld, Pharmazeutisches Institut, University of Bonn, Germany, for his kindness in supplying them with a sample of genisteine. One of us (N.J.L.) wishes to thank the Rockefeller Foundation for a fellowship and the National Research Council of Canada for the generous hospitality afforded during the summer of 1950.

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HYDROGEN OVERVOLTAGE AND POTENTIAL BUILD-UP AT COPPER CATHODES[1]

By A. K. Wiebe, W. Gauvin, and C. A. Winkler

Abstract

A given current (e.g., 10^{-4} amp.) results generally in a *nonlinear* hydrogen overvoltage – time relation at a copper cathode immersed in $N/5$ sulphuric acid. After a steady state value of the potential is reached, which may require several minutes, breaking the circuit allows the potential to fall slowly to the zero potential value. On again closing the circuit, a current of the same order as before causes, in a time of the order of seconds, a *linear* potential build-up to a value equal to the steady state hydrogen overvoltage. Taking the capacitance of a uniplanar surface as 20 μf. per cm.^{2}, the rate of the linear potential build-up permits estimation of cathode surface areas (Bowden and Rideal method). If it is now assumed that the nonlinear increase of hydrogen overvoltage with time is accompanied by deposition of a monatomic layer of hydrogen on the surface, the area occupied by this layer can be estimated. The area so calculated agrees as well as may be expected with that determined by the Bowden–Rideal method. It is concluded from these observations that the Bowden–Rideal measurement depends on the rate of charging a condenser, as distinct from the rate of increase of hydrogen overvoltage, which may be associated with deposition of a layer of hydrogen on the cathode surface. Evidence is further presented to indicate that the surface is completely covered with the layer of hydrogen at the maximum of hydrogen overvoltage, and that the Bowden–Rideal method therefore measures the true surface area of the cathode.

Introduction

Since it was first observed (20) that the hydrogen overvoltage at many cathodes increases with time at constant current, the behavior has been the subject of much investigation (2, 3, 6, 10, 12, 13, 17, 19), and has been explained in various ways. The main point of interest in such studies is, perhaps, to determine whether, at the maximum hydrogen overvoltage, there is a film of adsorbed hydrogen on the electrode surface. Study of systems in which the polarizing current is reversed between the limits of oxygen and hydrogen evolution from the electrode (4, 7, 8, 14, 15) has led to contradictory opinions on the matter. Experiments on the photoelectric effect in relation to adsorption of gases on the metal surface (15) indicate the soundness of an opinion held by others (1, 9) that an adsorbed film of hydrogen is responsible for hydrogen overvoltage. In the present paper additional evidence in support of this view is outlined.

Experimental

The cathode ray oscillograph unit and Leeds and Northrup type K potentiometer arrangement, used respectively for measurement of potential build-up and hydrogen overvoltage, were identical with those described in previous papers from this laboratory (16, 18). The electrolytic cell and the experimental

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methods were also the same in all essential respects. The hydrogen, water, and sulphuric acid were purified as in the earlier studies while the copper sulphate was recrystallized three times from redistilled water.

Results and Discussion

With a freshly prepared copper cathode in $N/5$ sulphuric acid, it was possible to obtain only a horizontal trace on the oscillograph screen immediately after the electrolyzing current was switched on. After the current had passed for about half a minute, it was switched off and the voltage measured on the potentiometer allowed to fall to a steady value. A slight potential build-up trace could then be recorded on the oscillograph. Further passage of current, followed by a sufficient time interval for the voltage to fall again to a steady value, allowed a second potential build-up trace on the screen to be obtained, the slope of which was greater than that of the first trace. With several repetitions of the procedure, the slope of the build-up trace was found to increase to a constant value, after which no further influence of current flow was detectable. Similar behavior was observed with several freshly prepared cathodes.

Further experiments were made in which the rate of increase of hydrogen overvoltage on freshly prepared cathodes was followed potentiometrically. These revealed that the maximum value corresponded approximately with the minimum time of current flow for constant slope of the potential build-up trace on the oscillograph screen. The possible significance of this correspondence prompted its further investigation in some detail.

Hydrogen overvoltage – time curves were determined potentiometrically, and rates of potential build-up at the maximum hydrogen overvoltage were determined with the oscillograph unit, for 62 different copper electrodes. From the latter measurements, the areas of the electrodes could be calculated in accordance with the Bowden–Rideal method. The electrode surfaces were prepared in a variety of ways, such as grinding or polishing with emery cloth of different grades, grinding with emery powder and water on a glass surface, scraping with a knife, electrodeposition, and electroetching. The surface areas obtained, determined by the rate of potential build-up, ranged from 32 × planar to 287 × planar, assuming a capacitance value of 20 μf. per cm.^{2} at a uniplanar surface (5, 11). Currents used in determining the rate of potential build-up varied from 1.05×10^{-5} amp. to 1.57×10^{-4} amp. Measurements with a given electrode using different currents in this range gave concordant values for the surface area. Hydrogen overvoltage – time relations were established with currents ranging from 1.03×10^{-5} amp. to 1.68×10^{-4} amp., these values being varied quite independently of those used in determining the rate of potential build-up with the oscillograph unit.

Typical hydrogen overvoltage – time curves are shown in Fig. 1, from which it will be noted that the maximum overvoltage value is reached only after a time of the order of minutes with the currents used. In sharp contrast with this

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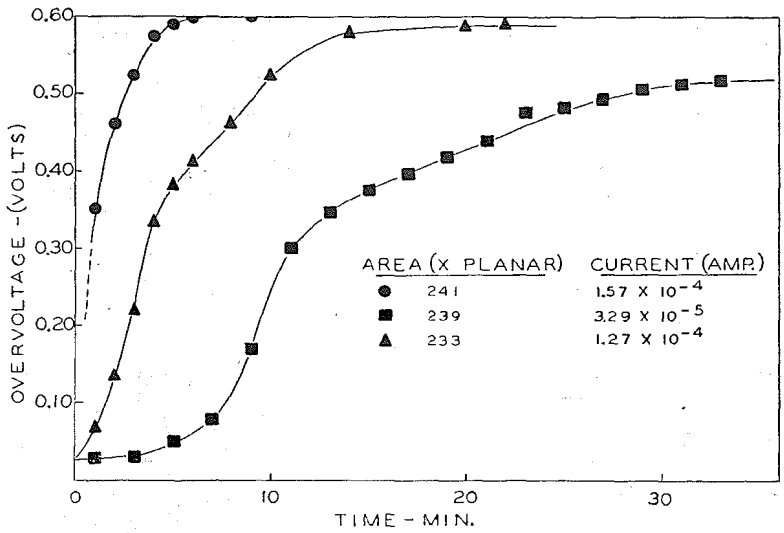

FIG. 1. *Typical hydrogen overvoltage-time curves at copper cathodes.*

was the behavior of the potential build-up trace on the oscillograph. When the maximum overvoltage had been reached, the potential was allowed to fall to zero, or very nearly zero, on open circuit, after which the potential build-up trace required only a few seconds to reach its maximum value (16), when the circuit was again closed. The maximum value of the potential build-up was equal to the maximum hydrogen overvoltage.

Applying Faraday's law to determine the amount of hydrogen deposited during the time required for the hydrogen overvoltage to reach its maximum value, a rough estimate was made of the area that would be covered by a "close-packed" monatomic layer of hydrogen on the cathode. For the calculation, the effective cross section of a hydrogen atom was taken as 1.8×10^{-16} cm.^{2}, and the time of current flow as the time for the hydrogen overvoltage to attain 98% of its maximum value. The calculation was made for all 62 electrodes investigated, and the areas so estimated were compared with those measured according to the Bowden–Rideal method. Typical results are given in Table I.

For 21 of the electrodes, the measured surface area was within about 25% of the calculated area for the hydrogen layer; for 47 of the electrodes, the agreement was within a factor of 2. Of the other 15 electrodes, four showed a disagreement larger than a factor of 3, the worst discrepancy being a factor of 6. The disagreement between the measured area of the electrode and the area calculated for the hydrogen layer appeared to be quite unrelated to the method of preparation of the cathode surface, to the length of any "induction period" in the hydrogen overvoltage – time curves, or to the current conditions used in either the Bowden–Rideal or hydrogen overvoltage measurements. Moreover, there was essentially equal probability of the measured surface area being greater or smaller than the area estimated for the hydrogen layer.

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TABLE I

Area by rate of potential build-up*		Area by hydrogen packing, cm.²	Deviation based on the potential build-up method,** %	Treatment of the cathode surface
×planar	cm.²			
233	85.3	117	+37	Ground with 120 mesh emery and water on glass
287	105	164	+56	As above
239	87.5	64.5	−26	As above
163	60	210	+252	As above
105	36.4	36.6	+0.6	Ground on 3/0 polishing paper
82	30	12	−60	Ground on 2/0 emery cloth
61	22.4	23.7	+5.8	Deposited 90 min. at 1 amp./dm.²
29.7	10.9	7	−36	As above
49	18	14.9	−17	Electroetched
38	13.6	9	−34	Ground with No. 2 emery cloth

* *Approximate electrode area, 0.4 cm.²*
** *For all 62 electrodes the average value of this deviation was +2%.*

In addition to the copper electrodes that have been examined, similar experiments have been made with 10 silver electrodes. It probably suffices to state that with these, the ratios of the areas calculated for the amount of hydrogen deposited at the maximum overvoltage to the areas measured by the Bowden–Rideal method lie within the limits 0.7 to 1.7.

In assessing the significance of the results outlined above, it must be realized that experiments of the type made may be subject to several uncertainties, none of which can yet be quantitatively evaluated. The most obvious possible source of error, perhaps, is the presence of traces of oxygen in the electrolyte or traces of oxide on the surface of the cathode prior to its immersion in the electrolyte. Both the Bowden–Rideal measurement and the time for attainment of maximum hydrogen overvoltage would almost certainly be influenced by the presence of such traces of oxygen or oxide. While very considerable precautions were taken to avoid error from this source, it is possible that these efforts were not completely successful, particularly during the grinding or polishing operations involved in preparation of many of the cathodes. Minute traces of impurities in the electrolyte might also affect significantly the measurements made on electrodeposited surfaces of which several were studied. Again, with several of the cathodes which were removed from the cell after surface area measurements and immediately resurfaced for further studies, retention of hydrogen on a portion of the surface could cause error in subsequent measurements.

Also, any traces of grease on the cathode surface are known to have a profound effect on the Bowden–Rideal measurement (6) and might well influence the hydrogen overvoltage. In spite of precautions to avoid them, such traces might inadvertently be introduced during the necessary manipulations.

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In view of the uncertainties mentioned above, and perhaps others not yet recognized, it is probably reasonable to conclude that, with copper and silver at least, the surface area measured by the Bowden–Rideal method is essentially equal to the area of a monatomic film of hydrogen adsorbed on the cathode at the maximum hydrogen overvoltage. It is possible that some of the larger observed discrepancies between these two areas are greater than the experimental error, but it will require very painstaking and time-consuming investigation to settle this point.

Approximate equality of the measured cathode area and the area of an adsorbed hydrogen film at the maximum hydrogen overvoltage, as well as the observed relation between the potential build-up trace and the hydrogen overvoltage – time curve, can be reasonably interpreted. It is necessary only to associate the hydrogen overvoltage with the presence of the adsorbed film of hydrogen, which in turn acts as the dielectric of a condenser of which the rate of charging is given by the rate of potential build-up measured on the oscillograph.

Considerable support for regarding the hydrogen overvoltage as a consequence of an adsorbed film of hydrogen would seem to be obtained from a series of experiments in which the cathode was left immersed in electrolyte for relatively long periods between successive measurements of the cathode area. No current was passed, but hydrogen gas was bubbled through the electrolyte, in the interval between measurements. When the current was again switched on, a potential build-up trace to the previous value, slightly convex to the x-axis, but of immediate occurrence and high rate, was observed on the oscillograph even after as much as two hours' immersion of the cathode. The condition of the cathode surface must have remained nearly the same after two hours in the absence of a depolarizing agent as it was after attainment of the maximum hydrogen overvoltage necessary for the first area measurement. Had the surface of the electrode returned to a condition comparable with that before passage of any current (i.e., before deposition of any hydrogen) the oscillograph trace would have been horizontal.

Although the experimental results so far presented enable distinction to be drawn between the increase of hydrogen overvoltage and the Bowden–Rideal rate of potential build-up, and associate the hydrogen overvoltage with an adsorbed hydrogen film, they provide no information about the extent of surface covered by the hydrogen film. Experiments were therefore made to clarify this last point. A copper cathode was prepared with emery cloth, as before, and placed in the electrolytic cell. A current of 1.07×10^{-5} amp. was passed until the maximum overvoltage value was reached. The potentiometer setting was then increased by 0.02 v. and the current suddenly increased to 9.05×10^{-5} amp. By determining the time required for the galvanometer to swing past the zero point, an estimate was made of the time required for the potential to increase by 0.02 v. A time of 1 sec. was recorded. From the measured capacitance of 1.0×10^{-3} farads, it may be calculated that it would require 0.22 sec.

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to increase by 0.02 v. the potential across a condenser of this capacity. The experiment was repeated with a second cathode, at a higher current level; the observed time for 0.02 v. increase in potential was 0.6 sec. and the calculated time 0.15 sec. The difference between the measured and calculated times is easily accounted for by the inertia of the galvanometer, together with a small initial deflection in a direction opposite to that of the final swing, due probably to a transient resulting from unbalance in the circuit. There can be little doubt that the increased current served only to increase the charge on a condenser already present, and that no further hydrogen deposition occurred to bring the potential to the higher value at the higher current. Had further deposition of hydrogen been necessary, it may be inferred from previous experiments that the time to attain the higher potential would have been of the order of minutes with the currents used.

Two interpretations of the above experiments are possible. It may be assumed that the surface of the cathode is only partially covered with hydrogen and that the fraction of the surface covered remains constant with different current densities. Alternatively, it may be assumed that, in the range of currents used, the surface becomes covered with a practically complete layer of hydrogen, the extent of which must therefore remain constant when the potential is increased at the higher current density. Of the two assumptions, the latter would seem to be the more reasonable, since the first implies that there are portions of the metal surface on which hydrogen deposition is forbidden, and this seems unlikely. It should be noted that the existence of centers of different activities on the surface is not denied by assuming that the hydrogen film is virtually complete over the surface. On the contrary, the segmented appearance of the hydrogen overvoltage – time curves indicates that hydrogen is more readily deposited on certain parts of the surface than on others. It is possible that with currents very much lower than those used in the present study, differentiation of such portions may become possible. It might be anticipated that sudden increase of the current to a higher value will then reveal a time required to attain a higher potential that is compatible with further deposition of hydrogen.

If it is accepted that there is a practically complete layer of hydrogen over the surface of the cathode at the maximum hydrogen overvoltage, two important conclusions may be drawn: (i) The Bowden–Rideal type of measurement gives a reasonable approximation to the true surface area of the cathode. (It should be emphasized that this conclusion involves acceptance also of equality between the areas calculated from the Bowden–Rideal measurement and the calculated area of the hydrogen film on the surface.) (ii) The increase of hydrogen overvoltage with current density corresponds to increased charge on the condenser of which the hydrogen film probably constitutes the dielectric. In view of the fact that the present experiments have been limited to copper and silver cathodes, it is probably not justified, however tempting, to attempt development of the second conclusion as it bears on existing theories of hydrogen overvoltage. Experiments are now in progress to examine other electrode

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materials, particularly mercury, with which the true electrode area (uniplanar) need not be in doubt. If the suggestions made previously receive confirmation in these studies, it might be possible to offer a substantial contribution to the problem of hydrogen overvoltage generally.

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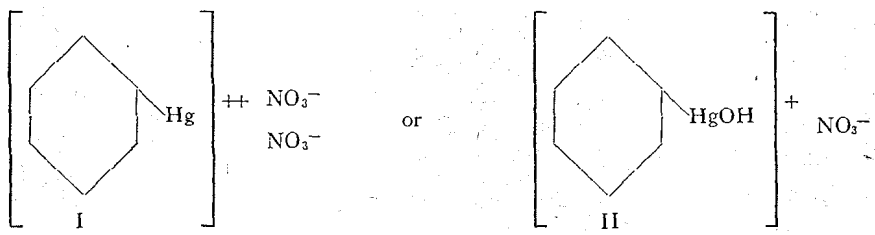
THE SIGNIFICANCE OF THE "MERCURINIUM ION" IN OXYMERCURATION[1]

By A. G. Brook and George F Wright

Abstract

The complex formed by mercuric nitrate with cyclohexene seems not to resemble similar argentous, cuprous, and platinous salt complexes, since it is stabilized by nitric acid while they are decomposed by acidic media. Furthermore, the cyclohexene – mercuric nitrate – nitric acid system is not stable as are the others in absence of air but decomposes to yield two equivalents of mercurous salt and one equivalent of formylcyclopentane. One or both of these products are presumed to be the material which earlier workers by implication defined as 1-hydroxy-2-nitratomercuricylohexane. It has now been found that this product could not have been formed under the reaction conditions used by these earlier workers. Finally the solubilization of cyclohexene in aqueous mercuric nitrate, on which the earlier workers based their concept of an alkene-mercurinium ion, does not have its counterpart in the solubilization of cyclohexene in aqueous mercuric acetate, since the rate of solution in the latter case is not faster than the rate of hydroxymercuration. In consequence there is no present evidence that such an ion is involved in oxymercuration of alkenes.

On the basis of their studies of the system: mercuric nitrate – nitric acid – water – cyclohexene, Lucas, Hepner, and Winstein (7) have concluded that a mercurinium ion (I) and/or a hydroxymercurinium ion (II) is present in this system.



Furthermore they consider these ions are functional in the reaction known as oxymercuration.

These authors have arrived at this conclusion on the basis of an elaborate quantitative phase distribution study in which they made various adjustments because of "secondary reactions" that were especially prominent at low acid concentrations. They did not evaluate these "secondary effects" qualitatively but enumerated them as follows:

1. Over a period of time the apparent mercury concentration, determined by thiocyanate titration, decreased a few per cent per hour at the start and some 27% in 13 hr.

2. Over a period of time the apparent amount of unsaturation is within experimental error of the theoretical for about one and one-half hours and then

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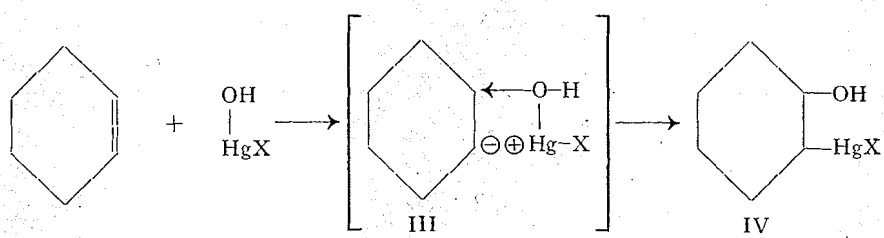
increases at an accelerating rate so that it is some 3% high after three hours and some 40% high after 17 hr. The unsaturation was determined by bromide-bromate titration as presumptive for cyclohexene.

3. Acidity increased with time.

4. After a time a solid separated from the mixture, especially at low acid concentrations. They considered that this material was probably 1-hydroxy-cyclohexane-2-mercuric salt (IV) which was derived via the mercurinium ion I or II.

Hydroxymercurials of cyclohexane (IV) have recently been prepared by us from cyclohexene (3). On the basis of observed second-order kinetics, stereochemical considerations, and the observation that methoxymercuration is faster than hydroxymercuration the ionic intermediate of Lucas, Hepner, and Winstein was considered less plausible as a mechanistic explanation than an intermediate molecular coördination complex (III) of cyclohexene with basic mercuric acetate.



In view of this difference of opinion it seemed worthwhile to examine whether 1-hydroxy-2-nitratomercuricyclohexane (IV, X = NO_3) would be stable in the environment where the mercurinium ion is supposed to exist.

Since easy interchangeability of X in the –HgX substituent is characteristic of oxymercurials such as IV, it was unnecessary to prepare 1-hydroxy-2-nitratomercuricyclohexane. The known 1-hydroxy-2-acetoxymercuricyclohexane was added instead to solutions of nitric acid in water. The concentration range of 0.04–0.55 mole per liter used by Lucas, Hepner, and Winstein was examined. After a few minutes the homogeneous solutions were poured into aqueous sodium chloride solutions from which the analogous chloromercurial (IV, X = Cl) would be precipitated almost quantitatively (3). In every case when nitric acid was present the odor of cyclohexene was apparent, thus indicating decomposition of the oxymercurial. The results in Table I show that the mercurial could not have been formed in appreciable amount under these reaction conditions.

Thus hydroxymercuration with mercuric nitrate is not a significant reaction in water. However, it is interesting to note that methoxymercuration of cyclohexene may be accomplished with mercuric nitrate in methanol to give an 80% yield of 1-methoxy-2-chloromercuricyclohexane after the initial product is

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TABLE I

SOLUTION OF 1-HYDROXY-2-ACETOXYMERCURICYCLOHEXANE (0.09 MOLE PER LITER) IN DILUTE NITRIC ACID AFTER 10 MIN.

Expt. No.	Conc. HNO_3 mole/liter	Yield of IV X = Cl	
		gm.	%
1	None	0.29	97
2	0.079	0.02	7
3[a]	0.159	0.01	3
4	0.159	0	0
5	0.248	0	0
6	0.397	0	0

[a] *0.095 mole per liter of sodium nitrate added.*

treated with aqueous sodium chloride. Evidently the lesser activity of nitric acid in the alcoholic reaction medium, as contrasted to the activity in water, is responsible.

Since it is evident from these experiments that the solid observed by Lucas, Hepner, and Winstein could not have been an oxymercurial of type IV (X = NO_3) we carried out experiments approximating their reaction conditions at concentrations shown in Table II in order to examine this solid.

TABLE II

MOLAR CONCENTRATIONS YIELDING MERCUROUS SALT IN ONE HOUR

Conc. $Hg(NO_3)_2$	Conc. HNO_3	Conc. C_6H_{10}	% HgCl
0.050	0.050	0.042	4
0.050	0.100	0.042	2
0.095	0.275	0.033	4.5
0.200	0.55	0.275	11.5

After one hour the interface between the carbon tetrachloride and aqueous phases contained a small amount of solid which was found to be mercurous chloride. The presence of this salt seemed not to be owing to impurities since purified reagents were used, nor was the extent of reduction affected by the presence of atmospheric oxygen. Its chloride moiety probably originated by slight hydrolysis of the carbon tetrachloride.

When the aqueous layer was treated with sodium chloride, from 2–12% of the total mercury was precipitated as mercurous chloride. The decrease in apparent mercury concentration and slow increase in acidity reported by Lucas, Hepner, and Winstein may therefore be explained simply by the fact that mercurous nitrate cannot be titrated quantitatively by thiocyanate and that acid is necessarily formed during the reduction. Likewise the increase in apparent unsaturation may be expected since the bromide-bromate reagent will oxidize mercurous nitrate quantitatively to the mercuric state.

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In order to ascertain the nature of the oxidation product corresponding to the reduction of mercuric salt we carried out an experiment at 25°C. using equimolar quantities of cyclohexene, mercuric nitrate, and nitric acid and omitted the carbon tetrachloride used by Lucas, Hepner, and Winstein. At no time was the odor of cyclohexene absent, but the nonaqueous phase disappeared after six minutes of violent shaking, and it reappeared after four hours, together with a small amount of solid and a characteristic disagreeable odor. This regenerated phase was removed after 16 hr. by azeotropic distillation under reduced pressure, leaving behind the solid.

Examination of the distillate showed that the nonaqueous phase comprised about half of the cyclohexene used initially, as well as formylcyclopentane in yield of about 37 mole % of the cyclohexene consumed. The actual yield of formylcyclopentane is slightly higher than this, because the nondistillable solid is the trimer of formylcyclopentane. This trimer has previously been reported as a polymer by Tiffeneau in a private communication relating to his report on formylcyclopentane (10) and later as a polymer of somewhat lower melting point (12). It can be formed from the aldehyde by treatment with 85% phosphoric acid, and it gives the same 2,4-dinitrophenylhydrazone. Since analysis with methyl Grignard reagent in the Kohler machine shows that it contains no active hydrogen or carbonyl group, we designate it as 2,4,6-tricyclopentyl-1,3,5-trioxane.

After the aqueous phase was chloroform-extracted to remove the trimer it was poured into aqueous sodium chloride. After the precipitate was extracted with methanol to remove a small amount of mercuric salt the remainder was found by its X-ray diffraction powder pattern to be essentially pure mercurous chloride in a molar yield of 90% of the mercuric nitrate used initially. The remaining 10% of mercuric salt is found in the methanolic extract and in the aqueous filtrate. When the mercuric salt is converted to the sulphide a few per cent of cyclopentanecarboxylic acid can be extracted from the aqueous filtrate. Under the conditions used in this experiment the reaction was rapid, since an aliquot removed after the first 20 min. showed that 10% of the mercuric salt was reduced to mercurous nitrate within this time.

The mechanism of this oxidation is at present obscure. The comparative consumption of reagents indicates that two molecules of mercuric nitrate are consumed per molecule of cyclohexene. None of the nitric acid is reduced to nitrous acid, but when insufficient mercuric nitrate remains in the system metallic mercury is precipitated. One might presume that the oxidation would produce either epoxycyclohexane or cyclohexandiol-1, 2 (*dl*, *ld* or *dd*, *ll*) and that one of these would undergo a Wagner–Meerwein type of 1, 2-rearrangement in the resultant solution. However, none of these substances shows any tendency toward rearrangement either in mercuric nitrate – nitric acid solutions or in similar solutions of mercurous nitrate.

The 1, 2-rearrangement of cyclohexandiol to formylcyclopentane has been reported as a pyrolysis over aluminum oxide (11) but these rearrangements

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have not been effected in water solution. On the other hand, Tiffeneau (10) has found that 2-iodocyclohexanol on treatment with silver nitrate is converted to formylcyclopentane. Although he does not define his reaction conditions, these are fixed approximately by the fact that he obtained cyclohexyl nitrate (together with cyclohexene) by treatment of cyclohexyl iodide with silver nitrate.

Since Tiffeneau's rearrangement thus seemed to proceed through the nitrate ester we have prepared the mono- and di-nitrate esters of *dd*, *ll*-1, 2-cyclohexandiol, but find that neither of these shows any tendency to rearrange to formylcyclopentane. We have as yet been unsuccessful in our attempts to esterify *dl*, *ld*-1, 2-cyclohexanediol with mixed nitric-phosphoric acid.

Discussion

In view of the extent to which the oxidation reaction occurs with the reagent concentrations used by Lucas, Hepner, and Winstein one may inquire as to why their evaluated equilibrium ratios (K_E) should have been sufficiently constant that they were able to average 2/3 of their results instead of extrapolating to zero time. Inspection of their equation, simplified by the fact that cyclohexene is almost insoluble in water,

$$K_E = \frac{\text{Conc. } C_6H_{10} \text{ in aqueous phase}}{\text{Conc. } C_6H_{10} \text{ in } CCl_4 \text{ [initial conc. Hg} - \text{ conc. } C_6H_{10} \text{ in aq. phase]}}$$

shows, however, that it is a function only of the relative concentrations of cyclohexene in the two phases. The oxidation reaction may be expressed by the equation

$$C_6H_{10} + 2Hg(NO_3)_2 + H_2O \longrightarrow C_6H_{10}O + 2HgNO_3 + 2HNO_3$$

Now it is evident by actual inspection of the reaction mixture without carbon tetrachloride that cyclohexene forms a complex with mercuric nitrate in the aqueous phase at a rate depending on the initial concentration of the mercuric salt. Lucas, Hepner, and Winstein assigned 20 min. for this establishment of equilibrium between the two phases. During this time, and subsequently, the cyclohexene in the aqueous phase would be consumed, but this would not be apparent by titration with bromide-bromate because the formation of 2 molecules of mercurous nitrate would compensate equivalently for the loss of cyclohexene. Compensating transfer of cyclohexene from the nonaqueous layer would be minimized by the consumption of mercuric nitrate with which it would otherwise form a complex in the aqueous solution. Fortuitous constancy would thus be obtained. However, K_E eventually would decrease because consumption of mercuric nitrate at twice the rate for that of cyclohexene would decrease the amount of initial complex and thus redistribute the cyclohexene into the nonaqueous phase.

On the basis of their results, Lucas, Hepner, and Winstein have defined the complex comprising mercuric nitrate, nitric acid, and cyclohexene as a mercurinium ion, although none of the criteria for authentic ions (electrolytic

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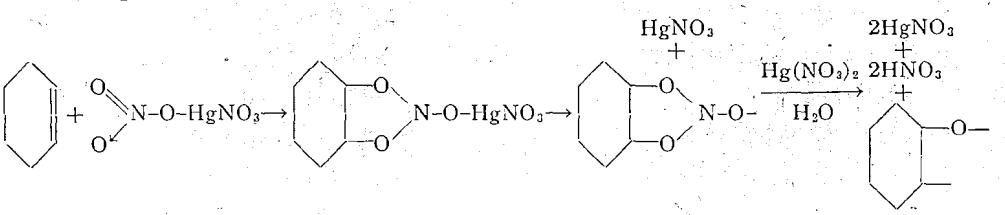
migration, abnormal depression of freezing point, etc.) were applied. Perhaps they did not mean an ion in the commonly accepted chemical sense, but rather a dipolar salt. However, they do consider the absorption of cyclohexene by aqueous mercuric nitrate as analogous with that of aqueous silver nitrate (7, p. 3102; 13) and presumably, with alkene-platinous halide (1, 5, 6, 9) and with alkene-cuprous halide complexes (8). But these complexes all have one common characteristic which would, indeed, seem necessary for complex cation formation: the complex forms with the lower valence state of the element. Thus olefins reversibly form complexes in neutral aqueous solution with argentous but not with argentic salts, with cuprous but not with cupric salts, and with platinous but not with platinic salts. One might then expect mercurous but not mercuric salts (since no higher valence is known) to form complexes with olefins. Actually undissociated complexes of alkenes with neutral mercurous salts have been observed (4).

Another significant difference between the argentous, cuprous, and platinous-alkene complexes and the mercuric nitrate – cyclohexene complex is found in the behavior toward acids. Although the former tend to decompose as the concentration of the acid is increased, the formation of the mercuric nitrate – alkene complex is enhanced by addition of nitric acid. Assuming that the acid is functioning to prevent the hydrolysis of mercuric nitrate, it is reasonable to assume that coordination occurs with the nitrato group. Decomposition of the resulting complex in presence of excess mercuric nitrate would result in the reaction products which have been isolated if the organic fragment were to rearrange to formylcyclopentane.



The nitrato group must be involved specifically in both the solubilization and oxidation process, since a 0.16 molar solution of mercuric chloride in 0.16 molar hydrochloric acid will not absorb a detectable amount of cyclohexene. This situation is unaltered when the acid concentration is increased tenfold or decreased to zero, although in the latter case the concentration of mercuric salt must be decreased in order to prevent its partial precipitation. This failure of mercuric chloride to form a complex with cyclohexene might be thought by some to be owing to its low degree of ionization. However, no such difficulty is encountered in coördination of mercuric chloride with tertiary amines, nor does the limited ionization of cuprous chloride prevent the mutual solubilization of the solid salt and the alkene in water (8).

The significance of the cyclohexene – mercuric nitrate – nitric acid complex, whether or not it be considered as a mercurinium ion, in oxymercuration is

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doubtful. Firstly it has been shown in this report that no oxymercurial is produced under conditions favorable for the complex. Secondly in a system such as cyclohexene – mercuric acetate – water, where hydroxymercuration occurs almost quantitatively, there is no evidence for an intermediate complex consisting of these components. If such a complex were significant to the oxymercuration reaction then its rate of formation would have to be faster than that of the hydroxyalkane-mercurial, but this seems not to be the case.

Thus visible evidence for the formation of the cyclohexene – mercuric nitrate – nitric acid complex is provided by the solubilization of the alkene into the aqueous phase. If disappearance of the nonaqueous phase is used as a criterion, the formation of 1-hydroxy-2-acetoxymercuricyclohexane is complete in 13 min. when 0.01 mole quantities of mercuric acetate and cyclohexene are shaken in 250 ml. of water. On the other hand, 30 min. are required before the second phase disappears when 0.1 mole of acetic acid is included in an otherwise identical experiment. The yield of 1-hydroxy-2-chloromercuricyclohexane was 50–63% when both reaction systems were poured into dilute aqueous sodium chloride.

If the cyclohexene – mercuric acetate – water system had behaved analogously with that comprising cyclohexene, mercuric nitrate, and water, the solubilization of the alkene ought to have been accelerated by addition of acid. Instead it was retarded. Actually this diminution in rate is in accord with the concept that basic mercuric acetate reacts directly with the alkene to form the hydroxyalkanemercurial, since the concentration of basic salt would be reduced by presence of acid. Furthermore it is improbable that a stable ionic intermediate is operative since the rate of solution of the alkene closely approximates the rate of formation of the oxymercurial.

While there is thus no evidence that an alkene – mercuric salt complex is involved in oxymercuration the oxidation reaction is frequently encountered. However, it is ordinarily slower than oxymercuration in water or methanol. It does not interfere except during rate studies with alkenes which alkoxymercurate quite slowly. In such cases the precipitation of mercurous acetate from the alcoholic medium coincides with the decay of the rate constant. There are certain cases (2) such as the treatment of *trans*-stilbene with mercuric acetate in absence of catalyst where oxidation to 1, 2-dimethoxy-1, 2-diphenylethane is the exclusive reaction. In this instance addition of peroxides will sufficiently accelerate the oxymercuration so that it takes precedence over the oxidation, but boron trifluoride evidently accelerates both reactions, since dimethoxydiphenylethane is the only product obtained. The difference in function of these two catalyst types is the basis of a study presently carried out in this laboratory.

Experimental*

Stability of 1-Hydroxy-2-acetoxymercuricyclohexane in Dilute Nitric Acid.

Freshly prepared 1-hydroxy-2-acetoxymercuricyclohexane (0.32 gm., 0.0009 mole) was added to 9 ml. of water containing various amounts of nitric acid

* *All melting points have been corrected against reliable standards.*

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(Table I) and the whole made up to 10 ml. volume with water. The compound dissolved after shaking for one minute. After 10 min. the whole was poured into dilute aqueous sodium chloride. The 1-hydroxy-2-chloromercuricyclohexane was filtered, dried, and weighed. In one experiment sodium nitrate was added to effect conversion to the nitratomercuri compound.

Methoxymercuration of Cyclohexene with Mercuric Nitrate

Experiments 1, 2, and 3 were carried out with 0.015 mole mercuric nitrate and 0.02 mole cyclohexene in methanol–water volumes of 50: 0; 25: 25, and 5: 45 ml. respectively. A trace of nitric acid was added as catalyst. The times after which no mercuric oxide was precipitated by alkaline treatment of a test portion were respectively six, three, and nine minutes. The yields after 15 min. (80, 70, and 10% respectively) were estimated from the precipitate of *trans*-1-methoxy-2-chloromercuricyclohexane obtained by pouring the reaction mixtures into aqueous sodium chloride. The products from Expts. 1 and 2 both melted at 113–114°C. The product from Expt. 3 was very impure, but a single crystallization from acetone showed that it was partly 1-methoxy-2-chloromercuricyclohexane, m.p. 112–114°C.

Reaction of Cyclohexene with Aqueous Mercuric Nitrate – Nitric Acid Solution

A solution of 81.2 gm. (0.25 mole) of mercuric nitrate and 15.7 ml. (0.25 mole) of 70% nitric acid in 500 ml. of water was treated with 25 ml. of freshly purified cyclohexene containing only a trace of peroxide. After three minutes' shaking less than half the cyclohexene remained; there was no separate phase after six minutes. The odor of cyclohexene prevailed throughout the reaction. No difference in results was obtained when the reaction was carried out under nitrogen. At the end of 20 min. a test portion, removed, extracted with ether, and treated with aqueous sodium chloride precipitated mercurous chloride equivalent to 0.1 of the original mercury content. The ether extract gave a positive carbonyl test with dinitrophenylhydrazine.

A separate phase separated after four hours. After 16 hr. the reaction mixture was distilled under 15 mm. pressure into an ice-cooled receiver and then into a trap cooled by dry-ice. The aqueous residue (200 ml.), containing an oily phase, was twice extracted with 30 ml. portions of chloroform. A test of the extracted aqueous residue with alkali did not indicate any mercuric ion. Treatment with 60 ml. of saturated aqueous sodium chloride gave a white precipitate which was filtered, washed with methanol, and when vacuum dried, weighed 52.8 gm. Since this solid was shown to be pure mercurous chloride by test with alkali and by its X-ray diffraction pattern it represents 89.5% of the total mercury introduced into the reaction. The methanol used to wash the white precipitate was diluted with water and nitric acid, and then was treated with hydrogen sulphide. The mercuric sulphide which precipitated was washed with methanol. Its weight, 5.83 gm., represents 10% of the mercury originally used.

The chloroform extract was evaporated to leave a gummy solid, which was crystallized wastefully from ether – petroleum ether (b.p. 40–60°C.) mixture.

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It weighed 0.25 gm. and melted at 123.5–124.5°C. When crystallized from hot 95% ethanol it melted at 128.5–129°C. When 70 mgm. of this compound was boiled with an equal amount of 2, 4-dinitrophenylhydrazine in ethanolic hydrochloric acid it formed the 2, 4-dinitrophenylhydrazone of formylcyclopentane, m.p. 163–164°C. after crystallization from boiling ethanol (30 ml. per gm.). Calc. for $C_{12}H_{14}N_4O_4$: C, 51.9; H, 5.05; N, 20.1%. Found: C, 51.8; H, 5.07; N, 19.9%.

The content of the dry-ice trap used in the vacuum distillation was dried with magnesium sulphate and distilled. The fraction, b.p. 81–83°C. weighed 9.2 gm. It was proved by methoxymercuration to be pure cyclohexene, which thus constitutes a 45% recovery of this starting material. The residue from this distillation was combined with the ether – petroleum ether liquors from which the solid, m.p. 124°C., was obtained, and also with an ether extract (dried with magnesium sulphate) of the aqueous distillate from the vacuum distillation. The accumulated oil was distilled to yield 4.45 gm., b.p. 80–81°C. (124 mm.), d_4^{20} 0.932, n_D^{20} 1.4428 and 0.8 gm. boiling approximately at 65°C. (8 mm.), n_D^{20} 1.4563. The first fraction, evidently formylcyclopentane, represents 37% of the cyclohexene consumed. The higher boiling fraction was redistilled at 215–216°C., corr., n_D^{20} 1.4532. Since these constants conform with those reported for cyclopentanecarboxylic acid, the crude yield is 5.6%.

The formylcyclopentane was redistilled, b.p. 133–134°C., n_D^{20} 1.44211, d_4^{20} 0.927. A portion was converted to the semicarbazone in 60% yield, m.p. 123–123.5°C. after crystallization from water. A third portion of the aldehyde was treated with 2, 4-dinitrophenylhydrazone in aqueous-ethanolic sulphuric acid. It yielded a dinitrophenylhydrazone the melting point of which was not depressed by admixture with the derivative described above.

2, 4, 6-Tricyclopentyl-1, 3, 5-trioxane

When 0.01 gm. of 85% phosphoric acid was allowed to flow into 0.20 gm. (0.002 mole) of formylcyclopentane solidification commenced at the interface. After two hours the solidification was complete. The solid was crystallized from boiling ethanol (25 ml. per gm.), m.p. 122.4–122.7°C., wt., 0.13 gm., or 65% of the theoretical yield. Recrystallization from the same solvent raised this melting point to 128–129°C. A mixed melting point with the solid compound obtained from the oxidation reaction was not depressed. The molecular weight determined by the Rast method initially gave a value of 292 (calculated 294) but this number decreased to 204 after repeated melting. Analysis in the micro-Kohler machine with methylmagnesium iodide showed absence of active hydrogen and carbonyl groups. Calc. for $C_{18}H_{30}O_3$: C, 73.5; H, 10.2%. Found: C, 73.5; H, 10.3%.

Reaction of Cyclohexene in Carbon Tetrachloride with Mercuric Nitrate and Nitric Acid in Water

A 250 ml. separatory funnel fitted with a sleeve-sealed stirrer was filled with 25 ml. of carbon tetrachloride and 200 ml. of water containing cyclohexene,

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mercuric nitrate, and nitric acid in concentration shown in Table II. The remaining air-space was negligible and results were identical when the funnel had previously been swept with nitrogen. After one hour of violent stirring the nonaqueous layer was drawn off together with a small amount of mercurous chloride. The aqueous layer was run into centrifuge jars containing 100 ml. of saturated aqueous sodium chloride. After 10 min. the centrifugate was filtered and the white precipitate washed with methanol until it no longer gave a test for mercuric chloride. It was then dried at 110°C. and weighed.

Absorption of Cyclohexene by Aqueous Mercuric Acetate

To a solution of 3.16 gm. (0.01 mole) of mercuric acetate in 250 ml. water at 25°C. was added 1 ml. (0.01 mole) of cyclohexene. The whole was shaken for 13 min., until the cyclohexene layer disappeared. The liquor was poured into 50 ml. of saturated aqueous sodium chloride. The 1-hydroxy-2-chloromercuricyclohexane which precipitated weighed 2.1 gm. or 63% of the theoretical amount.

The experiment was repeated except that the volume of 250 ml. was made up from water and 5.7 ml. (0.1 mole) of acetic acid. Thirty minutes of shaking elapsed before the nonaqueous phase disappeared. The yield of 1-hydroxy-2-chloromercuricyclohexane was 1.67 gm. or 50% of theoretical. In neither case was more than a trace of mercurous salt detected. In either reaction mixture the amount of product remaining in the aqueous solution was found to be 23–25% of that actually isolated.

Aqueous Mercuric Salts with Cyclohexene

When 1 ml. of cyclohexene was shaken for 24 hr. with 50 ml. of an aqueous solution 0.16 molar both in mercuric chloride and hydrochloric acid less than 1% of the cyclohexene was absorbed. This behavior was the same when the acid concentration was increased to 1.6 *N*. The absorption of 1 ml. of cyclohexene was likewise not measurable in 100 ml. of 0.08 molar aqueous mercuric chloride without any acid.

When the turbid solution of 6.50 gm. (0.02 mole) of mercuric nitrate in 50 ml. of water was shaken over five minutes with 1.6 ml. (0.02 mole) of cyclohexene the solution gradually became clear but only 35% of the cyclohexene layer disappeared; after 10 min. solution was complete. After 20 min. the solution was poured into aqueous sodium chloride and the mercurous chloride filtered off, washed with water, methanol and ether. It weighed 0.75 gm. or 16% of the theoretical yield for complete reduction of the mercuric salt.

When 8.2 gm. (0.1 mole) of cyclohexene was shaken for 10 min. under nitrogen with a solution of 28.06 gm. (0.1 mole) of mercurous nitrate in 6.3 ml. (0.1 mole) of 70% nitric acid and 100 ml. of water a precipitate of mercury began to appear. There remained 6.06 gm. of cyclohexene or 74% of the original amount. When this experiment was repeated with inclusion of 0.1 equivalent of mercuric nitrate the precipitation of mercury was hindered for about one hour, and only 20% of the cyclohexene was absorbed.

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Bromide-Bromate Titration of Mercurous Salt in Presence of Cyclohexene

The procedure of Lucas, Hepner, and Winstein (7) was followed in those runs where cyclohexene was present. In the absence of cyclohexene known amounts of potassium bromate and mercurous nitrate in dilute nitric acid were titrated with standard thiosulphate. Table III demonstrates the consumption of 1 equivalent of oxidizing agent by the mercurous salt or 2 equivalents by cyclohexene.

TABLE III

Expt. No.	Equiv. bromide-bromate	Equiv. $HgNO_3$	Equiv. unsaturation (0.5 equiv. C_6H_{10})	Equiv. $Na_2S_2O_3$	Total calc. equiv. unsaturation
1	0.00392	0	0	0.00391	0
2	0.00366	0.00034	0	0.00332	0.00034
3	0.00366	0.00103	0	0.00262	0.00104
4	0.00366	0	0.00151	0.00218	0.00148
5	0.00366	0.00034	0.00151	0.00185	0.00181

Treatment of Cyclohexanediols and Epoxycyclohexane with Mercury Salts

When cyclohexene was replaced by either *cis* or *trans* cyclohexanediol-1, 2 or epoxycyclohexane in the acidified mercuric nitrate reagents and the reaction mixtures were extracted with chloroform after 24 hr. no trace of formylcyclopentane could be detected in the extracts. Similar results were obtained when acidified solutions of mercurous nitrate were treated with the same substances. Finally, 0.005 mole of these substances was each treated over several days with a solution of mercuric nitrite prepared by admixture of mercuric chloride and sodium nitrite. Some mercurous salt precipitated but no formylcyclopentane could be detected. The dinitrophenylhydrazine test reagent is very sensitive for detection of this aldehyde.

dd, ll-1-Hydroxy-2-nitroxycyclohexane

To a solution of 11.2 gm. (0.1145 mole) of 1, 2-epoxycyclohexane in 110 ml. of anhydrous ether at −70°C. was added over one hour 4.8 ml. (0.1145 mole) of 100% nitric acid. The solution was stirred an additional half-hour, then let warm to 25°C. and washed with water and then with 2% aqueous sodium carbonate until the aqueous wash water was neutral. After drying with magnesium sulphate the solution was distilled finally at 3.5 mm. to give a main fraction, b.p. 100–105°C. weighing 10 gm. This 55% yield was redistilled at 100°C. (3 mm.), n_D^{20} 1.47892, d_4^{20} 1.225. M_D (calc.) 37.2; found 37.4. Calc. for $C_6H_{11}NO_4$: C, 44.6; H, 6.93; N, 8.71%. Found: C. 44.5; H, 7.02; N, 8.63%.

dd, ll-1, 2-Dinitroxycyclohexane

To a mixed acid prepared from 2.88 ml. (0.068 mole) of 100% nitric acid and 2.76 ml. (0.048 mole) of 96% sulphuric acid stirred and maintained at 0°C. was added 3.00 gm. (0.026 mole) of *dd, ll-1, 2*-cyclohexanediol over 30 min.

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After 15 min. longer at 0°C. the whole was drowned in ice water which was then ether-extracted. The ether extract, washed with water and sodium carbonate until neutral and dried with magnesium sulphate, was distilled finally at 0.5 mm. to yield 2.2 gm. (65%) b.p. 100–102°C. This was redistilled at 118–118.5°C. (5.5 mm.) n_D^{20} 1.47555, d_4^{20} 1.318. M_D calc. 44.1; found, 44.0. Calc. for $C_6H_{10}N_2O_6$: C, 34.9; H, 4.86; N, 13.6%. Found: C, 35.1; H, 4.88; N, 13.5%.

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EUTECTIC SOLIDIFICATION IN METALS[1]

By W. C. Winegard,[2] S. Majka,[3] B. M. Thall,[4] and B. Chalmers[4]

Abstract

A study has been made of the process of solidification of the alloys of tin and lead, the eutectic structure of which is typically lamellar. A technique was developed in which the rate and direction of solidification were controlled. It was demonstrated that freezing takes place by the simultaneous edgewise growth of the lamellae, the thickness of which depends on the rate of freezing. It was also shown that the interface between solid and liquid at any instant is corrugated, owing to the fact that one of the phases is in advance of the other. This is attributed to the difference in thermal conductivity of the two phases. A detailed description is given of the process of eutectic solidification.

1. Introduction

Eutectic solidification occurs in a binary system when a single liquid phase is transformed into two solid phases which are in equilibrium with the liquid at the eutectic temperature. There have been two detailed surveys (Brady (1) and Portevin (4)) of the structures that are found in binary eutectic alloys, but little has been written about the details of the process by which these structures are formed.

The commonest type of eutectic structure is that which is described as "lamellar". The appearance under the microscope of a suitably prepared surface is shown in Fig. 1, in which it will be seen that the two phases appear to exist as alternate layers.

The earliest attempt to account for the origin of this structure was by Tammann (8)*. His theory is that crystallization of one phase starts by nucleation and that this phase solidifies until the resulting change in the composition of the liquid is sufficient to cause the other phase to nucleate; the second phase then grows and the process is reversed. This results in the alternate solidification of the two phases. Fig. 2 represents a very small element of

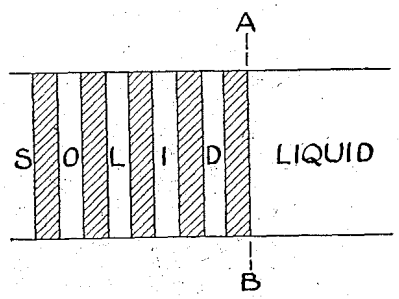

Fig. 2. *Eutectic solidification according to the Tammann theory.*

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* *Tammann's views, developed in much earlier work, are summarized in this book.*

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PLATE I

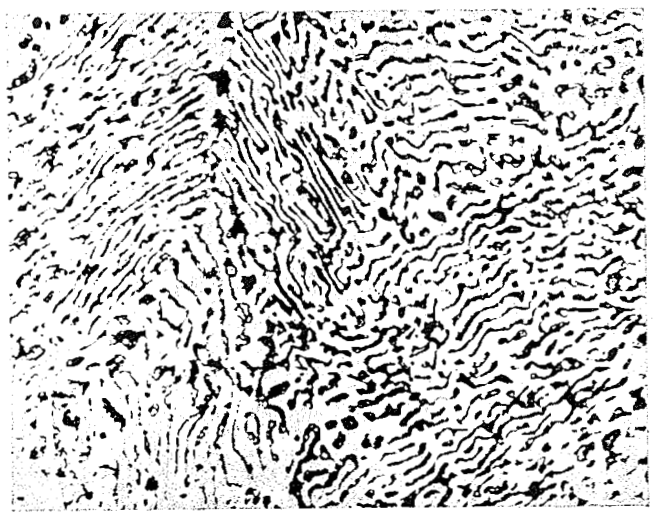

FIG. 1. *Typical lamellar eutectic structure in Pb–Sn system.* × *1000.*

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the material during solidification. The interface between solid and liquid is represented by AB, with solid to the left and liquid to the right. The region considered is small enough for the interface to be represented as a plane. The direction of heat flow is from right to left and, according to Tammann's theory, the lamellae should form perpendicularly to the direction of heat flow, or parallel to the interface between solid and liquid.

A different view was taken by Vogel (10); he considered that the lamellar appearance corresponded to the existence of the two phases in the form of rods, or more accurately polygonal prisms, with their axes perpendicular to the interface. Crystallization of the two phases would occur simultaneously, and the instantaneous condition would be as represented in Fig. 3.

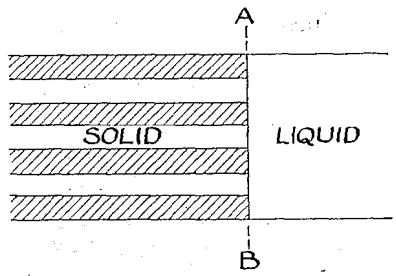

FIG. 3. *Eutectic solidification according to the Vogel theory.*

Experimental investigation of this question by Straumanis and Braaks (6, 7) proved that, in five alloys which were examined, the structure was lamellar and that the lamellae were approximately perpendicular to the interface. This appears to have been the only investigation in which the direction of heat flow was known, and it offers very strong support for the views of Vogel as opposed to those of Tammann. Recent work by Elwood and Bagley (3) has shown the existence of definite crystallographic relationships between the interpenetrating components of a eutectic grain.

Recent work by Thall and Chalmers (9) on the structure of aluminum–silicon eutectic alloys shows that the modification of the structure, by rapid freezing or by the addition of sodium, can be accounted for by making certain assumptions with regard to eutectic freezing. One of these assumptions is that the two phases are formed simultaneously (as in Fig. 3) and another is that, instead of the interface being smooth, it has the form represented in Fig. 4, in

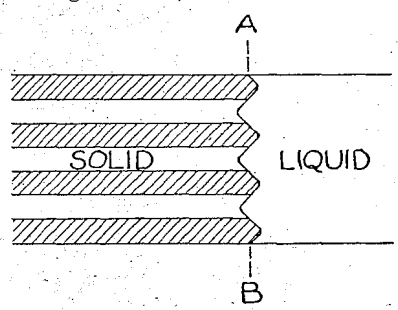

FIG. 4. *Eutectic solidification as envisaged by Thall and Chalmers.*

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which the interface between the dark phase and the liquid is in advance of the interface between the light phase and the liquid. This assumption is made on the basis of the fact that the rate of advance of the interface is determined by the heat flow across it and by the latent heat of fusion of the solid phase. The surface of one phase will tend to lead if its thermal conductivity is higher and if its volume latent heat is lower than those of the other phase.

The present investigation was undertaken in order to examine the validity of these assumptions and to provide further experimental evidence about the process of eutectic solidification.

2. Experimental Considerations

The object of the experimental work was to study the geometry of the structure and of the solid–liquid interface in relation to the direction of heat flow. In order to achieve this result, it is necessary for freezing to occur under conditions which allow the direction of heat flow and the speed of solidification to be determined. It is also necessary to be able to examine the solid–liquid interface.

These requirements are all satisfied by the experimental technique previously described by Chalmers (2), in which solidification takes place in a graphite "boat" and the heat flow is controlled by means of a movable furnace. A temperature gradient can be set up and maintained so that solidification proceeds from one end of the sample to the other at any required speed. For this purpose, the furnace is moved mechanically. Provision was also made for rapid tilting of the boat at any desired time. This causes rapid removal of the liquid from the boat, and allows the preservation of the solid surface for detailed examination. The present paper deals with an investigation of tin–lead alloys. The use of these alloys has the advantage that the experiments can be performed in air, as oxidation and evaporation are relatively slow. In addition, the low melting-point simplifies the experimental technique. According to Raynor (5), the equilibrium diagram for the lead–tin system is as shown in Fig. 5.

3. Direction of Growth of Lamellae

The directions of heat flow and of the interface are known in specimens prepared in the way described above. The structure, as determined from microsections, can therefore be related to the direction of heat flow. Sections were accordingly taken in the horizontal plane (i.e., perpendicular to the interface) and in a vertical plane parallel to the interface. Typical photomicrographs of these two sections in a eutectic sample are shown in Figs. 6 and 7 respectively.

It must be concluded that the structure is lamellar, and that the lamellae are approximately parallel to the direction of heat flow. It is also observed that the lamellae are in groups, those in each group being equally spaced and inclined at the same angle to the horizontal plane. A group of similarly inclined lamellae may be referred to as a "eutectic grain".

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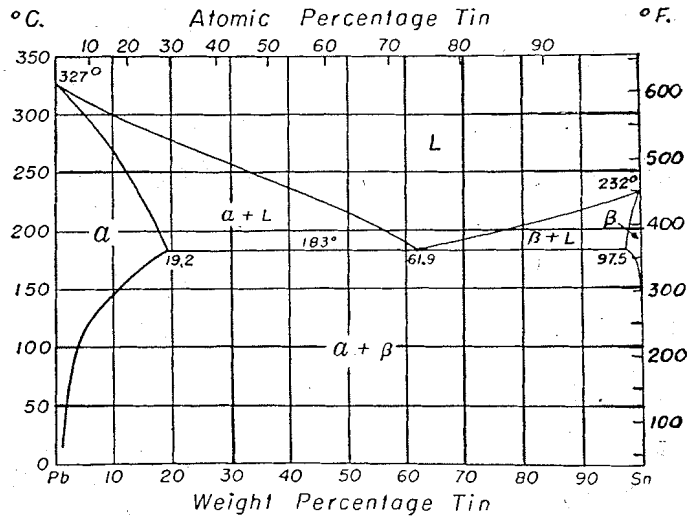

FIG. 5. *Lead-tin equilibrium diagram.*

4. Macroscopic Appearance of Alloys

If the composition of an alloy is not that of the eutectic, then the first material to solidify will consist mainly of the element which is present in excess, with some of the other element in solid solution. Primary solidification continues until the remaining liquid has reached the eutectic composition.

In order to examine the process of primary crystallization, alloys of 70% Sn and 30% Pb, and of 55% Sn and 45% Pb were allowed to solidify at the rate of 0.02 mm. per min. The former alloy presented the characteristic appearance shown in Fig. 8.

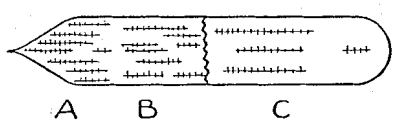

FIG. 8. *Characteristic appearance of slowly cooled 70% Sn-30% Pb alloy.*

The structure appeared to have three distinct zones. In the first (A), Fig. 8, the solid consisted entirely of a solid solution of lead in tin, with a dendritic structure. In the second zone (B), a fine eutectic surrounded the dendrites of the tin-rich solid solution, while in the third (C) the dendrites were fewer and the eutectic coarser. The second alloy is of such composition as to cause primary crystallization of the lead-rich phase. The structure obtained is shown in Fig. 9. The structure was quite different from that of the alloy with the higher tin content, and was as follows: Zone (A), Fig. 9, consisted of distinct crystals of

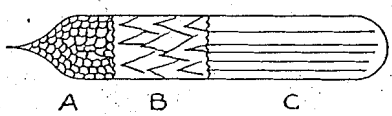

FIG. 9. *Characteristic appearance of slowly cooled 55% Sn-45% alloy.*

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lead and of tin; the second zone (B) consisted of fine eutectic, and the third zone had a coarse lamellar structure. The main difference between the two structures is in their primary constituents. In the tin-rich alloy, they were manifest in the form of dendrites, while in the lead-rich alloy no dendrites were evident.

The formation of dendrites can be explained if the solid has a higher thermal conductivity than the liquid; the experimental results suggest that the thermal conductivity of the liquid is intermediate between those of the two solid phases; the tin-rich solid solution must have a greater conductivity than the liquid in order to account for its tendency to form dendrites.

5. Shape of Solid–Liquid Interface

Examination of the interface between solid and liquid is not possible while freezing is in progress. The interface existing at any instant can, however, be preserved for subsequent examination by sudden removal of the liquid.

The interface was first examined in an alloy containing 70% Sn and 30% Pb. When the interface was preserved by sudden decanting of the liquid, the tin dendrites projected from the remainder of the interface to such an extent that examination at high magnification with the metallographic microscope was impossible.

It was possible, however, to obtain a formvar replica of the surface and to examine it in the electron microscope after shadow casting. The authors are indebted to Dr. D. Scott of the Physics Department, University of Toronto, who undertook this aspect of the investigation. Considerable difficulty was encountered in achieving satisfactory contrast, because the replica had to be made thick to avoid disturbance by the dendrites. An electron micrograph is shown in Fig. 10.

It is apparent that the surface of the replica was "corrugated" in a way that corresponds to an interface shape of the type represented in profile in Fig. 4. An interpretation is that one phase advances into the liquid ahead of the other.

In order to avoid the difficulties caused by the presence of dendrites, similar experiments were conducted on an alloy with the eutectic composition. Examination of the unetched surface by phase contrast microscopy* confirmed the previous deduction that the surface was "corrugated". An example of the appearance of the surface at a magnification of 1500 is shown in Fig. 11. An estimate of the "depth" of the corrugations was made by using the extreme sensitivity with which focusing can be adjusted. It was found that, in the case under review, the depth was 0.2 to 0.5 micron; the lateral spacing of the laminations was about 2 microns.

* *In phase contrast microscopy, very high resolution normal to the surface is obtained by using a type of illumination in which slight changes in level give large differences in brightness of the image.*

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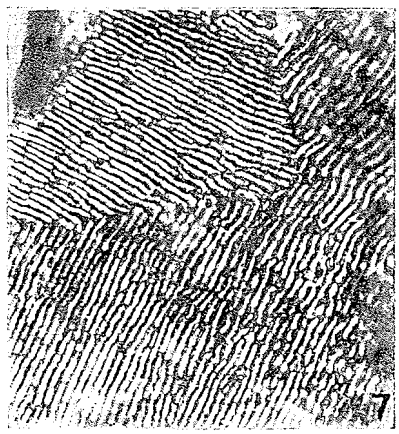

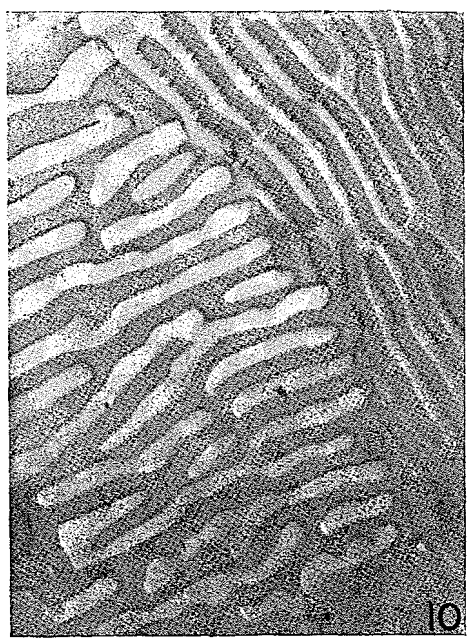

FIG. 6. *Lead-tin eutectic, microsection perpendicular to interface.* × *1000.*
FIG. 7. *Lead-tin eutectic, microsection parallel to interface.* × *750.*
FIG. 10. *Electron micrograph of Pb-Sn eutectic interface.* × *10,000.*
FIG. 11. *Phase contrast micrograph of the Pb-Sn eutectic interface.* × *1500.*

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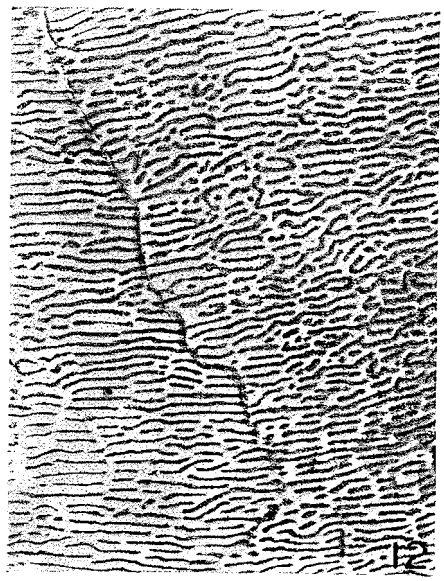

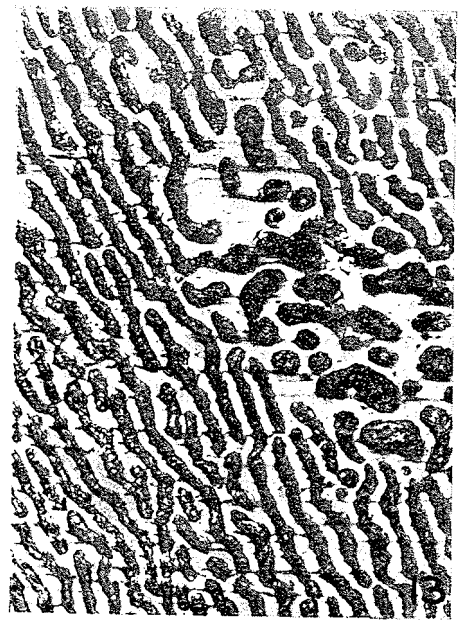

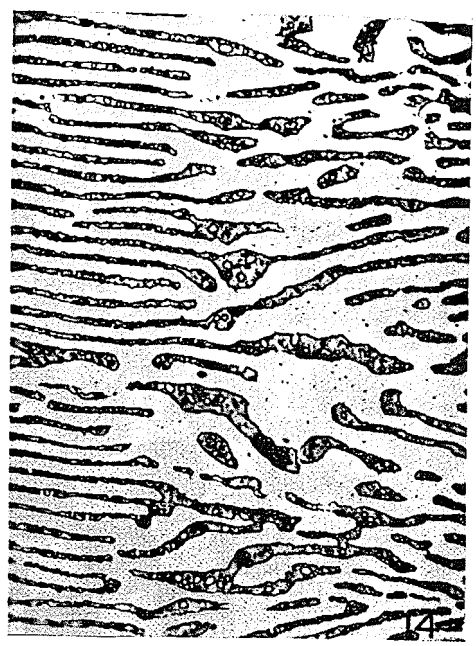

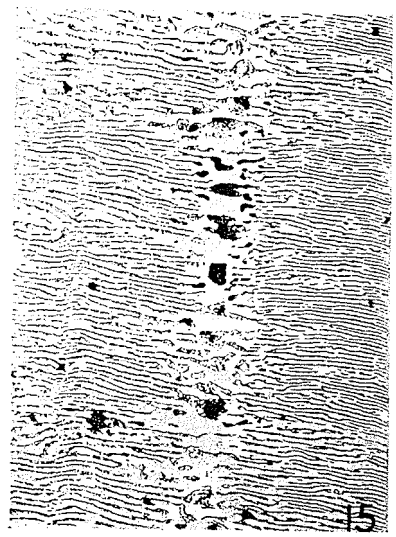

FIG. 12. *Hollow conic micrograph of Pb-Sn eutectic interface.* × *2000.*
FIG. 13. *Photomicrograph of Pb-Sn eutectic (normal lighting).* × *1000.*
FIG. 14. *Photomicrograph of Pb-Sn eutectic showing precipitation in Pb phase.* × *1000.*
FIG. 15. *Photomicrograph showing variation of thickness with speed of growth.* × *200.*

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Somewhat similar results were obtained by the use of hollow conical illumination; an example is shown in Fig. 12. In this photograph, the leading parts of the surface are white, and the hollows are dark.

6. Identification of the "Leading Phase"

It will be seen in Fig. 12 that the white parts of the field have an appearance of continuity, while the dark regions are of characteristically limited extension. It is next necessary to prove that these two parts of the surface correspond to the two phases of the eutectic, and to determine which is in advance. Metallographic examination of the surface after polishing and etching reveals the appearance illustrated in Fig. 13. It will be seen that the distribution of the light and dark areas is generally similar to those of Fig. 12. In Fig. 13, the light and dark regions correspond to the two phases of the eutectic, since they are revealed by etching, which has different effects on the two phases. It follows that the light phase in the etched section (Fig. 13) corresponds to the light areas of Fig. 12—that is, to the more advanced parts of the interface. This phase can be identified as follows: it is observed that, if a section similar to Fig. 13 is made after the alloy has been heated, the dark phase contains white spots, which can be recognized as precipitated particles of the other phase. An example is shown in Fig. 14. Reference to the equilibrium diagram shows that the solubility of tin in lead decreases rapidly below the eutectic temperature; it is therefore to be expected that precipitation of tin should occur in the lead-rich phase. The dark phase may, therefore, be tentatively identified as lead-rich. This is confirmed by the anisotropy of the light (tin-rich) phase, as revealed by polarized light. It is concluded that the leading phase in the tin–lead eutectic is the tin-rich phase.

Since the latent heat and thermal conductivity of the tin-rich phase are both higher than those of the lead-rich phase, it follows that the thermal conductivity is the controlling factor in determining which phase will be in advance. It is probable that with such slow freezing rates the latent heat does not exert as great an influence as it would at the higher cooling rates which occur in practice.

7. Thickness of the Lamellae

Some observations on the thickness of the lamellae may also be recorded. The actual thickness of the lamellae can only be measured on a section taken parallel to the interface, while in other directions there is no certainty that the section is perpendicular to the lamellae. On the other hand, it is not possible to examine the constancy of the thickness of a particular group of lamellae by means of a section parallel to the interface. To investigate the influence of speed of growth on the thickness of the lamellae, it is necessary to examine a section perpendicular to the interface. Fig. 15 shows a photomicrograph of such a surface in a region where the speed of advance of the interface

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was reduced and increased again. It is seen that the lamellae become thicker at lower speeds. Fig. 14 is a more detailed view of the same section. Quantitative relationships have not been established.

8. Mechanism of Eutectic Solidification

It is now possible to describe the mechanism of eutectic freezing in some detail. It is probable that the process commences with the formation of a nucleus of one of the phases. A crystal of this phase will grow until the surrounding liquid has become rich enough in the other constituent for the second phase to nucleate. The two initial crystals that form in this way will grow side by side; if growth is radial (as it must be at this stage) each crystal will grow wider as it grows outward from its point of nucleation "P" (Fig. 16A). The extent to which the crystals can grow wider depends on the speed of growth, since diffusion in the liquid is necessary to keep the surface of each phase supplied with the appropriate atoms for continuous solidification. The greater the speed of solidification, the less will be the time available for lateral diffusion and the less will be the maximum thickness of the lamellae. When the maximum thickness is reached, the concentration of phase B at the point C will reach such a level that solidification of phase A is replaced by solidification of phase B. This can occur either by fresh nucleation or by the growth of phase B from above or below the plane represented by the diagram. The process will be repeated whenever the maximum thickness is attained. This is illustrated in Fig. 16B between P and XX. Branching does not occur unless it is necessitated by the diffusion criterion, because it results in an increase of the area and, therefore, of surface free energy of the interface between the phases. Under conditions of parallel as distinct from radial heat flow, Fig. 16B, XX to YY, no further branching will occur so long as speed of growth is constant. The structure is then lamellar. Once a lamellar structure has been established, it is maintained by the growth of both phases simultaneously, the lamellae growing "edgewise" into the liquid.

Although the experiments refer only to the lead–tin system, it is suggested that the conclusions are of general application.

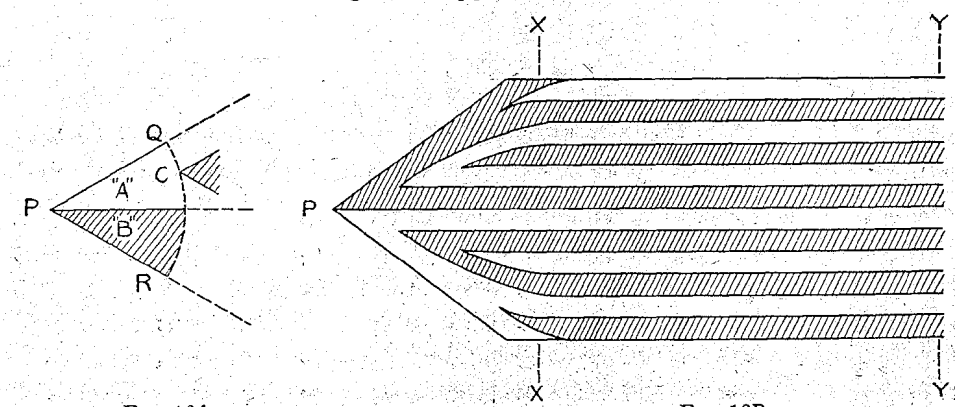

FIG. 16A. FIG. 16B.

FIG. 16. *A and B represent eutectic solidification according to the theory proposed in this paper.*

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CONTRIBUTION TO THE STUDY OF 4-MONOSUBSTITUTED-3-AMINO-5-PYRAZOLONES[1]

By Paul E. Gagnon, Jean L. Boivin,[2] and Jacques Giguere[3]

Abstract

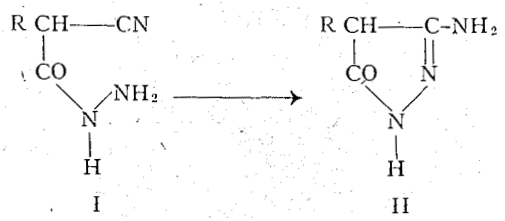
The condensation of monosubstituted cyanoacetic esters with hydrazine gave rise to 4-R-3-amino-5-pyrazolones. The pyrazolones prepared were those in which R = *o*-chlorobenzyl, β-*p*-methylphenoxyethyl, γ-*p*-methylphenoxypropyl, β-*p*-ethylphenoxyethyl, β-*p*-chlorophenoxyethyl, γ-*p*-chlorophenoxypropyl, γ-*p*-bromophenoxypropyl, or *n*-dodecyl.

The ultraviolet absorption spectra of these pyrazolones were determined in neutral, acid, and alkaline medium.

Introduction

Ethyl cyanoacetate, when treated with hydrazine, forms the corresponding hydrazide. The latter in the presence of an alkaline catalyst gives rise to 3-amino-5-pyrazolone (1, 5). Substituted and disubstituted cyanoacethydrazides treated with strong alkalies yield 4-mono- or 4, 4-disubstituted-3-amino-5-pyrazolones (2).

In this paper, the preparation of eight new 3-amino-5-pyrazolones with alkyl or phenoxyalkyl substituents in position 4 is described.



I II

All these compounds were made by preparing the corresponding monosubstituted cyanoacethydrazides (I) and treating them with sodium hydroxide. When the alkaline solution was neutralized with acetic acid, pyrazolones (II) usually precipitated as white solids which were recrystallized several times from dilute ethanol. They were soluble in ethanol, acids, and bases, and slightly soluble in water. They were insoluble in ether and benzene. All compounds gave a red color with ferric chloride.

The physical properties and analyses of the pyrazolones prepared are given in Table I together with their spectrophotometric data.

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TABLE I

4-MONOSUBSTITUTED-3-AMINO-5-PYRAZOLONES

Substituent	Formula	M.p., °C.*	Analysis, % Nitrogen		Ultraviolet absorption maxima					
					Neutral		Acid		Alkaline	
			Calc.	Found	Log E_m	Å	Log E_m	Å	Log E_m	Å
n-Dodecyl	$C_{15}H_{29}ON_3$	152–154	15.7	15.7	3.54 3.45	2520 2800	3.85 3.25	2360 2800	3.83	2300
o-Chlorobenzyl	$C_{10}H_{10}OClN_3$	170	18.8	19.1	4.01	2450	4.07	2360		
β-*p*-Methylphenoxyethyl	$C_{12}H_{15}O_2N_3$	184–185	18.0	17.7	4.18 4.04 3.45 3.39	2260 2450 2780 2850	4.28 3.30 3.22	2280 2780 2840	3.99 3.05	2240 2760
γ-*p*-Methylphenoxypropyl	$C_{13}H_{17}O_2N_3$	159–160	16.9	17.1	4.06 3.74 3.62 3.62	2240 2480 2790 2850	4.14 3.62 3.56	2260 2780 2850	4.09 3.33	2240 2760
β-*p*-Ethylphenoxyethyl	$C_{13}H_{17}O_2N_3$	170–171	16.9	16.7	4.29 3.98 3.53	2240 2440 2770	4.32	2270	4.37	2240
β-*p*-Chlorophenoxyethyl	$C_{11}H_{12}O_2ClN_3$	204–205	16.6	17.0	4.24 3.42	2300 2820	4.42 3.24	2300 2800	4.33 3.33	2270 2780
γ-*p*-Chlorophenoxypropyl	$C_{12}H_{14}O_2ClN_3$	203–204	15.7	15.4	4.11 3.61	2280 2820	3.97 3.60	2280 2800	4.13 3.23	2270 2780
γ-*p*-Bromophenoxypropyl	$C_{12}H_{14}O_2BrN_3$	214–216	13.7	13.9	4.30 3.69	2270 2820	4.18 3.67	2280 2800	4.08 3.41	2260 2780

* *All melting points are uncorrected.*

Preparation of Pyrazolones

4-Monosubstituted-3-amino-5-pyrazolones

The hydrazide (0.1 mole) of the ethyl monosubstituted cyanoacetate was treated with two equivalents of sodium hydroxide (40%) and stirred for a few minutes. The mixture was allowed to stand for three hours and diluted with water (250 ml.). The solution was then acidified with acetic acid (50%) and the mixture was allowed to cool slowly. The resulting crystalline compound was filtered, washed with water, and recrystallized several times from dilute ethanol. The yields were excellent. A positive color test was obtained with a dilute ferric chloride solution. The results are given in Table I.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were taken on a Beckman spectrophotometer Model DU in the same way as previously described (2). Results are listed in Table I and some of the data are plotted in Figs. 1 and 2.

Examination of Fig. 1 reveals that in neutral solution 4-*n*-dodecyl-3-amino-5-pyrazolone exhibits two absorption bands, at 2520 and 2800 Å, with intensities of 3.54 and 3.45 (log E_m) respectively.

In acid medium, the curve is shifted towards a shorter wave length. Both peaks are still present, but the intensity of the first one has increased to 3.85

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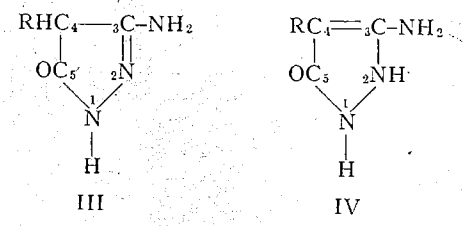
(log E_m) at 2360 Å whereas the intensity of the other one which has not been displaced was lowered to 3.25 (log E_m). In alkaline medium, there is also a hypsochromic displacement; the intensity of the first maximum is the same as in acid medium, but the second peak at 2800 Å has completely disappeared.

To explain these different spectra in neutral, acid, and alkaline media, one must keep in mind that pyrazolones may exist in many tautomeric forms; two of these are represented by the following formulas III and IV.



III IV

Examination of these two structures reveals that the double bond in the heterocyclic ring may be between positions 2 and 3 or 3 and 4. According to the position of the double bond, spectra might be different. This point was discussed for 4-benzyl-3-amino-5-pyrazolone (2, 3); in that case two absorption bands of different intensities were obtained in neutral medium, but in acid solution only one appeared with a greater intensity. The 4-*n*-dodecyl-3-amino-5-pyrazolone

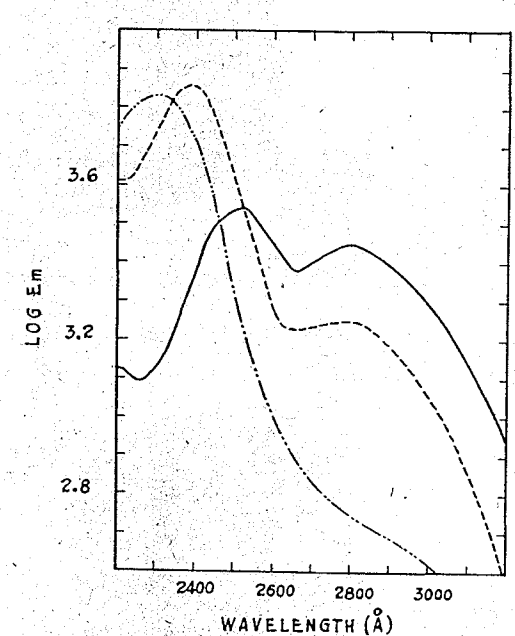


FIG. 1. *Ultraviolet absorption spectra.*
——— *4-n-Dodecyl-3-amino-5-pyrazolone (ethanol)*
– – – – – – – – " " " *(0.1 N hydrochloric acid in 90% ethanol)*
– · – · – · – · – " " " *(0.01 N sodium hydroxide in 90% ethanol)*

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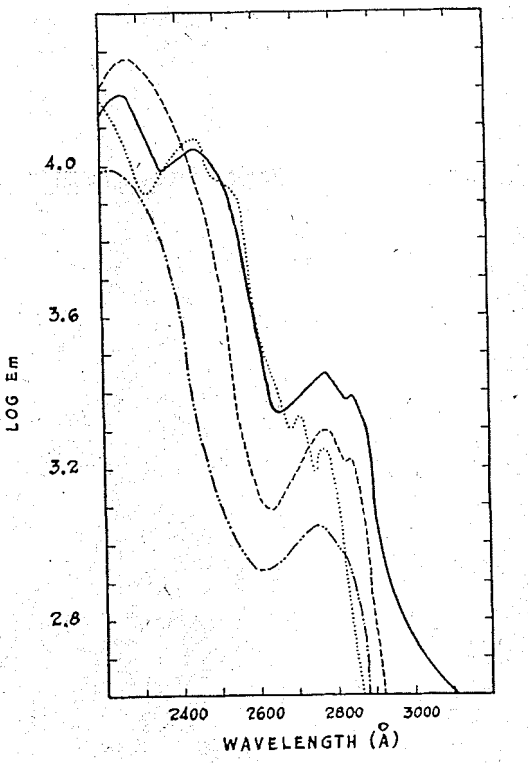
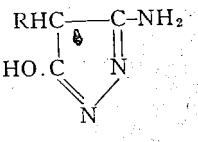


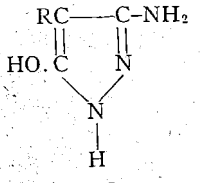
FIG. 2. *Ultraviolet absorption spectra.*
——— *4-β-p-Methylphenoxyethyl-3-amino-5-pyrazolone (ethanol)*
– – – – – *" " " (0.1 N hydrochloric acid in 90% ethanol)*
. . . . . *" " " (0.01 N sodium hydroxide in 90% ethanol)*
. . . . . *4-β-Phenoxyethyl-3-amino-5-pyrazolone (ethanol).*

exhibits almost the same behavior. In acid medium, there might be a mixture of both forms III and IV. Moreover, in acid medium the peak at 2520 Å is shifted to 2360 Å and has a greater intensity.

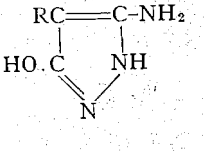
In alkaline medium, three tautomeric structures might be possible, V, VI, and VII.



V



VI



VII

The hypsochromic displacement is still more pronounced than in acid medium, but the absorption intensity is the same. If the position of the maximum and its intensity are considered, it may be concluded that, in alkaline medium, the substance has the structure VII.

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The spectra of 4-β-p-methylphenoxyethyl (Fig. 2), 4-γ-p-methylphenoxypropyl (Table I), and 4-β-p-ethylphenoxyethyl (Table I) derivatives of 3-amino-5-pyrazolones are almost similar in neutral, acid, and alkaline media. Four maxima are exhibited in all the three spectra, appearing at about the same wave lengths. Two little peaks appear at about 2800 Å and 2850 Å and are probably due to the effect of the substituent in position 4. Similar maxima were already observed with the spectra of 4-β-phenoxyethyl and 4-γ-phenoxypropyl pyrazolones (Fig. 2), and it has been shown that the bands were due to the absorption of the phenoxyalkyl group (2, 3).

In acid medium, there are three maxima in the spectra of the three pyrazolones. The maxima at 2450–2500 Å have disappeared. The same effect was observed with 4-benzyl-3-amino-5-pyrazolone (2, 3). This implies the possibility that the three pyrazolones in acid solution might have structure IV. There is also a hypsochromic displacement of the curve which has been previously explained (2, 3, 4).

In alkaline medium, the curves of the same three pyrazolones (Fig. 2) are shifted hypsochromically. Moreover, another maximum at about 2800 Å has disappeared. The curves are similar to that of 4-β-p-chlorophenoxyethyl-3-amino-5-pyrazolone (Table I). Maximal intensities are the same and their wave lengths differ only by some 20 Å. The similarity of the spectra of these three pyrazolones indicates that their structure is the same.

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THE POLYMERIZATION OF STYRENE SENSITIZED BY ACETYL RADICALS[1]

By G. L. Osberg[2] and D. J. Le Roy

Abstract

A study has been made of the polymerization of styrene in the liquid phase, initiated by acetyl radicals from the photolysis of diacetyl. The rate of consumption of monomer was proportional to the square root of the rate of light absorption; the rate of consumption of diacetyl was proportional to the first power of the rate of light absorption. The ratio of the rate constant for chain propagation to the square root of the rate constant for chain termination was found to be 3.9×10^{-3} liter$^{1/2}$ mole$^{-1/2}$ sec.$^{-1/2}$ at 20°C. The quantum yield of diacetyl consumption was 4.0×10^{-3}. By relating the kinetic data to the observed intrinsic viscosities, the exponent of the number average molecular weight in the modified Staudinger equation was found to be 0.65. The values of the corresponding K factors for homogeneous and heterogeneous polymers were 6.5×10^{-3} and 8.2×10^{-3}, respectively, when the assumption was made that chain termination was by recombination; for chain termination by disproportionation the values were 8.7×10^{-3} and 12.9×10^{-3}, respectively, for concentrations in base moles per liter.

Studies of the addition polymerization of vinyl compounds made by a number of workers have shown the over-all process to be a chain reaction occurring in three stages: initiation, propagation, and termination. Various initiation processes have been used: thermal production of radicals from the pure monomer (18), thermal production of radicals from an added initiator (16), photochemical production of radicals from the pure monomer (3, 7, 15, 22), and photochemical production of radicals from an initiator (8). The photochemical techniques possess the advantage of yielding more data concerning the rate constants involved in the polymerization; with the fourth method it is often possible to have fairly accurate knowledge of the nature of the radical which initiates polymerization.

A number of investigations of the photolysis of diacetyl (21) have indicated that this substance undergoes a primary split into acetyl radicals, even at wave lengths as long as 4047 and 4358 Å (1, 2). At these wave lengths diacetyl absorbs strongly and seemed to be well suited as an initiator for the polymerization of styrene, which shows almost negligible absorption in this range. It was, accordingly, used as an initiator for the photosensitized polymerization of styrene in the liquid phase.

Since this research was undertaken several papers have appeared in which diacetyl has been used as an initiator of vinyl polymerization. Blout and Ostberg (6) showed that the decomposition of diacetyl by ultraviolet light accelerated the polymerization of allyl methacrylate. Cohen, Ostberg, Sparrow, and Blout (9) showed the effective wave length to be 4000 to 4600 Å, and that the decrease in the yellow color indicated that diacetyl was consumed in the process. More recently Matheson, Auer, Bevilacqua, and Hart (14) have used the photolysis of diacetyl to initiate the polymerization of methyl methacrylate.

[1] *Manuscript received November 14, 1950.*
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Experimental Methods

Reagents

Styrene, obtained from Polymer Corporation, Sarnia, was treated in a number of ways to remove impurities; the most satisfactory method was found to be simply a distillation under oxygen-free nitrogen at a pressure of 10 to 14 mm., taking the middle third. The distillate was transferred, under nitrogen, to the flask G_1 of Fig. 1, where it was frozen, pumped, melted, and distilled back and forth a number of times between G_1 and G_2. Care had to be taken to exclude oxygen, as it not only increased the light absorption but affected both the thermal (dark) and photochemical rates.

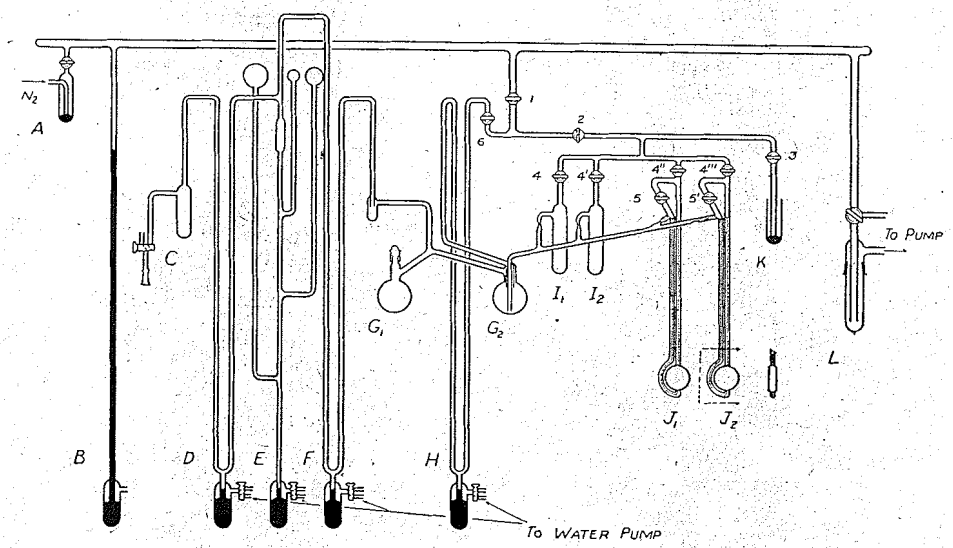

FIG. 1. *Apparatus used to prepare the solutions and fill the dilatometer cells.*

The effect of oxygen on the light absorption of styrene is shown in Fig. 2. The extinction coefficient ϵ is defined by the relation $I_T = I_0 10^{-\epsilon l}$, where l is the path length in centimeters. Pure oxygen-free styrene was used in the reference cell and measurements were made on a Beckman ultraviolet spectrophotometer. Curve A was obtained with a sample through which air was bubbled for one-half hour; Curve B, for a sample through which oxygen was bubbled for 10 min.; Curve C was obtained after bubbling pure nitrogen through sample B for one hour. It is apparent that not all of the light-absorbing complex can be removed by nitrogen.

Diacetyl, obtained from Eastman, was refluxed under nitrogen and then distilled through a Vigreux column. It was then transferred, under nitrogen, to the storage bulb C (Fig. 1) where it was thoroughly degassed and isolated by the mercury cutoff D. In the later experiments the storage bulb was kept at Dry Ice temperature. The purified diacetyl had a boiling range of 88.5° to 89.2°C.

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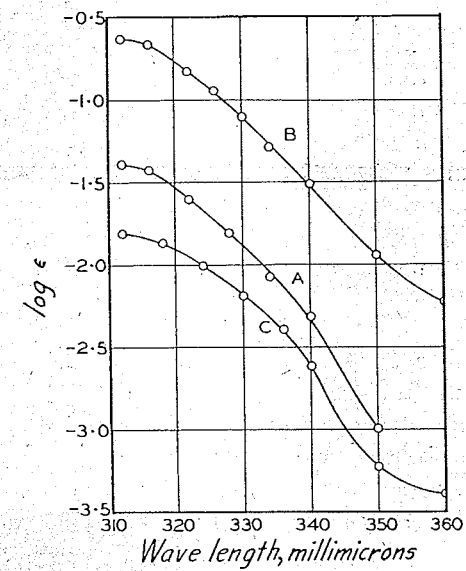

FIG. 2. *Effect of oxygen on the light absorption of liquid styrene. (A) Air bubbled through sample for one-half hour. (B) Oxygen bubbled through sample for 10 min. (C) Nitrogen bubbled through Sample (B) for one hour. The extinction coefficient* ϵ *is defined by the relation* $I_T = I_0 10^{-\epsilon l}$, *where* l *is the path length in centimeters. All measurements were made relative to pure air-free styrene.*

Nitrogen was purified by passing it through Fieser's solution (10), lead acetate solution, concentrated sulphuric acid, and finally over Drierite.

Preparation of Solutions

The diacetyl was measured in the gas phase. By freezing the material in the storage volume C, lowering the mercury in the cutoff E to the required point and then allowing the diacetyl in C to warm up, vapor could be admitted to one or more of the calibrated volumes. The mercury in the cutoff D was then raised, the diacetyl in C frozen with liquid air, and the pressure of the vapor in the calibrated volumes read on the cutoff D. The measured volume of diacetyl was then condensed onto the weighed, degassed styrene in G_2 through the cutoff F. This cutoff was then closed, and compressed air was admitted to its reservoir to raise the mercury level to a height which would permit a pressure differential of over 1 atm. between its two arms. Nitrogen at atmospheric pressure was then admitted through 1, 6, H, 2, 4, 4′, 4″, and 4‴. The solution was kept at Dry Ice temperature until ready for filling the cells.

Filling the Cells

The temperature of the diacetyl–styrene solution in G_2 was adjusted to 20°C. and the nitrogen pressure in the manifold adjusted until it bubbled out through K. With stopcocks 1, 2, 3, 6, and 4″ open and 4′, 4‴, 5 and 5′ closed, the dilatometer cell J_1 was filled by partly closing 2. This displaced some of the solution

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into J_1. When sufficient solution was added to the dilatometer the flow was stopped by opening 5 and 2. The dilatometer was kept at 20°C. during the filling operation. The other dilatometer, J_2, and the sample bulb I_2 were filled with solution in the same manner. Before sealing these off at the constrictions and removing them from the filling system by breaking off the tubes above the stopcocks 4′, 4″, and 4‴, the connecting lines were cleared of solution by closing 3 and passing nitrogen through them and out through G_1, the cap of which was loosened slightly. The sample bulb I_1 was previously filled with pure styrene in the same manner as described for the solution.

The Dilatometer Cells

The polymerization was followed by measuring the decrease in volume of the solution. The dilatometer cells, shown as J_1 and J_2 in Fig. 1, were Pyrex cylinders 47 mm. in diameter with plane parallel Pyrex windows 15 mm. apart inside. Two capillary tubes were attached as shown and extended 33 cm. above the top of the cell. Each tube had an engraved line at the top. Changes in liquid height were measured with reference to these lines by means of a mirror scale. The volume of each cell was approximately 25 cc.; the smallest capillary used was 0.74 mm. in diameter, the largest, 1.10 mm. The volumes of the cells and the volumes per unit length of capillary were calibrated with mercury. For most of the experiments the dilatometers were kept in a water bath at 20.00 ± 0.03°C. Allowance was made for the portion of the capillaries outside the thermostat.

Optical Arrangement

A UA-2 250 w. Uviarc was used as the light source. The slowness of the reaction made it impossible to use a collimated beam. The arc was placed close to the water bath, 6 cm. from the front face of the cell. Corning filters, used to obtain monochromatic light, were placed inside the water bath in a brass support which also held the cell in a reproducible position. The cell was kept dark by means of a shutter until the light from the lamp had reached a constant intensity.

Actinometry

The light intensities were measured by photolysing uranyl oxalate – oxalic acid solutions in the dilatometer cells. The intensities incident on the front face of the cell solution for various filter combinations are given in Table I. Each tabulated value of the light intensity is the average of three determinations. The mean deviations were all less than 2%. The greatest source of error was in the determination of the percentage of light absorbed by the actinometer solution. The values were determined on the Beckman instrument, 5.0% at 4358 Å, 5.9% at 4047 Å.

Determination of Diacetyl in Diacetyl–Styrene Solutions

The concentration of diacetyl in the original solution was obtained from transmission measurements on the sample which was displaced into the bulb I_2

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TABLE I

INCIDENT LIGHT INTENSITIES

Wave length Å	Corning filter number	Intensity, einsteins $cm.^{-2}$ $hr.^{-1}$
4047	3060 + 4308 + 5970	$3.7_1 \times 10^{-6}$
4358	5113 + 3389	19.4×10^{-6}
4358	$2 \times 5113 + 2 \times 3389$	$3.0_7 \times 10^{-6}$
4358 + 4047	3060	84.5×10^{-6}

during the filling operation. Values were obtained for 422 and 436 mμ. The solutions were found to obey Beer's law over the range 0.07 to 3.2 gm. per liter; pure styrene, from bulb I_1 was used as the reference solution. The extinction coefficient a in the expression $I_T = I_0\ 10^{-acl}$, where c is the concentration in moles per liter and l the path length in centimeters, was evaluated by two methods: (1) weighing the diacetyl, (2) estimating the weight by the gas volume method described above. By the weight method a was found to be 23.7 at 422 mμ, 21.0 at 436 mμ; by the volume method, 23.6 and 21.2, respectively. The probable error by the volume method was somewhat greater and in practice initial diacetyl concentrations were found by the light transmission method using the values 23.7 and 21.0 for a.

Determination of Diacetyl in Solutions Containing Polystyrene

In order to determine the diacetyl consumed during an experiment it was necessary to obtain its concentration in solutions containing polystyrene as well as styrene. Smakula (19) has shown that polystyrene solutions obey Beer's law, at least under the conditions used by him, and it was assumed that, relative to pure styrene, the absorption of a solution containing styrene, diacetyl, and polystyrene would be given by the expression $\log I_0/I_T = acl + bc'l$, in which a, c, and l are as defined previously and b and c' are, respectively, the extinction coefficient and concentration (in grams per liter) of the polystyrene in the solution. Values of b were determined for each experiment by evaporating a portion of the final solution until a constant (maximum) transmission was obtained. This usually required the evaporation of 1/3 to 1/2 of the styrene. The polymer content was determined by analysis, as described below. The correction required as a result of the absorption by polymer, while small by comparison with the absorption by diacetyl, was quite significant in determining changes in diacetyl concentration.

Determination of Polystyrene

The amount of polymer formed during an experiment was determined by pumping down a 5 gm. sample until the diacetyl and the bulk of the styrene had been removed, leaving a thin layer of residue. The remaining volatile matter was removed by the method of Lewis and Mayo (13). The residue was dissolved in benzene and the solution frozen with Dry Ice. The frozen solution

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was then immersed in an ice–water mixture and pumped until only the spongy residue remained. This was pumped at room temperature until a constant weight was obtained. The agreement between duplicate samples was within a fraction of 1%.

Relation Between Volume Changes and Polymer Formation

It was found experimentally that there was a linear relation between the weight per cent of polymer and the per cent change in volume as determined by the dilatometers. The average of five determinations gave

$$\text{Wt \% polymer} = 100\Delta V/V \times 6.20 \pm 0.12 \qquad (1)$$

Linear relations were also found by Starkweather and Taylor (20) and by Schulz and Harborth (17) for the liquid phase polymerization of methyl methacrylate. Goldfinger and Lauterbach (12) measured the densities of styrene–polystyrene solutions but reported their results in the form of a graph showing no experimental points. The value of the factor calculated from their graph is 5.9. Our value of 6.2 was used in the calculations of this paper.

Any change in monomer concentration is readily calculated from the volume change. Thus, if $[M]$ is the concentration of monomer in moles per cubic centimeter, V' is the volume of the final solution, f the molecular weight of the monomer, and m and p are the weights, in grams, of the monomer and polymer, respectively, then

$$-\Delta m/(m+p) = p/(m+p) = 6.20\,\Delta V/V',$$

or

$$-\Delta[\mathrm{M}] = -\Delta m/(fV') = (1/fV')\,6.20\,(m+p)\Delta V/V. \qquad (2)$$

For the small conversions obtained in this work the quantity $(m+p)/V'$ may be taken to be the density of styrene at 20°C., 0.907.

Hence

$$-\Delta[\mathrm{M}] = 5.40 \times 10^{-2}\Delta V/V. \qquad (3)$$

Results

Effect of Dissolved Air

Comparison experiments showed that dissolved air had a positive catalytic effect on the photosensitized polymerization of styrene alone, and on both the thermal (dark) and photosensitized polymerization of diacetyl–styrene solutions. These photochemical experiments were done with a wave length of 4047 Å. The impurity introduced as a result of contact with air (presumably a peroxide) appeared to be consumed during polymerization. One of these solutions had an initial thermal rate of 10×10^{-7} mol. cc.$^{-1}$ hr.$^{-1}$, but after illumination for three hours the subsequent thermal rate was 3.2×10^{-7}.

Typical Photosensitized Polymerization

Two dilatometer cells were filled with the same solution, as described above. Both were placed in the thermostat but one was kept darkened in order to obtain the thermal rate. In Fig. 3 is shown a plot of volume change against time for a typical photosensitized polymerization. The sudden increase in volume (a) on illumination corresponded to an increase in temperature of

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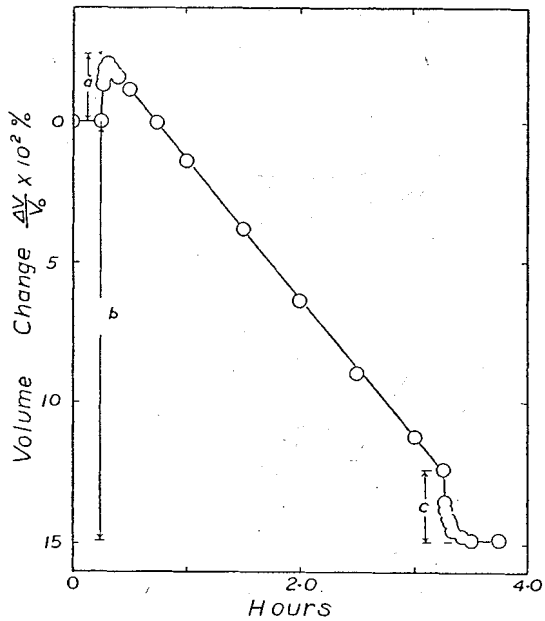

FIG. 3. *Relative volume change vs. time for a typical experiment.*

approximately 0.2°C. The decrease in volume on cutting off the light (*c*) was not as abrupt, although of about the same magnitude. In other experiments, in which the rate of light absorption was greater, *c* was considerably greater than *a*. This was undoubtedly the result of the "after effect", studied by Bamford and Dewar (3). However, the difficulty of disentangling this from the thermal effect made further study of this phenomenon unprofitable.

The absence of an induction period indicates that inhibiting impurities were removed. The rate calculated from the linear portion of Fig. 3 corresponded to a monomer consumption of 2.68×10^{-5} mol. cc.$^{-1}$ hr.$^{-1}$. The corresponding thermal rate from the darkened cell was 1.2×10^{-7}.

Effect of Light Intensity of the Rate of Polymerization

The absorbed light intensity depends on both the incident light intensity and the diacetyl concentration.* Both of these quantities were varied. The most extensive measurements were made with monochromatic light of wave length 4358 Å. Fourteen experiments were performed with different diacetyl concentrations, ranging from 0.14 to 19.4 millimoles per liter, and with an initial incident light intensity 19.4×10^{-6} E. cm.$^{-2}$ hr.$^{-1}$. In the case of seven of these the experiment was interrupted after the rate had been established

* *The absorbed light intensity, $\bar{I}_a$ is given by the expression $\bar{I}_a = (I_0/l)(1 - 10^{-acl})$, in which I_0 is the light intensity incident on the front face of the solution in einsteins cm.$^{-2}$ hr.$^{-1}$, l is the length of the cell in centimeters, a is the extinction coefficient defined previously, and c is the concentration of diacetyl in moles per liter. It is clear that $\bar{I}_a$ may be varied by changing either I_0 or c.*

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and was continued again with an incident light intensity of $3.0_7 \times 10^{-6}$. In all, the average rate of light absorption, $\bar{I}_a$, was varied from 1.32×10^{-7} to 98.9×10^{-7} E. cm.$^{-3}$ hr.$^{-1}$.

As can be seen from Fig. 4, the rate of polymerization is proportional to $\bar{I}_a^{1/2}$. This is in contrast to the polymerization of vinyl acetate photosensitized by benzoyl peroxide (8), where the exponent of $\bar{I}_a$ approached unity as the benzoyl peroxide concentration increased. The value of k in the observed rate expression

$$-d[M]/dt = k\bar{I}_a^{1/2} \tag{4}$$

was $5.8 \pm 0.6 \times 10^{-3}$ for 4358 Å. The average value of k for four experiments with 4047 Å was $6.6 \pm 0.6 \times 10^{-3}$. The difference between the values for the two wave lengths is scarcely significant.

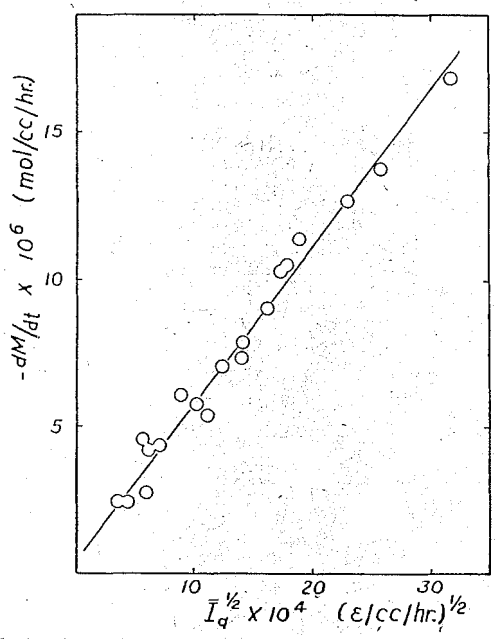

FIG. 4. *Relation between rate of polymerization and absorbed light intensity.*

Effect of Light Intensity on the Rate of Diacetyl Consumption

These measurements were difficult because of the small changes encountered, as well as the absorption of light by the polymer. The corrections for polymer absorption were made as described above. To obtain the maximum rate of change of diacetyl concentration, five experiments were made using the combined wave lengths, 4047 and 4358 Å (*v.* Table I). In addition, two experiments were made with a single set of 4358 Å filters. The diacetyl concentrations were determined during each experiment by removing the cell and measuring the transmission at 436 or 422 mμ on the Beckman spectrophotometer.

The effect of the absorbed light intensity on the rate of diacetyl consumption is shown in Fig. 5. The crosses are the values obtained when no correction for

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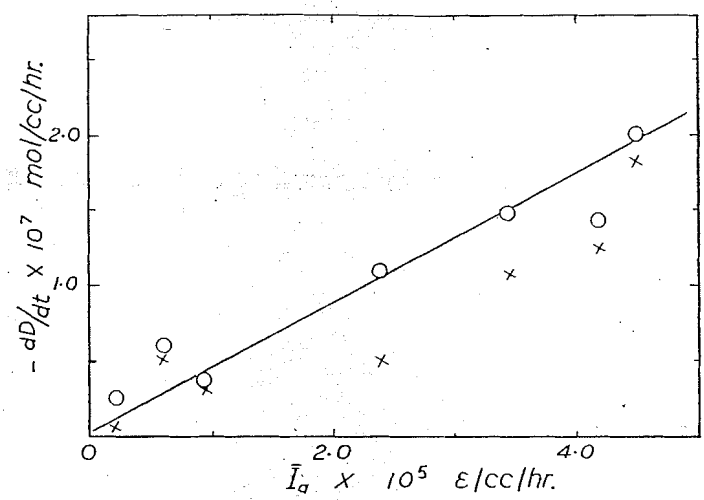

FIG. 5. *Relation between rate of consumption of diacetyl and light intensity, with (circles) and without (crosses) correction for absorption by polymer.*

absorption by polymer was made; the circles are the corrected values. For the two lowest light intensities (monochromatic 4358 Å) the values of $\bar{I}_a$ were calculated from the expression

$$\bar{I}_a = (I_0/l)\ (1 - 10^{-21.0[D_0]1.53}), \tag{5}$$

in which $[D_0]$ is the initial concentration of diacetyl and l is the length of the cell, 1.53 cm. For the dichromatic light, 4047 Å accounted for 31.2%, 4358 Å for 68.8% of the incident light intensity, and hence

$$\bar{I}_a = (I_0/l)\ (0.688(1 - 10^{-21.0[D_0]l}) + 0.312(1 - 10^{-16.4[D_0]l})\ ). \tag{6}$$

Although the values of $\bar{I}_a$ in Fig. 5 are for the initial conditions they suggest that the rate of consumption of diacetyl is directly proportional to the absorbed light intensity, i.e., that

$$-d[D]/dt = \phi \bar{I}_a. \tag{7}$$

An approximate value of ϕ may be obtained from Fig. 5; a more accurate value can be obtained by integrating (7) over the duration of each experiment. For the monochromatic light the expression is

$$\phi = l/I_0 t\ ([D_0] - [D_t]) + 1/(21.0\ I_0 t) \log\ (1 - 10^{-21.0[D_0]l})/(1 - 10^{-21.0[D_t]l}). \tag{8}$$

The expression for the dichromatic light is more complicated and will not be given here. The mean value of ϕ obtained was 4.0×10^{-3} mole of diacetyl consumed per einstein absorbed, with a mean deviation of 0.6×10^{-3}; the value corresponding to the slope of Fig. 5 is 4.3×10^{-3}.

Interpretation of Results

The results may be interpreted on the basis of the following mechanism, in which D represents a diacetyl molecule, M a styrene molecule, A an acetyl radical, X_i a polymeric free radical and Q_i a stable polymer molecule.

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Initiation	$D + h\nu = 2A$		θI_a
	$A + M = X_1$		k_i
Propagation	$X_i + M = X_{i+1}$		k_p
Termination	$X_n + X_m = Q_{n+m}$		k_s
	or $X_n + X_m = Q_n + Q_m$		

From the usual steady-state relations it is seen

that $$[A] = 2\theta I_a/(k_i[M]) \tag{9}$$

and that $$[X] = (2\theta I_a/k_s)^{1/2}, \tag{10}$$

in which $[X] = \sum_i [X_i]$.

For long chains the rate of monomer consumption would be given by the expression

$$-d[M]/dt = k_p[M][X] = k_p[M](2\theta I_a/k_s)^{1/2}. \tag{11}$$

The predicted rate of diacetyl consumption would be

$$-d[D]/dt = \theta I_a. \tag{12}$$

Under the experimental conditions the *local* rate of light absorption, I_a, can be assumed to be identical with the average rate of light absorption, $\bar{I}_a$. Further, if it can be assumed that the only reaction leading to diacetyl consumption is the dissociation into radicals then $\theta = \phi = 4.0 \times 10^{-3}$ and $k_p/k_s^{1/2} =$

$$\frac{5.8 \times 10^{-3}}{(2 \times 4.0 \times 10^{-3})^{1/2}[M]} = 7.45 \text{ cc.}^{1/2} \text{ mole}^{-1/2} \text{ hr.}^{-1/2}$$

$$= 3.9 \times 10^{-3} \text{ liter}^{1/2} \text{ mole}^{-1/2} \text{ sec.}^{-1/2}. \tag{13}$$

From the data of Bamford and Dewar (3) $k_p/k_s^{1/2}$ was equal to 1.12×10^{-2} at 25°C., 5.1×10^{-3} at 0°C., for the polymerization of styrene alone.

The above mechanism is in agreement with the observation (Fig. 4) that the only effect of diacetyl concentration on the rate of polymerization is in determining the rate of acetyl radical formation, i.e., the rate of initiation. Several interpretations of the low value of θ may be offered. (1) Excited diacetyl molecules are deactivated by collision. In this case θ would be equal to the ratio of the probability of dissociation to the probability of (dissociation + deactivation). (2) The quantum yield for the dissociation reaction is unity, but diacetyl is re-formed by association of acetyl radicals. This, however, would lead to a rate of polymerization proportional to $\bar{I}_a^{1/4}$, which is contrary to experiment. (3) The possibility that diacetyl undergoes predissociation by collision is not in disagreement with the results.

Molecular Weight Distribution

Gee and Melville (11) and Bawn (5) have worked out the distribution functions for a number of different mechanisms. The chain length distribution corresponding to the mechanism outlined above was evaluated first for the case of chain termination by recombination.

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If $[M_r]$ is the concentration of polymer of chain length r, it is seen that

$$d[M_r]/dt = 1/2\, k_s \sum_{j=1}^{j=r-1} [X_j][X_{r-j}], \tag{14}$$

with $r - 1$ terms in the summation. Under steady state conditions

$$[X_j] = [X_1]\, q^{j-1} \text{ and } [X_{r-j}] = [X_1]\, q^{r-j-1}, \tag{15}$$

where $q = [X_j]/[X_{j-1}] = k_p[M]/(k_p[M] + k_s[X])$. (16)

Also, under steady-state conditions,

$$[X_1] = 2\theta I_a/(k_p[M] + k_s[X]), \tag{17}$$

$$\text{and} \quad [X] = (2\theta I_a/k_s)^{1/2}. \tag{10}$$

Making these substitutions, and noting that

$$d[M_r]/-d[M] = (d[M_r]/dt)/(-d[M]/dt),$$

it follows that

$$[M_r]/-\Delta[M] = d[M_r]/-d[M] = 1/2(r-1)\delta^3(1+\delta)^{-r}, \tag{18}$$

in which the function δ is equal to $(2\theta I_a k_s)^{1/2}/(k_p[M])$. Equation (18) shows the strong dependence of chain length distribution on I_a. The calculated distribution for one of the experiments, for which δ was equal to 3.4×10^{-3}, is shown in Fig. 6.

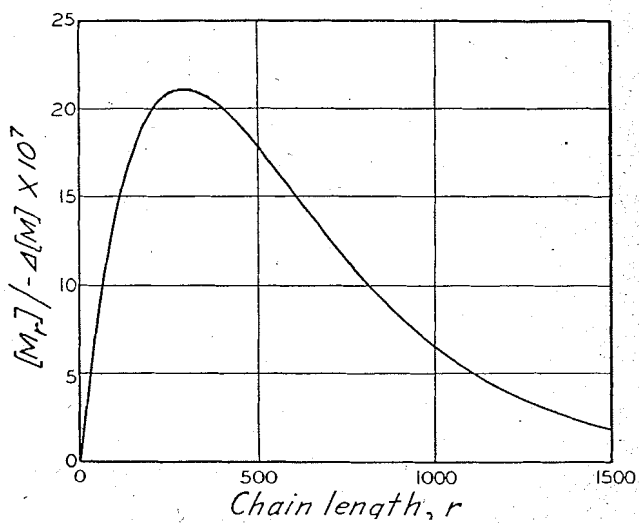

FIG. 6. *Calculated chain length distribution for $\delta = 3.4 \times 10^{-3}$ and chain termination by recombination.*

Photo-initiation by diacetyl could, on the basis of this mechanism, be used to prepare polymers of any required average molecular weight. The number average chain length, $\bar{r}_n$, is given by the relation

$$\bar{r}_n = \frac{\sum r[M_r]}{\sum [M_r]} = 2/\delta. \tag{19}$$

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The weight average, $\bar{r}_w = \dfrac{\sum r^2 m_0[\mathrm{M}_r]}{(-\Delta[\mathrm{M}])m_0} = 3/\delta,$ (20)

in which m_0 is the molecular weight of the monomer. If chain termination is by disproportionation the corresponding values of $\bar{r}_n$ and $\bar{r}_w$ are $1/\delta$ and $2/\delta$, respectively.

Intrinsic Viscosity of the Heterogeneous Polymer

From the distribution function (18), and a knowledge of the appropriate constants in the expression for the intrinsic viscosity it should be possible to predict the intrinsic viscosity for any experimental condition. Agreement with observed values might then be assumed to confirm the kinetic mechanism.

Using the modified Staudinger equation, the intrinsic viscosity of a homogeneous polymer of molecular weight m_r is given by the relation

$$[\eta]_r = Km_r^a. \tag{21}$$

If w_r is the weight of polymer of chain length r, the intrinsic viscosity of a heterogeneous polymer would be

$$[\eta] = \frac{\sum_r [\eta]_r w_r}{\sum_r w_r} = \frac{K\sum_r m_r^a w_r}{\sum_r w_r}. \tag{22}$$

Substitution from (18) gives

$$[\eta] = \frac{Km_0^a \sum_r r^{a+1}(r-1)(1+\delta)^{-r}}{\sum_r r(r-1)(1+\delta)^{-r}}. \tag{23}$$

The solution of (23), since $\delta \ll 1$, is

$$[\eta] = Km_0^a\, \Gamma(a+3)/2\delta^a, \tag{24}$$

in which $\Gamma(a+3)$ is the gamma function of $(a+3)$.

From (19), the number average molecular weight is $2m_0/\delta = \bar{m}_n$, and hence the intrinsic viscosity of a heterogeneous polymer formed by this mechanism is given by the relation

$$[\eta] = K'\bar{m}_n^a, \tag{25}$$

where $K' = K\Gamma(a+3)/2^{a+1}$. Bamford and Dewar (4) have derived the relation between K' and K for a number of different mechanisms.

The values of $[\eta]$ calculated from Equation (24) or (25) will be strongly dependent on the value of a, less so on the value of K or K'. Bamford and Dewar (4) have tabulated some of the values of a found in the literature for different polymers. In their own work they found a to be close to 0.65, and K equal to 3.04×10^{-3} (for concentrations in base moles per liter) at 25°C., using toluene as the solvent. They used the method of end-group analysis to obtain $\bar{m}_n$ and calculated K from the relation between K and K' appropriate to their mechanism. From Equations (19) and (25) it is clear that for a series of different light intensities log $[\eta]$ should be a linear function of log δ with slope

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$-a$ and intercept $\log K' + \log (2m_0)^a$. The results of a number of experiments were plotted in this way but it was found that the points could not be fitted to a straight line. This was traced to the fact that the viscosity determinations were made 24 hr. or more after the termination of the photolysis, and, although the amount of polymerization which took place in the interval was quite small, the high molecular weight of this thermal polymer had a large effect on the intrinsic viscosity. In the case of three experiments, viscosity determinations were made immediately after the end of the photolysis, using styrene as the solvent. The data for these are given in Table II.

TABLE II

DEPENDENCE OF $[\eta]$ ON δ

Expt.	$\delta \times 10^3$	$\overline{m}_n \times 10^{-3}$	$[\eta]^*_{obs}$
19	6.8	30.6	7.0
20	3.4	61.3	10.4
21	1.8	115.7	16.7

* *Concentrations in base moles per liter.*

For these experiments $\log [\eta]$ was a linear function of $\log \delta$, from which a was found to be 0.65 and K' to be 8.2×10^{-3}. The corresponding value of K is 6.5×10^{-3}.

If chain termination is by disproportionation the relation between $[\eta]$ and $\overline{m}_n$ takes the form

$$[\eta] = K''\overline{m}_n{}^a, \tag{26}$$

in which $K'' = K\Gamma(a + 2)$. The value of K'' was found to be 1.29×10^{-2}; the corresponding value of K is 8.7×10^{-3}. Although the value of K based on the assumption that chain termination occurs by recombination is closer to that of Bamford and Dewar, it is not felt that the present work can be interpreted as favoring either termination mechanism. The close agreement in the value of a is of some interest, for although both sets of measurements are based on the validity of kinetic mechanisms, the polymerization reactions were entirely different. Bamford and Dewar (4) produced their polymer thermally, using benzoyl peroxide as the catalyst and carbon tetrachloride as a solvent. Through chain termination and chain transfer each polymer molecule was assumed to contain four chlorine atoms. The average molecular weights were obtained by chlorine analysis, and ranged from 4850 to 44,000.

Acknowledgment

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THE STRUCTURE OF SEDAMINE[1]

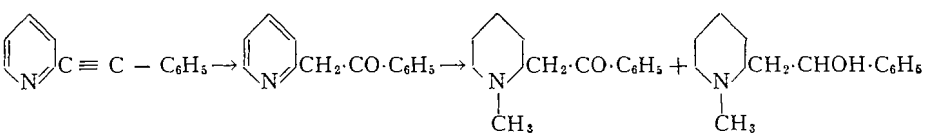
BY LÉO MARION, ROBERT LAVIGNE, AND LIONEL LEMAY

Abstract

The infrared absorption spectrum of sedamine, an alkaloid occurring in *Sedum acre* L., is exactly superposable on that of synthetic 1-methyl-2-(β-hydroxy-β-phenylethyl)-piperidine. The melting points of the bases and their hydrochlorides, alone and in admixture, indicate that sedamine is probably one of the optically active forms of the synthetic diastereomer.

The alkaloid sedamine was found in *Sedum acre* L., by Kolesnikov and Shvartsman (3) who assigned to it the empirical formula $C_{17}H_{24}O_2N$. Later it was isolated again from the same source by one of us (4) who found that it is accompanied by nicotine and who corrected the formula to $C_{14}H_{21}ON$. An investigation of the species *Sedum sarmentosum* Bunge had shown that this plant contained two alkaloids, i.e., N-methylisopelletierine and the corresponding dihydro-base, 1-methyl-2-(β-hydroxypropyl)-piperidine, the latter being one of the optically active isomers of that structure (5). The occurrence of such bases in another species of *Sedum*, together with an examination of the empirical formula of sedamine, prompted the assumption that sedamine might be an N-methylpiperidine carrying in the 2-position a β-hydroxy-β-phenylethyl group (IV). The correctness of this assumption has now been established by the synthesis of the base IV and the direct comparison of this base with sedamine.

The synthesis was carried out with the condensation product of α-picoline and benzaldehyde as starting material, following the procedure outlined by Scheuing and Winterhalder in connection with their synthesis of lobeline (6). The product was treated with bromine and the adduct converted to 1-α-pyridyl-2-phenylacetylene (I) which by the action of concentrated sulphuric acid gave rise to α-phenacylpyridine (II). Howton and Golding (1) report that the platinum oxide-catalyzed hydrogenation of the methobromide of II gives



I II III IV

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a good yield of 1-methyl-2-phenacylpiperidine (III), but that further hydrogenation yields a compound in which they tentatively assume that the phenyl group has been reduced to a cyclohexyl group. In the present instance, however, the metho-*p*-toluenesulphonate of II was prepared and the platinum oxide-catalyzed reduction of this salt was found to give a mixture in which the main component, 1-methyl-2-phenacylpiperidine (III), was accompanied by an appreciable quantity of the desired product, 1-methyl-2-(β-hydroxy-β-phenylethyl)-piperidine (IV). A compound of this structure contains two asymmetric C atoms and must, therefore, exist in two diastereoisomeric pairs. From it was obtained a crystalline fraction melting at 88°C.

Recrystallization of sedamine did not alter the melting point (88–89°C.), but reanalysis of the alkaloid showed the formula to be $C_{14}H_{21}ON$, without the third of a mole of water of crystallization reported earlier (4). The melting point of sedamine was not visibly depressed by admixture with the synthetic base (IV). However, while sedamine hydrochloride melted at 205°C., the hydrochloride of synthetic IV melted at 185°C. as also did the mixture of the two salts. Nevertheless, the infrared absorption spectra of the two bases (Fig. 1) are superposable and, therefore, the bases must be identical. The discrepancy in the melting points of the hydrochlorides is likely attributable to the fact that sedamine is presumably optically active—although insufficient material is available for the determination—while the synthetic base is racemic.

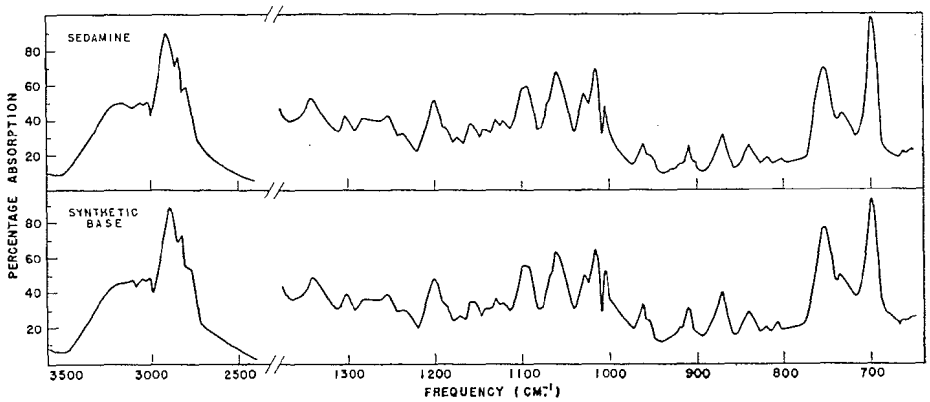

FIG. 1. *Infrared spectra of sedamine and the synthetic base, measured on a Perkin–Elmer 12B single beam spectrometer with sodium chloride prism, 1 mm. cell. The alkaloids were in carbon disulphide solution, 10 mgm. per ml.*

Amongst the minor alkaloids of *Lobelia inflata* L., Wieland and his coworkers (7) have reported two isomeric bases of formula $C_{14}H_{21}ON$, one melting at 103°C. the other at 81°C. The latter when oxidized gave rise to α-N-methylpiperidyl-carboxylic acid and was tentatively assigned structure IV which has now been shown to be that of sedamine. It is impossible to state whether the lower melting of the two *Lobelia* alkaloids is identical either with sedamine or its optical antipode or whether it is one of the other diastereoisomeric pair.

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Experimental*

Sedamine

The analytical figures reported previously (4) for this alkaloid agreed with the formula $C_{14}H_{21}ON.1/3H_2O$. Sedamine was recrystallized from petroleum ether and this did not alter its melting point, 88–89°C. It was dried in an evacuated desiccator before analysis. Calc. for $C_{14}H_{21}ON$: C, 76.68; H, 9.65; N, 6.39%. Found: C, 76.46; H, 9. 46; N, 6.28%.

α-Phenacylpyridine

1-α-Pyridyl-2-phenylacetylene was prepared by the method of Scheuing and Winterhalder (6). A quantity (31.6 gm.) of this substance was added to water (71 cc.) and concentrated sulphuric acid (64.5 cc.) and the mixture heated for 20 min. on the steam bath. After cooling, water (64.5 cc.) was added, the solution was alkalized with ammonia and extracted with ether. The ether extract was dried over sodium chloride and distilled on the steam bath to remove the solvent. The residual base after distillation, b.p. 130–135°C. at 0.6 mm., consisted of a yellow oil that solidified on cooling to yellow needles, m.p. 51°C. After sublimation and recrystallization from ether–hexane, it melted at 58–59°C. The literature gives m.p. 54°C. (2) and 59.1–60.7°C. (1). Yield, 29.7 gm. (85.5%). Calc. for $C_{13}H_{11}ON$: C, 79.18; H, 5.58%. Found: C, 79.29, 79.30; H, 5.41, 5.39%. The oxime melted at 117–118°C. (the literature records m.p. 116°(1)).

α-Phenacylpyridine metho-p-toluenesulphonate

To a solution of α-phenacylpyridine (17.3 gm.) in benzene (32 cc.), methyl *p*-toluenesulphonate (26.2 gm.) was added and the resulting solution heated on the steam bath for one hour. After a few minutes, the solution turned red and crystals separated. After one hour benzene (100 cc.) was added, the mixture allowed to cool and filtered. The filtered crystalline product, after recrystallization from methanol–ether, consisted of pale yellow prisms, m.p. 149–150°C. Weight, 21.8 gm. Calc. for $C_{21}H_{21}O_4NS$: C, 65.85; H. 5.48; N, 3.60. Found: C, 65.85, 65.70; H, 5.33, 5.37; N, 3.64, 3.58%.

α-Phenacyl N-methylpiperidine

α-Phenacylpyridine metho-*p*-toluenesulphonate (17.3 gm.) was dissolved in glacial acetic acid (170 cc.) and hydrogenated for 30 hr. in the presence of platinum oxide catalyst (0.2 gm.) at 50 lb. pressure. The catalyst was filtered and the filtrate distilled under reduced pressure on the steam bath. There remained a residue that was dissolved in water (150 cc.), the solution was alkalized with sodium hydroxide and extracted with ether. The combined ether extract was dried over sodium sulphate and evaporated to dryness. A pale yellow oil remained that boiled at 125–130° at 0.2 mm.; wt. 9.27 gm.

* *All melting points are corrected.*

The oily product (9.27 gm.) was dissolved in hot methanol (50 cc.) and added to a hot solution of picric acid (13 gm.) in methanol (100 cc.). Boiling was continued for 15 min. and the solution allowed to cool. A crystalline picrate separated (10.43 gm.) that, after recrystallization from boiling methanol, consisted of bright yellow aggregates, m.p. 159–160°C. (The literature (1) reports 159.2–159.4°C. as the melting point.) Calc. for $C_{20}H_{22}O_8N_4$: C, 53.81; H, 4.93; N, 12.56%. Found: C, 53.63, 53.81; H, 4.92, 5.03; N, 12.38, 12.41%. The base recovered from the pure picrate was an oil.

The picrate (2 gm.) was decomposed by shaking with dilute hydrochloric acid and ether. The aqueous solution was neutralized with potassium carbonate and extracted repeatedly with ether. The combined extract was dried over sodium sulphate and distilled on the steam bath. A yellow oil was left that was distilled *in vacuo*, b.p. 125–130°C. at 0.6–0.8 mm.; wt., 0.837 gm. The distillate was dissolved in absolute ether and the solution saturated with hydrogen chloride. A white gum separated that was crystallized from ethanol–acetone and recrystallized several times from ethanol–ether. The hydrochloride consisted of small colorless prisms, m.p. 166–167°C. Calc. for $C_{14}H_{19}ON \cdot HCl$: C, 66.26; H, 7.94; N, 5.40%. Found: C, 66.36; 66.11; H, 8.04, 7.80; N, 5.50%.

1-Methyl-2-(β-hydroxy-β-phenylethyl)-piperidine

The methanolic mother liquor from which the picrate of α-phenacyl-N-methylpiperidine had first separated was diluted with water, the solution made strongly acid with hydrochloric acid, and repeatedly extracted with ether to remove the liberated picric acid. The aqueous solution was then alkalized with sodium hydroxide and extracted with ether. This ether extract was dried over sodium sulphate and evaporated to dryness. There remained an oily residue that was distilled *in vacuo*, b.p. 165–170°C. at 1.7–2 mm.; wt. 3.38 gm. On standing, the distillate partially crystallized; it was dissolved with warming in petroleum ether and the solution on cooling deposited a crop of crystals. After several recrystallizations from petroleum ether the product was obtained as colorless elongated plates, m.p. 88°C. Calc. for $C_{14}H_{21}ON$: C, 76.68; H, 9.65; N, 6.39%. Found: C, 76.57, 76.79; H, 9.33, 9.48; N, 6.29, 6.40%. The infrared absorption spectrum of this compound reveals the presence of a hydroxyl group but shows no absorption in the carbonyl region. The total spectrum (Fig. 1) is superposable on that of sedamine.

A small quantity of the base was dissolved in methanol and neutralized to Congo red by the dropwise addition of methanol containing concentrated hydrochloric acid. The solution was then evaporated on the steam bath, the residue dissolved in methanol and the solution again evaporated to dryness. The final residue was dissolved in a few drops of methanol and the cooled solution diluted with absolute ether to incipient turbidity. Inoculation with a small crystal of sedamine hydrochloride initiated crystallization. The salt was recrystallized twice from methanol–ether from which it separated as colorless needles, m.p. 185°C. In admixture with sedamine hydrochloride it melted at 183°C.

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Acknowledgment

The absorption spectra were taken by Dr. R. N. Jones and Mr. R. Lauzon, National Research Council, whose courtesy is gratefully acknowledged. Our thanks are also due to the Office de Recherches Scientifiques de la Province de Québec, for the award of a Fellowship to one of us (R.L.).

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THE STRUCTURE OF JABORANDINE, THE ALKALOID OF *PIPER JABORANDI* VELLOSO. I.[1]

By K. Wiesner

Abstract

Jaborandine, the active principle of *Piper jaborandi* Velloso, has been shown to be an ester of *p*-aminobenzoic acid and an amino alcohol which contains a tertiary nitrogen with an N–CH_3 group and has the formula $C_{11}H_{23}ON$.

The Brazilian plant *Piper jaborandi* used as a local anaesthetic in popular medicine has been shown by Oscar Ribeiro and Antenor Machado (1) to contain an alkaloid which is responsible for the anaesthetic properties of the plant. We have had the opportunity of examining a small amount of the alkaloid, and we present our first results in this communication. The alkaloid forms a crystalline hydrochloride which melts at 134°C., resolidifies, and remelts at 154–156°C. A picrolonate, m.p. 148–149°C., was also prepared. The base itself can be distilled in high vacuum and solidifies to a low melting crystalline solid. The analyses of these derivatives agree with the formula for the base $C_{18}H_{28-30}O_2N_2$, some of the analyses seemingly agreeing better with the H_{30} than with the H_{28} formula. The base forms salts with one equivalent of acid and contains one N–CH_3 group. The result of a potentiometric microtitration showed only one basic nitrogen with the dissociation constant pK (cellosolve) = 8.14. The second nitrogen must therefore be very weakly basic or nonbasic. The ultraviolet spectrum in alcohol shows a maximum at 294 mμ (log ϵ = 4.52). As the infrared spectrum of the alkaloid indicated a possibility of an ester group, a small amount of the base was hydrolyzed with alcoholic potassium hydroxide. The hydrolyzate was separated into the basic and acidic fractions. The basic fragment was a liquid, which after distillation gave analytical figures agreeing with $C_{11}H_{23}ON$. It shows also the presence of one N–CH_3 group. A basic monobenzoyl derivative of this compound was prepared which gave a crystalline picrolonate. The analyses of these derivatives support the formula $C_{11}H_{23}ON$ and also show that the compound contains a hydroxy group and a tertiary nitrogen.

The acidic component was extracted from the hydrolysis mixture after acidification with hydrochloric acid in a continuous ether extractor. The analysis showed that it actually was a hydrochloride of an amino acid $C_7H_7O_2N$. This amino acid gave, with a slight excess of diazomethane, an ester $C_8H_9O_2N$, m.p. 110°C. This melting point is identical with the melting point of methyl *p*-aminobenzoate and was not depressed by admixture of the ester with an authentic specimen. Also the infrared spectra of methyl *p*-aminobenzoate and our ester were identical. The amino acid had ultraviolet spectra

[1] *Manuscript received December 22, 1950.*
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both in acidic (maxima 222 mμ, log ε = 4.08; 290 mμ, log ε = 4.25) and alkaline (maximum 266 mμ, log ε = 4.29) alcohol identical with those of *p*-aminobenzoic acid. It is therefore clear that the formula $C_{18}H_{28}O_2N_2$ is to be preferred for jaborandine and that this alkaloid is the *p*-aminobenzoic ester of amino alcohol I.

$$HO - C_{10}H_{19} = NCH_3$$
$$\text{I}$$

No further experiments have yet been done on the structure of this compound but it seems likely that it contains the nitrogen in a ring, which would probably classify it among either the piperidine or pyrrolidine alkaloids. The dehydrogenation with selenium (350 mgm.) carried out on 100 mgm. of base I, at 350°C. for eight hours in a sealed tube, gave in a 15% yield a basic product which distilled at approximately the same temperature as base I and had an absorption maximum at 263mμ, log ε 3.45. This leaves not much doubt that the dehydrogenation product is a substituted pyridine derivative and therefore base I a substituted N-methylpiperidine alcohol.

Experimental Part

Jaborandine hydrochloride

The compound was recrystallized seven times from alcohol to a constant melting point, 134°C. Sometimes the compound resolidified and melted at 154–156°C. For analysis it was dried in a high vacuum for 24 hr. at 70°C., Calc. for: $C_{18}H_{31}O_2N_2Cl$: C, 62.9; H, 9.13; N, 8.16; Cl, 10.34; N methyl, 4.37%. Calc. for: $C_{18}H_{29}O_2N_2Cl$: C, 63.35; H, 8.58; N, 8.21; Cl, 10.41; N methyl, 4.40%. Found: C, 62.61; H, 8.93; N, 8.18; Cl, 10.91; N methyl, 4.62%. *The picrolonate* was recrystallized six times to a constant melting point of 148–149°C. and dried in a high vacuum at 80°C. for 24 hr. Calc. for: $C_{28}H_{38}O_7N_6$: C, 58.9; H, 6.73; N, 14.71%. Calc. for: $C_{28}H_{36}O_7N_6$: C, 59.1; H, 6.38; N, 14.78%. Found: C, 58.97; H, 6.49; N, 14.92. The free base was liberated from the recrystallized hydrochloride and distilled in a collar flask. It boiled at 190–200°C. (outside) at 0.5 mm. Calc. for: $C_{18}H_{30}O_2N_2$: C, 70.5; H, 9.88; N, 9.14%. Calc. for: $C_{18}H_{28}O_2N_2$: C, 70.9; H, 9.29; N, 9.19%. Found: C, 70.23; H, 9.72; N, 9.42%.

Hydrolysis of Jaborandine

Jaborandine (150 mgm.) was refluxed for six hours with 8 cc. of 10% alcoholic potassium hydroxide. After this time the alcohol was taken off in a vacuum and 30 cc. of water added. The solution was extracted exhaustively with ether. The ether extract was dried and evaporated to dryness, leaving 78 mgm. of an oily base. This compound was purified by filtering through a column of 3 gm. of alumina in chloroform and fractionally distilled in a collar flask in high vacuum. It boiled sharply at 85–90°C. (outside temperature) at 2–3 mm. The middle fraction was analyzed. Calc. for: $C_{11}H_{23}ON$: C, 71.2; H, 12.52; N, 7.55; 1 active H, 0.54, N methyl, 8.1%. Found: C, 70.67; H, 12.08; N, 7.65; active H, 0.6%; N methyl, 5.26%. The base showed no ultraviolet absorption.

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As the base failed to give crystalline salts and it was obviously desirable to purify it through a solid derivative, 100 mgm. was benzoylated by the usual procedure with benzoyl chloride and pyridine. A quantitative yield of a basic benzoyl compound was obtained which gave a crystalline picrolonate. The picrolonate after six recrystallizations from methanol melted sharply at 104–105°C. and was dried at 80°C. for 24 hr. in high vacuum. Calc. for: $C_{28}H_{35}O_7N_5$: C, 60.7; H, 6.38; N, 12.66%. Found: C, 60.65; H, 6.54; N, 12.83%. The free benzoylated base was liberated from the picrolonate and distilled for analysis in a collar flask. It boiled at 1 mm. at 140–150°C. (outside temperature). Calc. for: $C_{18}H_{27}O_2N$: C, 74.7; H, 9.44; N, 4.84%. Found: C, 74.61; H, 9.56; N, 5.00%. The aqueous alkaline layer after extraction of the base $C_{11}H_{23}ON$ was acidified with hydrochloric acid and extracted continuously with ether for three days. After evaporation of the ether approximately 70 mgm. of a crystalline solid remained. It was recrystallized from alcohol–ether, and after two crystallizations it melted around 200°C. with decomposition. It was shown by qualitative test to be a hydrochloride. A small sample was dried for analysis at 90°C. in high vacuum. Calc. for: $C_7H_7O_2NHCl$: C, 48.4; H, 4.61; N, 8.06%. Found: C, 47.94; H, 4.69; N, 7.98%.

The rest of the compound together with a sample obtained in a second experiment (130 mgm. in all) was dissolved in 5 cc. of methanol and just sufficient diazomethane solution was added to make the solution permanently faintly yellow. After standing for 15 min. the solution was filtered, evaporated to dryness, and the ester which formed a slowly crystallizing white oil recrystallized from a methanol–water mixture. After four crystallizations the ester had a constant melting point, 110°C., which showed no depression on admixture of the ester with a sample of methyl *p*-aminobenzoate of the same melting point. For analysis the compound was sublimed in high vacuum at 100°C. Calc. for: $C_8H_9O_2N$: C, 63.56; H, 6.00; N, 9.27; OCH_3, 20.40%. Found: C, 63.62; H, 6.08; N, 9.37; OCH_3, 20.35%. The compound gave an infrared spectrum identical with the spectrum of methyl *p*-aminobenzoate.

Acknowledgments

The author expresses his gratitude to Drs. O. Ribeiro and A. Machado, Rio de Janeiro, for their kind co-operation and a gift of crystalline jaborandine hydrochloride with which the work was performed.

This work was performed on a grant from the National Research Council, Ottawa. The analyses were done in the Microanalytic Laboratory of Dr. Rob. Dietrich in Zurich. The infrared spectra were taken partly in the National Research Laboratories, Ottawa, and partly by Messrs. Samuel P. Sadtler & Son, Inc., Philadelphia.

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THE SYNTHESIS OF DEHYDROLUPANINES AND THE STEREOCHEMISTRY OF THE C_{15} LUPIN ALKALOIDS[1]

By Léo Marion and Nelson J. Leonard

Abstract

Two new dehydrolupanines, $C_{15}H_{22}N_2O$, have been prepared: (1) by the mercuric acetate dehydrogenation of the alkaloid *d*-lupanine, and (2) by the N-bromosuccinimide dehydrogenation of *d*-lupanine. The conversion of *d*-lupanine to its diastereoisomeric alkaloid *d*-*a*-isolupanine has been effected by mercuric acetate dehydrogenation followed by catalytic hydrogenation. On the basis of evidence and knowledge at present accumulated it has been possible to assign absolute stereochemical structures to a number of C_{15} lupin alkaloids.

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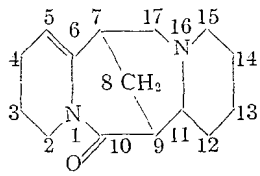
Of the three lupin alkaloids of molecular formula $C_{15}H_{22}N_2O$ thus far characterized, namely aphyllidine (10), monspessulanine (11), and "P1" (8), the structure of only the first has been established (I). The molecular formula suggested the possible biogenetic derivation of the other $C_{15}H_{22}N_2O$ alkaloids from either lupanine (II) or hydroxylupanine (III). Accordingly, laboratory methods have been investigated for the conversion of the well known alkaloid II to compounds of composition $C_{15}H_{22}N_2O$, characterized by the formation of derivatives and hydrogenation products.



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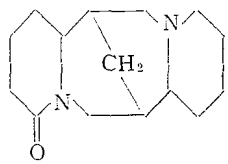

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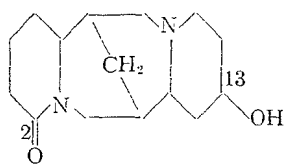


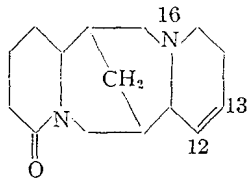
III

The position of attachment of the hydroxyl group in hydroxylupanine (III) has been ascertained as C–13[2] by Galinovsky, Pöhm, and Riedl (3) on the basis of products obtained on exhaustive chromic acid oxidation of III. Dehydration of hydroxylupanine would be expected to yield either Δ^{12}-dehydrolupanine (IV) or Δ^{13}-dehydrolupanine (V), both possible products having the unsaturation β, γ to the amino nitrogen (N–16) provided no rearrangement attended the

[1] *Manuscript received January 9, 1951.*
Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2367.

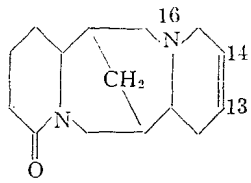
[2] *C–12 on J. F. Couch's numbering system.*

III →



IV

or



V

dehydration. Phosphorus pentoxide was employed by Galinovsky and Pöhm (2) for the dehydration of hydroxylupanine during the process of establishing the constitution of this alkaloid, but the product was not isolated. Instead, the crude intermediate was hydrogenated over palladium on charcoal directly to *d*-lupanine (II). It might be that the $\Delta^{12(13)}$-dehydrolupanine (IV or V) could be obtained more efficaciously by a milder dehydration process such as the Chugaev reaction.[3]

A new dehydrolupanine was obtained by the mercuric acetate dehydrogenation of *d*-lupanine and will be referred to as "dehydrolupanine (MA)," in the absence of an absolute determination of the double-bond position. The same reaction had been carried out by Kneuer (4), but he found that the product obtained upon loss of two atoms of hydrogen from lupanine was too unstable to be characterized. Our experience paralleled Kneuer's in that the quantity of mercurous acetate precipitated indicated the abstraction of two hydrogens from the *d*-lupanine molecule, and the "dehydrolupanine (MA)" formed was especially sensitive to air. However, we found that if the base was kept bound in the salt form by means of acetic acid, catalytic hydrogenation of the probable $C_{15}H_{22}N_2O$ intermediate could be effected before too much decomposition had taken place. When the "dehydrolupanine (MA)" in acetic acid was hydrogenated over platinum, two products were isolated in the pure state: *l*-α-isosparteine, $C_{15}H_{26}N_2$, identified as the free base and picrate, and *d*-α-isolupanine, $C_{15}H_{24}N_2O$, identified as the perchlorate.

The conversion of *d*-lupanine to these two products of the *iso* series indicates that inversion at one of the asymmetric centers of *d*-lupanine must have occurred in the dehydrogenation–rehydrogenation process. The successful conversion of *d*-lupanine to its diastereoisomer *d*-α-isolupanine is similar to the change from *l*-sparteine to *l*-α-isosparteine, effected by Winterfeld and Rauch (12) by means of mercuric acetate dehydrogenation to α-didehydrosparteine followed by catalytic hydrogenation. In both instances, the conversions must involve the same asymmetric carbon atom, and since the dehydrogenation process probably introduces unsaturation α, β to the basic nitrogen (N–16 in *d*-lupanine, both nitrogens in *l*-sparteine), it is possible to postulate the structure of the unisolated "dehydrolupanine (MA)" as Δ^{11}-dehydrolupanine (VI). The vinyl tertiary amine grouping would in part account for the instability of this

[3]*See, for example: Alexander, E. R. and Mudrak, A. J. Am. Chem. Soc. 72: 1810. 1950; Adams, R., McKenzie, S. Jr. and Loewe, S. J. Am. Chem. Soc. 70: 664. 1948; Djerassi, C. Chem. Revs. 43: 271. 1948.*

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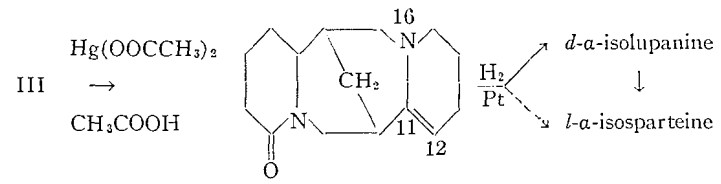
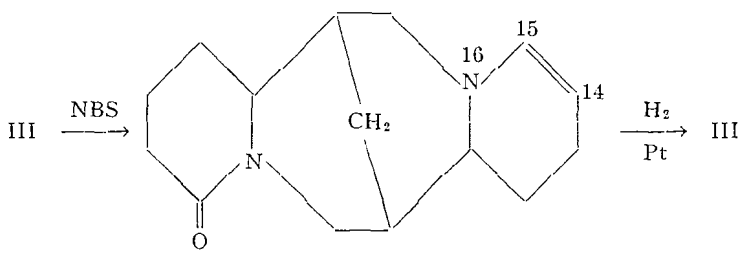


VI

dehydrogenated lupanine, in contrast to the relatively stable $\Delta^{12(13)}$-dehydrolupanine obtained in the dehydration of hydroxylupanine. The formation from VI of *l*-α-isosparteine along with the expected *d*-α-isolupanine is somewhat surprising since the catalytic hydrogenation of *d*-α-isolupanine to *l*-α-isosparteine has in the past required 2*N* hydrochloric acid solution (1), rather than glacial acetic acid, which was the solvent used in the hydrogenation of "dehydrolupanine (MA)."

Another dehydrolupanine was obtained by the dehydrogenation of *d*-lupanine by means of N-bromosuccinimide, a reagent whose application appears to be novel in the alkaloid field. The "dehydrolupanine (NBS)", $C_{15}H_{22}N_2O$, underwent decomposition when distillation of the free base was attempted, but it was readily characterized by formation of the perchlorate, m.p. 240.5–241.5°C. (dec.), $[\alpha]_D^{26}$ −125° (water). The rehydrogenation of "dehydrolupanine (NBS)" in the presence of platinum catalyst in acetic acid solution furnished *d*-lupanine in near quantitative yield, which indicated that an asymmetric center was probably not involved in the dehydrogenation–rehydrogenation process, or at least that position C-11 was not involved (as in the action of mercuric acetate). Since sparteine, with no amide linkage, undergoes reaction with N-bromosuccinimide (5) and since the reagent probably introduces unsaturation α, β to the basic nitrogen (N–16) in *d*-lupanine, the structure of the "dehydrolupanine (NBS)" may be represented tentatively as Δ^{14}-dehydrolupanine (VII).



VII

The ease of dehydrogenation of *d*-lupanine with N-bromosuccinimide was somewhat surprising. It was necessary only to mix the two reactants in chloroform solution, and the product was worked up immediately. Neither peroxide nor heat nor an extended reaction time had any beneficial effect on the dehydrogenation process. The action of N-bromosuccinimide in the dehydrogenation of amines is being investigated further.

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On the basis of evidence and knowledge at present accumulated, it should be possible to assign absolute stereochemical structures to the members of the C_{15} family of lupin alkaloids. With the alkaloid thermopsine identified by Cockburn and Marion (1) as structurally similar but stereochemically different from anagyrine, the two racemates of $C_{15}H_{20}N_2O$ (ring A = α-pyridone) have been satisfactorily characterized as *dl*-anagyrine and *dl*-thermopsine. *d*-Anagyrine is the only one of the four optically active forms which has not yet been found in nature. Considering only one of the enantiomorphs of each racemate, the configuration of the diastereoisomers can be represented by formula VIII in which the relation of the 7, 9-methylene bridge to the C_{11}-hydrogen is *cis* and by that in which the relation is *trans* (IX) (see Fig. 1). The $C_{15}H_{24}N_2O$ compounds (ring A = α-piperidone) can exist in four racemic forms due to the *different* asymmetric carbons C_6 and C_{11} and the $C_{7,9}$-asymmetric center. With only one enantiomorph of each racemic pair indicated in Fig. 1, the relations between the C_6-hydrogen, the $C_{7,9}$-methylene bridge, and the C_{11}-hydrogen in these four diastereoisomeric forms are indicated as follows: *cis-cis* (X), *trans-cis* (XI), *cis-trans* (XII), and *trans-trans* (XIII). One of the racemates corresponds to *dl*-lupanine, of which both forms have been found in nature, and a second racemate corresponds to *dl*-α-isolupanine (*dl*-tetrahydrothermopsine), of which only the *d*-form has thus far been found in nature (9). It is as yet unknown whether the $C_{15}H_{24}N_2O$ alkaloidal products: nonalupine, sophocarpine, and dihydromonspessulanine have the same basic ring structure as lupanine; therefore, the distribution of the other two racemates structurally related to lupanine and α-isolupanine remains in doubt at present. The $C_{15}H_{26}N_2$ compounds, by contrast, have two *similar* asymmetric carbons, C_6 and C_{11}, and the asymmetric center at $C_{7,9}$. Three racemates exist, and the relations between the asymmetric centers in a representative of each, as indicated in Fig. 1, are as follows: *cis-cis* (XIV), *cis-trans* (XV), and *trans-trans* (XVI). Both *d*- and *l*-sparteine have been found in nature, and *l*-α-isosparteine has recently been isolated from natural sources for the first time by Marion, Turcotte and Ouellet (9). "β-Isosparteine" has not yet been characterized.

A provisional stereochemical structure has been assigned to sparteine (6) on the basis of accumulated evidence as to the structural similarity but configurational difference between rings B and C in sparteine and its derivatives. The stereochemical structure is represented by the *cis-trans* form (XV) in Fig. 1. If this structure is correct, then the lupanine and anagyrine progenitors of sparteine must be, respectively, either the *trans-cis* $C_{15}H_{24}N_2O$ (XI) and the blank-*cis* $C_{15}H_{20}N_2O$ (VIII), *or* the *cis-trans* $C_{15}H_{24}N_2O$ (XII) and the blank-*trans* $C_{15}H_{20}N_2O$ (IX). The key to the configuration of the progenitors of sparteine lies in the stereochemical course of the hydrogenation reaction which converts anagyrine to lupanine; i.e., whether the hydrogen becomes attached to the 6-carbon of anagyrine *cis* to the $C_{7,9}$-methylene bridge or *trans* to it. A careful inspection of scale molecular models (Fisher–Hirschfelder–Taylor and Stuart) indicates that there is a real difference between the two faces of the $C_{15}H_{20}N_2O$ molecule in ease of approach toward hydrogen on a catalyst surface.

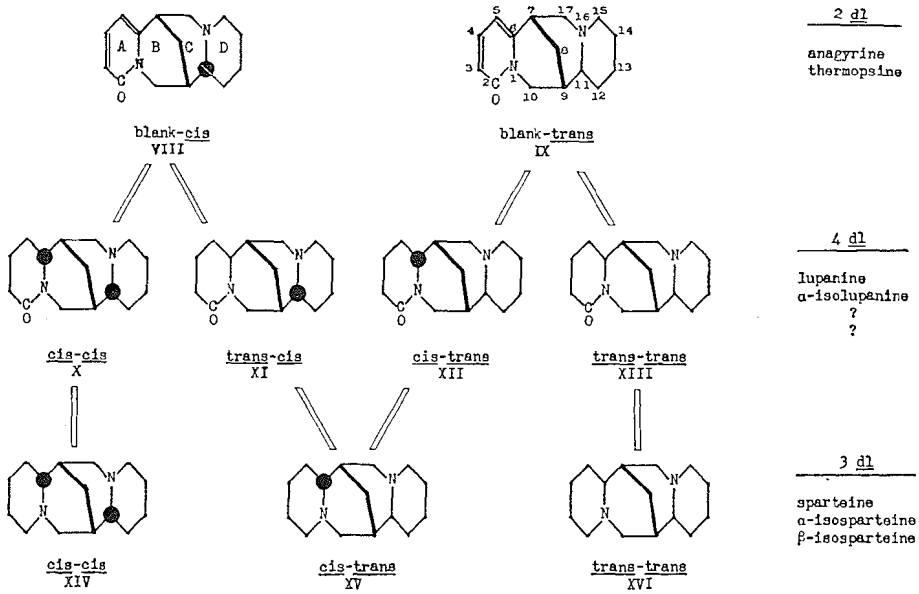

FIG. 1. *Stereochemical family—C_{15} lupin alkaloids.*

Approach at C_6 *trans* to the methylene bridge is appreciably masked by the atoms of rings B, C, and D, whereas approach at C_6 *cis* to the $C_{7,9}$-methylene bridge is relatively unhindered. On the basis of this model inspection and the recognized surface nature of the catalytic hydrogenation process (7), the assumption can therefore be made that hydrogen enters the anagyrine molecule *cis* to the $C_{7,9}$-methylene bridge in the formation of lupanine. This limits the structure of lupanine to either the *cis-cis* or the *cis-trans* $C_{15}H_{24}N_2O$ type, and a decision can be made in favor of the latter (XII), since sparteine, which is obtained from lupanine, has the *cis-trans* $C_{15}H_{26}N_2$ structure (XV) and only the *cis-trans* $C_{15}H_{24}N_2O$ type can be its precursor. Thus, it becomes possible to assign stereochemical structures to the entire sparteine family. Lupanine (both *d* and *l*) has the *cis-trans* configuration (XII), and its precursor anagyrine (both *d* and *l*) can only have the blank-*trans* configuration (IX). On the basis of this sole assumption that hydrogen enters the $C_{15}H_{20}N_2O$ molecule at C_6 *cis* to the methylene bridge, it also becomes possible to assign stereochemical structures to thermopsine, α-isolupanine (tetrahydrothermopsine), and α-isosparteine. (An inspection of the scale models shows that *cis* approach to the methylene bridge is easier than *trans* no matter whether the C_{11}-hydrogen is *cis* or *trans*.) Thermopsine has been shown to be convertible to α-isolupanine (tetrahydrothermopsine) by hydrogenation over platinum in acetic acid, and α-isolupanine, to α-isosparteine by hydrogenation over platinum in hydrochloric acid (1, 9). Thermopsine must have the blank-*cis* $C_{15}H_{20}N_2O$ structure (VIII) since it is diastereoisomeric with anagyrine; *cis*-hydrogenation at C_6 would produce the *cis-cis* $C_{15}H_{24}N_2O$ structure (X), which is therefore α-isolupanine. These blank-*cis* (VIII) and *cis-cis* (X) progenitors require that

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α-isosparteine, $C_{15}H_{26}N_2$, have the structure *cis-cis* (XIV). It will be noted that there is thus stereochemical consistency in the two families: anagyrine → lupanine → sparteine; thermopsine → α-isolupanine → α-isosparteine.

It was shown earlier that sparteine can be converted to isosparteine by mercuric acetate dehydrogenation followed by catalytic hydrogenation (12), and in the present work, the conversion of lupanine to α-isolupanine by a similar process has been described. The conversion of lupanine, with the *cis-trans* structure (XII), to α-isolupanine, with the *cis-cis* structure (X), necessitates the introduction of a double bond at C_{11}. If the subsequent hydrogenation (over platinum in acetic acid) is to produce the *cis-cis* $C_{15}H_{24}N_2O$ molecule, the hydrogen must enter *cis* to the $C_{7,9}$-methylene bridge. This is entirely consistent with the assumption as to stereospecificity of hydrogenation reached earlier on the basis of the scale models. The dehydrogenation–rehydrogenation of sparteine (XV) must proceed in an analogous manner: introduction of a double bond at C_{11}, followed by catalytic addition of hydrogen at C_{11} *cis* to the $C_{7,9}$-methylene bridge to produce the *cis-cis* α-isosparteine (XIV).

Experimental*

Dehydrogenation of d-Lupanine by N-Bromosuccinimide. "Dehydrolupanine (NBS)"

A solution of 1.812 gm. (5.2 millimoles) of *d*-lupanine perchlorate in water was treated with concentrated ammonium hydroxide, and the basic solution was extracted with chloroform. The combined chloroform extracts were evaporated to dryness, and the residue was redissolved in anhydrous chloroform. To this solution was added 1.07 gm. (6.0 millimoles) of N-bromosuccinimide in 125 ml. of anhydrous chloroform. The resulting yellow solution was shaken briefly (two to three minutes), then extracted several times with aqueous sodium hydroxide. The chloroform layer was washed with water, and the chloroform was removed by distillation, finally *in vacuo*. The residue was dissolved in methanol, and to the methanolic solution was added 72% perchloric acid until the solution was just acid to Congo red. An immediate separation of colorless triangular plates resulted, and a total of 1.333 gm. (74%) of *perchlorate* was collected. After two recrystallizations from methanol containing a trace of ether the perchlorate melted at 240.5–241.5°C., with decomposition; $[\alpha]_D^{26}$ −125° ± 1° (c = 1.10, water). Found: C, 51.65; H, 7.22; N, 8.03%. Calc. for $C_{15}H_{22}N_2O \cdot HClO_4$: C, 51.94; H, 6.68; N, 8.08%.

Hydrogenation of "Dehydrolupanine (NBS)"

When an attempt was made to distil the free base, obtained by basification with aqueous sodium hydroxide followed by chloroform extraction and evaporation of the chloroform, no distillate was obtained at 0.2 mm. up to 230°C. and intensive resinification occurred. For catalytic hydrogenation, 300 mgm.

* *All melting points are corrected.*

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(1.2 millimoles) of "dehydrolupanine (NBS)" was used, as obtained from a solution of the perchlorate by basification and chloroform extraction followed by evaporation of the chloroform. A solution in 10 ml. of glacial acetic acid did not absorb hydrogen when palladium on charcoal was used as the catalyst, but absorbed one molar equivalent of hydrogen in two hours when platinum oxide catalyst was used. The solution was filtered, and the filtrate was evaporated to dryness *in vacuo*. The residue was treated with 5% aqueous sodium hydroxide and extracted with chloroform. The chloroform extracts were washed with water and evaporated to dryness. The residue was distilled at 0.15 mm. and a bath temperature of 135–145°C. The distillate was converted directly to the perchlorate by adding perchloric acid to a methanol solution; m.p. 210–211°C., undepressed on mixture with an authentic sample of *d-lupanine perchlorate* (m.p. 210–211°C.). The specific rotation was also identical with that of *d*-lupanine perchlorate, as determined in aqueous solution.

Attempted Further Dehydrogenation of "Dehydrolupanine (NBS)"

A solution of "dehydrolupanine (NBS)" in chloroform, made by decomposition of 1.20 gm. (3.46 millimoles) of "dehydrolupanine (NBS)" perchlorate, was treated with a solution of 0.678 gm. (3.81 millimoles) of N-bromosuccinimide in 100 ml. of chloroform. The resulting solution changed from colorless to yellow to orange, then back to straw yellow, just on shaking a few minutes. The chloroform solution was extracted three times with aqueous sodium hydroxide, washed with water, and evaporated to dryness. The product was not homogeneous, as evidenced by the perchlorate which separated as a mixture of reddish oil and crystals that resisted purification.

Dehydrogenation of d-Lupanine by Mercuric Acetate. "Dehydrolupanine (MA)"

A solution of *d*-lupanine in chloroform obtained by decomposition of 1.406 gm. (4.03 millimoles) of *d*-lupanine perchlorate, was evaporated to dryness, and the residue was redissolved in 50 ml. of 5% acetic acid in water. To this acetic acid solution was added 10.3 gm. (32.2 millimoles) of mercuric acetate, and the resulting solution was stirred under a nitrogen atmosphere on the steam bath for five hours. The mixture was cooled and filtered, and 1.9 gm. (7.3 millimoles) of mercurous acetate was collected. This corresponds to the removal of two hydrogen atoms from lupanine. The filtrate was saturated with hydrogen sulphide and the insoluble mercuric sulphide was removed by filtration. The final filtrate was evaporated to near dryness *in vacuo*, a small amount of 10% sulphuric acid was added to dissolve the residue, and excess aqueous sodium hydroxide and chloroform were added. The aqueous layer was rapidly extracted with further portions of chloroform, the combined chloroform extracts were washed with water, and glacial acetic acid was added to the chloroform solution. If the precaution of adding acetic acid was not followed, decomposition of the base in chloroform solution occurred very rapidly. It was not possible to isolate the "dehydrolupanine (MA)", and attempts to form perchlorate or picrate derivatives were not successful.

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Hydrogenation of "Dehydrolupanine (MA)"

The chloroform – acetic acid solution was evaporated to dryness *in vacuo*, and the residue was redissolved in 35 ml. of glacial acetic acid. Hydrogenated at room temperature and atmospheric pressure over 300 mgm. of platinum oxide catalyst, the material (assuming it to be $C_{15}H_{22}N_2O$) absorbed one mole equivalent of hydrogen. The catalyst was removed by filtration and the acetic acid, by evaporation *in vacuo*. The residue was treated with 5% aqueous sodium hydroxide and chloroform, and the aqueous layer was further extracted with chloroform. The combined extracts were washed with water and evaporated to dryness *in vacuo*. The residue was distilled *in vacuo* and two fractions were collected: 66.1 mgm. of colorless needle crystals which sublimed at 0.07 mm. and a bath temperature of 70–80°C.; 140.5 mgm. of colorless oil which distilled at 0.08 mm. and a bath temperature of 125–140°C. The solid fraction was resublimed for analysis. Found: C, 75.62; H, 11.28%. Calc. for $C_{15}H_{26}N_2$: C, 76.86; H, 11.18%. For $C_{15}H_{26}N_2 \cdot H_2O$: C, 71.38; H, 11.18%.

The analysis was suggestive of *l-α-isosparteine* partially hydrated, as was the melting point behavior (melting at 104°C., clearing at 115°C.). When mixed with a sample of freshly sublimed *l-α*-isosparteine, the melting point behavior was identical. A *picrate* of the solid fraction was made in ethanol and recrystallized from methanol; m.p. 221°C., with decomposition, undepressed on mixture with an authentic sample of *l-α*-isosparteine picrate (m.p. 221°C., with decomposition).

The second or liquid fraction (see above) was converted to the perchlorate in methanol solution. A fractional crystallization of the crude salt which first separated gave a more soluble perchlorate, recrystallized from methanol–ether, which melted with decomposition at 248–249°C. This perchlorate was not depressed in melting point when mixed with the perchlorate of an authentic sample of *d-α-isolupanine* (m.p. 248–249°C. with decomposition). The less-soluble perchlorate fractions appeared to be mixtures, indicating the presence but not the identity of a second constituent of the high boiling fraction resulting from dehydrogenation–hydrogenation.

Acknowledgment

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THE SEPARATION OF THE RARE EARTHS BY ION-EXCHANGE PROCEDURES[1]

By F. T. Fitch and D. S. Russell

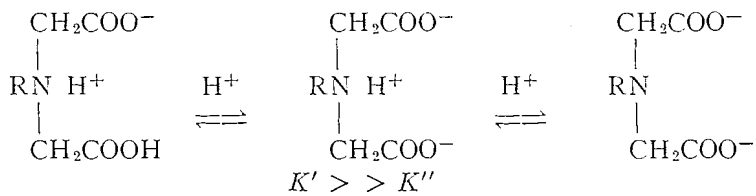
Abstract

The iminodiacetic acids have been examined as possible complexing agents in the chromatographic separation of the rare earths with cation exchange resins. The ammonium salts of these acids form complex ions involving both one and two iminodiacetate ions of increasing stability with the rare earth elements of greater atomic number. Methods greatly reducing the time and material requirements are presented for the separation of the cerium group elements with nitrilotriacetic acid.

Introduction

Considerable success in the separation of the rare earth elements has been achieved recently in the application of chromatographic techniques to cation exchange resins (6, 18, 21). Elution with a complexing agent, generally citric acid, was found to move the adsorbed rare earth ions through an exchanger bed at different rates. The elements of higher atomic number, which formed the more stable complex ions with citric acid, were collected in correspondingly earlier portions of the eluate. Careful control of pH and ion concentrations was necessary to achieve the desired ion-exchange and exploit to a maximum the slight differences in behavior of the elements (19, 20). However, with the large volumes of eluate and further separations required, the purification of appreciable quantities of these elements still remained laborious.

The iminodiacetic acids, $RN(CH_2COOH)_2$, are excellent complexing agents for most di- and trivalent cations, and interest in the present work has centered on their development as eluting agents for the rare earth elements. These compounds are weak acids with "zwitterion" or dual type ion formation causing considerable difference in the dissociation of the acid groups.



$K' > > K''$

When partially neutralized, these acids readily form complex ions with most cations, chelate formation occurring through the nitrogen and acid groups. In many cases, basic ions are indicated at high pH values and often the metal hydroxide may be precipitated on addition of strong base.

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Hydrogen ion is liberated from the zwitterion in chelate formation. Titration of the acids with base in the presence of various cations gives some indication of the extent of complex ion formation at different pH values and may permit an estimation of both the acid dissociation and complex ion instability constants. With nitrilotriacetic acid, Schwarzenbach and Biedermann (14) have reported that a mixture of both the mono- and di-acid complex ions was formed by lanthanum or cerous ions with some indication of greater stability for the complexes of the latter element. Beck (2) has found in fractional precipitation experiments additional evidence for the greater stability of the complex ions of nitrilotriacetate with the rare earths of higher atomic number and also confirmed the existence of the di-acid complex ion, $M(N(CH_2COO)_3)_2^{---}$, by precipitation with $Co(NH_3)_6^{+++}$.

At pH 5 to 7, in which range the elution of the rare earths was found to occur, the iminodiacetic acids are present almost entirely as either the HA^- or HA'^{--} anion. Titration experiments have indicated that the complex rare earth ions would be MA^+ and largely MA_2^-, where M represents the trivalent cation. The principal equilibria involved in the complexing and exchange reactions between the eluting solution and the ammonium form of the resin may be written as follows:

$$HA^- \overset{K''}{\rightleftharpoons} H^+ + A^=,$$

$$MA^+ \overset{K_c'}{\rightleftharpoons} M^{+++} + A^=,$$

$$MA_2^- \overset{K_c''}{\rightleftharpoons} MA^+ + A^=,$$

$$\text{and } M^{+++} + 3NH_4R \overset{K_{ex}}{\rightleftharpoons} 3NH_4^+ + MR_3,$$

where R represents the anionic species of the resin. Applying the mass law to these equilibria, an expression similar to that applied to the citric acid system (7) may be obtained for the rare earth distribution coefficient, K_d, as follows:

$$K_d = \frac{(MR_3)}{(MA^+) + (MA_2^-)}$$

$$= \left(\frac{1}{1 + \dfrac{K''(HA^-)}{K_c''(H^+)}}\right) \frac{K_{ex}K_c'}{K''} \frac{(NH_4R)^3}{(NH_4^+)^3} \frac{(H^+)}{(HA^-)}$$

With the rare earth present to a large extent as the di-acid complex ion, MA_2^-, under the elution conditions, the distribution coefficient would tend to approach the following expression:

$$K_d = \frac{K_{ex}K_c'K_c''}{(K'')^2} \frac{(NH_4R)^3}{(NH_4^+)^3} \frac{(H^+)^2}{(HA^-)^2}$$

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Thus, an increase in pH, iminodiacetic acid or ammonium ion concentration could be expected to increase the proportion of rare earth in solution and quicken the elution of the cation from the exchanger. The displacement of ammonium ion from the resin by appreciable quantities of a foreign cation or rare earth ion should decrease the distribution coefficient. It has been found convenient to use a separation factor (7, 9), namely, the ratio of the respective distribution coefficients, in estimating the possibility of separating a pair of cations. The data available are insufficient to permit prediction of the separation factors for the rare earth elements but the difference in effect of neodymium and lanthanum on the titration curves was great enough to indicate convenient separations throughout the group. The use of the iminodiacetic acids as eluting agents has been investigated and, in particular, procedures employing nitrilotriacetic acid have been developed for the separation and purification of the cerium group elements.

Experimental

Materials

Resin.—Amberlite I.R. 120, 20–35 mesh, Resinous Products and Chemical Company.

Rare earth.—Crude didymium oxide, Lindsay Light and Chemical Co., and resulting column preparations.

Iminodiacetic acids.—A number of these acids were synthesized by heating solutions of the corresponding amino acid (or hydrazine) and chloroacetic acid with controlled addition of the calculated quantities of potassium hydroxide or carbonate to remove the resulting hydrochloric acid. The products were recovered either as the insoluble acid or metal salt as described in the literature. This general procedure was followed in the preparation of nitrilotriacetic acid (10), hydrazinodiacetic acid (1), benzyl iminodiacetic acid (3), and *o*-carboxyaniline-N-N-diacetic acid (17). In the preparation of nitrilotriacetic acid, yields of about 80% theoretical were obtained using chloroacetic instead of iodoacetic acid, but often larger quantities of hydrochloric acid than those indicated were necessary for the precipitation of the product.

Rare Earth Analysis

Total rare earth was determined gravimetrically by precipitation with oxalic acid and ignition to the oxide. Careful control of precipitation conditions and reagent quantities was necessary, particularly with lanthanum, to avoid small filtrate losses apparently due to a slight solubility of the precipitate (8, 13). The rare earth was precipitated from solution, heated just to boiling, by the addition of 10% oxalic acid (4 ml. per 100 ml. sample) and then allowed to stand for two hours on a steam bath. After cooling rapidly to 0°C. in a salt–ice bath with frequent stirring, the precipitate was filtered from solution and ignited at 800°C. for weighing. These precipitation conditions with a final cooling in tap water were followed roughly in the recovery of rare earth from

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the large volumes of column eluate, and material losses of only 2–3% were encountered throughout the extensive handling of a column run.

Samarium, neodymium, and praseodymium were determined by their absorption spectra as described by Rodden (12) and Moeller and Brantley (11), employing a Cary Recording Spectrophotometer, Model 11M. Special cells with a light path of 2 cm. were designed to handle 2–3 ml. solutions of the oxide samples dissolved in 2% hydrochloric acid. For this determination absorption bands were employed at the following wave lengths: Pr, 444.5 mμ; Nd, 521 mμ; Sm, 402 mμ. Oxides, that had been purified extensively by column elution, were used in the preparation of samples and synthetic mixtures to obtain standard curves. As the examination of the absorption spectra of these materials gave no suggestion of contamination, the purity was better than 99.5% for Pr and Nd and 99% for Sm. Only at high concentrations did the absorption bands give any indication of deviation from Beer's law and these elements appeared to have negligible effect on the absorption spectra of one another. In mixed oxides samples of 200 mgm., these elements could be determined down to approximately 1% Pr, 2% Nd, and 3% Sm and detected at appreciably lower concentrations.

Titration of the Iminodiacetic Acids

The iminodiacetic acids may be titrated to a sharp end point prior to neutralization of the last acid group (16, 17). The additional acid liberated owing to complex formation was determined throughout the pH range of this end point by titration of the various acids with sodium hydroxide (0.1 and 0.5 *N*) in the presence of neodymium and lanthanum chloride. A Beckman pH meter, model G, was used in the titrations, and special care was required to reach equilibrium values in the initial stages owing to the relative insolubility of many of these acids.

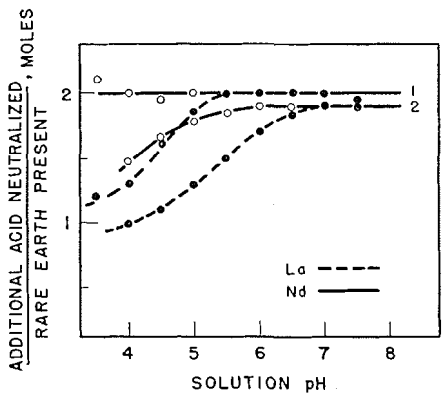

FIG. 1. *Nitrilotriacetic acid neutralized per mole rare earth due to complex formation. Rare earth, 0.33 millimole; initial volume, 100 ml. Nitrilotriacetic acid: 1. 5.0 millimole 2. 1.0 millimole.*

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The acid liberated through complex formation has been shown for several cations to approach a definite mole ratio, acid/cation, indicative of the ion formed (15). Both neodymium and lanthanum, as representative of the cerium group, were found to form a complex ion under optimum conditions involving two nitrilotriacetate groups as shown in Fig. 1. At lower pH values and concentrations, incomplete reaction led to a mixture of the mono- and di-acid complex ions. Under these conditions, neodymium tended to react more completely, indicative of complex ions of greater stability for the rare earth elements of higher atomic numbers.

In general, the reactions of the various iminodiacetic acids resembled those of nitrilotriacetic acid, indicating both a greater stability for the complexes of neodymium and the formation of a di-acid complex ion under optimum conditions. However, the iminodiacetic acids possessing the greater number of acid groups of possible use in complex formation were found to form ions of greater stability as suggested in Fig. 2. These titration curves were helpful in evaluating the probable elution characteristics of the various acids, indicating the extent of complex formation and the differences in behavior of the rare earths. For example, column experiments readily confirmed the advantages of using nitrilotriacetic acid (Fig. 1) as an eluting agent at low pH's.

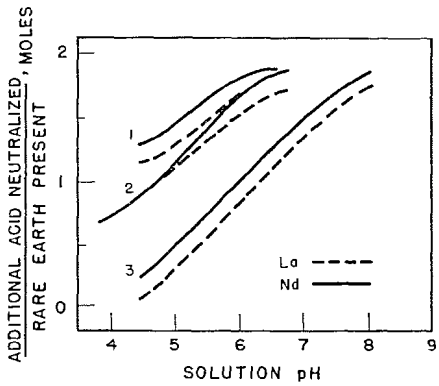

FIG. 2. *Acid neutralized per mole rare earth due to complex formation. Rare earth, 0.33 millimole; initial volume, 100 ml. 1.0 millimole acid: 1. o-Carboxy aniline-N-N-diacetic acid 2. Hydrazinodiacetic acid 3. Benzyl iminodiacetic acid.*

Elution Procedures

A column bed was prepared on a base of sand similar to those used with citric acid (5) and connected to the sampling apparatus as shown in Fig. 3. The resin was conditioned before use by treating it several times alternately with hydrochloric acid 1:3 and ammonium chloride 15%. A long illuminated tube fitted with a small spectroscope permitted the identification of the elements in the eluate by their characteristic absorption spectra as they were removed from the column.

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Continuous sampling during unattended operation was accomplished by allowing the eluate to overflow at different levels from the delivery tube into closed liter Erlenmeyer flasks with standing tubes to force delivery into the following receiver. The small losses of mixed eluate and the slight contamination from level adjustments were negligible compared to the total sample volumes. With small volumes of eluate, sampling was accomplished by an intermittent siphoning pipette with an extended delivery arm. An escape mechanism actuated by the weight of each sample caused the pipette to deliver into consecutive receivers.

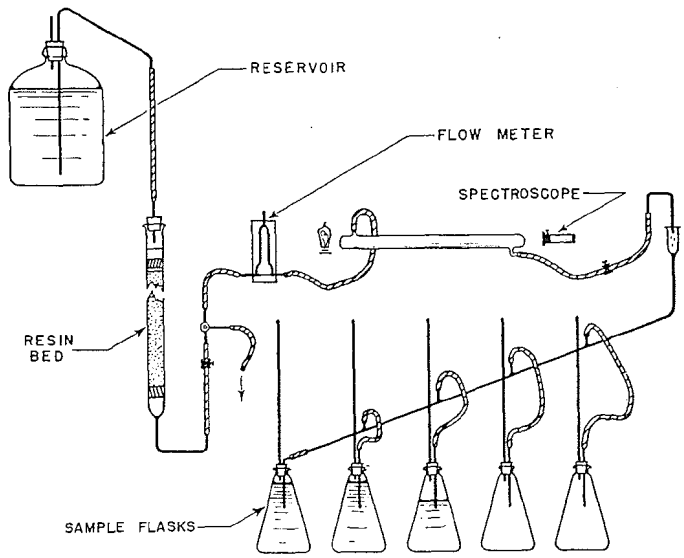

FIG. 3. *Apparatus for column separations.*

All of the various iminodiacetic acids were found to elute the rare earths from the resin bed with varying degrees of separation. The best results were obtained with complexing agents capable of forming complex ions of appreciably different strengths with the various earth elements and of a suitable stability to produce the desired exchange on passage through the column. Desirable elution characteristics and a convenient preparation in large quantities made nitrilotriacetic acid most suitable for general use and, thus, the following description is concerned mainly with this acid.

The rare earth was adsorbed on the resin (ammonium form) from a chloride solution of approximately pH 2. A nitrilotriacetic acid solution, partially neutralized with ammonium hydroxide, was passed slowly through the resin bed to elute the earth elements in order of decreasing atomic number. Allowance was made for the slower movement of the latter elements, as the elution progressed, by increasing the strength of the eluate, generally with the addition of ammonium acetate buffer. An initial treatment with eluate at low concentrations served both to remove the traces of the head elements and to band more clearly on the adsorbent the major constituents which then were removed

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with excellent separations at increased concentrations. Careful control of conditions in this manner resulted in a sharp separation, on the resin, of the last element in the sample, generally lanthanum, which was recovered rapidly with stripping solution, a buffered concentrated elutriant for the quick removal of cations.

In treating a sample from 25 gm. of crude didymium oxide, the rare earth was adsorbed from a liter of the chloride solution, pH 2, on amberlite I.R. 120 resin, to form the upper 32 cm. of a resin bed, 3.2 by 160 cm. After an additional water wash of several liters, a 0.5% nitrilotriacetic acid solution at pH 5.0 was passed through the column at a rate of approximately 40 to 50 ml. per sq. cm. per hr. to remove the traces of head elements and most of the samarium. Then the eluate was buffered with 0.25% ammonium acetate at the same pH to recover neodymium, praseodymium, and cerium consecutively at much higher concentrations. At this point lanthanum remained adsorbed on the resin bed, and prolonged elution was avoided by removing the lanthanum rapidly with a stripping solution of 1% nitrilotriacetic acid and 4% ammonium chloride at pH 7 to 8. In this way, the separation of this mixture was accomplished with only 40 to 50 liters of eluate, as shown in Fig. 4. The resin bed was treated with hydrochloric acid (1:3) and then 15% ammonium chloride solution before further use.

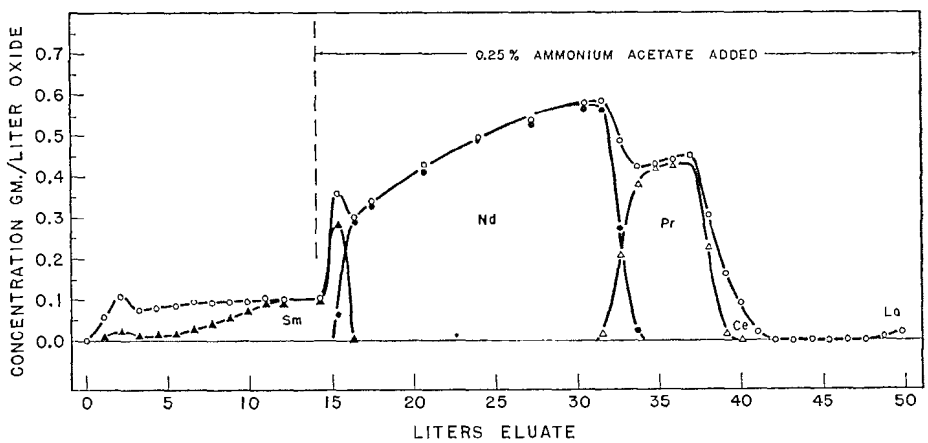

FIG. 4. *Elution curve of crude didymium with nitrilotriacetic acid.*

Although the small quantities of samarium and head elements were separated rather indifferently during the initial elution at low concentrations, the advantage of this treatment was demonstrated in the later separations of the major constituents. These elements overlapped to only a minor extent, with lanthanum actually remaining adsorbed on the resin bed during the passage of several liters of eluate. In the greater part of these elements collected, the amounts of impurities present were below detectable limits. Certain features of the elution curve reflected the operating technique, particularly the peak due to the rapid removal of samarium with the change in elution conditions.

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The scale of these procedures could readily be reduced with minor modifications in concentrations, flow rate, and pH. Columns 1 by 50 cm., separating 3 gm. didymium oxide gave elution concentrations of 3 mg. per ml. at a flow rate of 10 cm. per sq. cm. per hour. Long narrow resin beds, i.e., 0.6 by 70 cm., and smaller samples, 100 to 250 mgm., with unbuffered nitrilotriacetic acid solution were used to accentuate the separations sufficiently to produce a pronounced break in the elution between lanthanum and the group elements. With another acid, hydrazinodiacetic acid, this characteristic was pronounced enough to be of possible analytical use in the separation of lanthanum (4).

Discussion

More effective separations were obtained at pH values of nearly 5 with nitrilotriacetic acid, a range in which the titration curves had indicated an appreciable difference to exist between lanthanum and neodymium in the extent of complex formation. A decrease in pH occurred in the eluate on passage through the bed which appeared to be indicative largely of the resulting complex formation and movement of the earth. Under set operating conditions, only slight variations in output pH were noted between the various elements, of little help in controlling operations. Since these solutions have negligible buffering action in this range, the rate of elution appeared to be somewhat self-regulating with the extent of complex formation rather than the input pH being the controlling factor so that little difference was noted between pH 5 to 7. With ammonium acetate added as buffer, the rate of elution became more dependent upon the input pH, and the more uniform exchange conditions existing throughout the resin bed appeared to be an additional advantage. With this buffer a higher elution rate was found which was attributed largely to the increased ammonium ion concentration. Although difficult to assess, flow rate did not appear to be a critical factor in the ranges indicated.

The elements of higher atomic number were removed earlier and at higher concentrations from the resin bed. Elution of the earths began almost immediately and generally was continuous through the series, with eluate concentrations varying for individual quantities and relative sample size. Little cross-contamination occurred between the concentration bands and, thus, the quantities of preceding material influenced the point at which any element was eluted from the resin bed. A few cations were found to act as separating elements between these concentration bands but their use was not developed fully. Of most interest with nitrilotriacetic acid was the effect of cadmium in spreading the samarium and neodymium bands further apart.

The effect of the column dimensions was roughly the same as in the case of citric acid (19, 20). Little further separation was gained by increasing the length of a column beyond a definite limit, although with a fixed volume of resin the characteristics of the elution curves became more pronounced as the ratio of length to diameter was increased.

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Raising the elutriant above room temperature appeared to increase the exchange occurring in the resin bed, leading to a more definite banding of the elements and requiring greater eluate volumes. This effect was sufficiently marked at 50°C. to yield comparable results from resin beds, one third to one fifth the usual volume, in smaller volumes of more concentrated eluate.

Although not examined in detail, the column action showed appreciable deviation from the ideal picture of well defined concentration bands displaced in a regular manner through the adsorbent. Sectional analysis indicated a tendency to marked banding in a region of high concentration on the upper section of the column but with low diminishing concentrations extending downward through the greater part of the resin bed. The elution action appeared to combine this initial banding operation with the rapid washing of the most soluble ion through the remainder of the bed, limited exchange in this region leading to some further purification. As the bulk of the more soluble elements was removed some approach to a more normal banding and displacement action was indicated.

Acknowledgment

The authors wish to express their gratitude to Dr. R. N. Jones and Mr. D. S. Keir of the National Research Laboratories, for their aid in conducting the spectrophotometric analysis of the rare earths. The assistance of Mr. W. G. Humphreys in carrying out some of the operations is gratefully acknowledged.

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EXCHANGE REACTIONS OF ALICYCLIC IODIDES WITH SODIUM IODIDE[1]

By Sylvia F. Van Straten, R. V. V. Nicholls, and C. A. Winkler

Abstract

The activation energies for the exchange reactions between sodium iodide and cyclopentyl, cycloheptyl, cycloöctyl, cyclopentadecyl, and 2-heptyl iodides were all in the range 21 ± 1 kcal. per mole. For cyclohexyl iodide the value was 25.6 kcal. per mole. This difference seems to be explained from a consideration of the initial potential energies of the various rings. An inverse relation appears to exist between log PZ and $\frac{1}{N}$, the reciprocal of the number of carbon atoms in the iodides investigated, for all the iodides except cyclopentyl iodide. This might be due to a change in the number of equivalent constellations in the activated state.

Introduction

Several studies with substituted alicyclic compounds (4-6, 8-11), in particular those involving nucleophilic substitution reactions of alicyclic halides (2, 12), have demonstrated an apparently anomalous behavior of cyclohexyl derivatives. With a view to obtaining more information about such systems, the type of reaction involved has been made as simple as possible in the present investigation, by studying the exchange reaction between iodide ion and alicyclic iodides. The exchange of iodide ion with 2-heptyl iodide was also studied for purposes of comparison, since exchange occurs at a secondary carbon atom in this compound, as in alicyclic iodides.

Experimental and Results

Radioactive iodine, I^{131}, was obtained from the National Research Council, Atomic Energy Project, Chalk River, Ontario, as carrier-free sodium iodide.

Sodium iodide (Merck Reagent grade) dried for several days at 110°C. was used as diluent.

Absolute ethanol was used as solvent.

The alicyclic iodides were all prepared by treating the corresponding alcohol with 57% hydriodic acid.

Cyclopentanol, cyclohexanol, and 2-heptanol were obtained commercially (Eastman Kodak). Cycloheptanol was prepared by cyclizing suberic acid (City Chemical Company, New York) to cycloheptanone (13), followed by reduction of the ketone with aluminum isopropoxide and isopropyl alcohol. Cycloöctanol and cyclopentadecanol were also obtained in a similar manner by reduction of the corresponding ketones.*

[1] *Manuscript received in original form June 30, 1950, and, as revised, February 27, 1951. Contribution from the Chemistry Laboratories, McGill University, with financial assistance from the National Research Council of Canada.*

* *We are indebted to the University Chemical Laboratory, Cambridge, England, and to Firmenich and Company, Geneva, Switzerland, for gifts of the cycloöctanone and cyclopentadecanone ("exaltone") respectively.*

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The exchange reactions were followed by withdrawing samples from appropriate thermostats at suitable time intervals, and separating the organic and inorganic iodides by benzene–water extraction. Silver iodide was precipitated from each fraction by the addition of alcoholic silver nitrate. The precipitate was washed with methanol to remove benzene, heated on a steam bath with concentrated nitric acid until brown fumes appeared, washed again twice with water and twice with methanol, and slurried in dry methanol. A sample of the slurry, contained within a glass ring, was evaporated on a glass plate and the rate of exchange determined from the change in specific activity, using standard counting equipment.

Two series of experiments were made with each alicyclic iodide, except cycloöctyl iodide, which was available in amount sufficient only for one limited series of experiments. The order of the reaction was determined for each compound by varying the initial concentrations, and the activation energy determined for a range of temperature of 20°–30°C.

The reactions were all found to conform satisfactorily to second order behavior. There was some discrepancy, for which no satisfactory explanation can be given, between the values of the second order rate constants at a given temperature in the two series of reactions with a given organic iodide. However, the activation energies obtained for the two series agreed within 400 cal. per mole, except with cyclopentyl iodide where the two values differed by 800 cal. per mole. The activation energy lines for one series of experiments with each compound (except cycloöctyl iodide) are shown in Fig. 1.

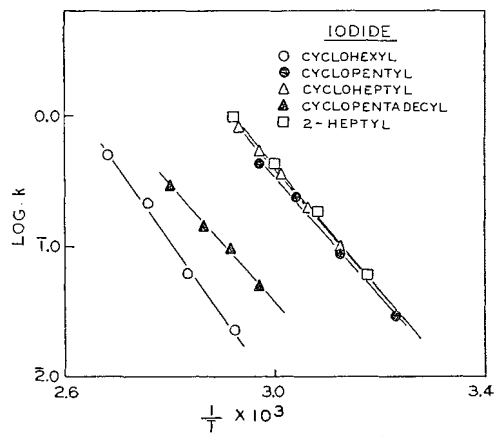

FIG. 1. *Typical Arrhenius lines.*

The data given in Tables I and II are typical of the results obtained in the study as a whole. For calculation of activation energies, the value of k used at each temperature was the average of the individual values, usually at least four, for different reaction times.

In Table III are summarized the results for the various reactions studied.

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TABLE I

THE EXCHANGE OF CYCLOHEXYL IODIDE WITH SODIUM IODIDE
Concentration: RI, 0.30 *M.*; NaI, 0.30 *M*

Temp., °C.	Reaction time, min.	% Exchange	k(cc.$-$mole$^{-1}-$sec.$^{-1}$) $\times 10^2$
69.0	198	7.3	0.023
	258	7.8	0.024
	318	11.9	0.024
	383	13.5	0.022
79.9	180	17.8	0.065
	181	17.1	0.062
	240	22.2	0.063
	300	25.2	0.060
	360	30.0	0.060
89.8	120	32.0	0.195
	150	40.2	0.208
	190	50.0	0.223
	240	58.2	0.222
100.0	30	24.5	0.576
	45	28.5	0.464
	60	43.0	0.577
	80	44.0	0.442

TABLE II

THE EXCHANGE OF CYCLOPENTYL IODIDE WITH SODIUM IODIDE IN ETHANOL SOLUTION

Temp., °C.	Reactant concentration (molarity)		Maximum exchange, %	k(cc.$-$mole$^{-1}-$sec.$^{-1}$) ($\times 10^2$)
	RI	NaI		
Series A				
36.6	0.30	0.30	16	3.0
47.0	0.30	0.30	31	9.0
56.0	0.30	0.30	25	23.3
	0.20	0.40	37	24.4
64.0	0.45	0.15	26	47.2
	0.30	0.30	56	42.0
	0.15	0.45	43	42.5
	0.50	0.10	51	44.2
Series B				
36.6	0.30	0.30	19	3.3
50.7	0.30	0.30	37	14.1
56.0	0.30	0.30	36	26.9
64.0	0.30	0.30	70	55.6

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TABLE III

SUMMARY OF RESULTS FOR THE EXCHANGE REACTIONS BETWEEN ALICYCLIC IODIDES AND SODIUM IODIDE IN ETHANOL SOLUTION

Alicyclic iodide	k(at 25°C) $\times 10^2$ cc.$-$mole^{-1} $-$sec.$^{-1}$*	E** kcal/mole	log PZ**
Cyclopentyl iodide	0.88	21.0	13.4
Cyclohexyl iodide	0.0084	25.6	14.7
Cycloheptyl iodide	1.2	21.3	13.7
Cyclooctyl iodide	0.28	22.0	13.6
Cyclopentadecyl iodide	0.099	20.1	11.8
2-Heptyl iodide	0.77	21.8	13.9

* *Calculated from* $k = PZ\, e^{-E/RT}$, *using the values recorded for* E *and* log PZ.

** *Each value recorded is the average of the two values obtained for series A and series B experiments (except for cycloöctyl iodide, where only one limited series of experiments was possible). The probable error in the average values is approximately 3%.*

Discussion

The apparently anomalous behavior of a cyclohexyl derivative, referred to previously, appears to be confirmed in the present study. The considerably lower rate of exchange of cyclohexyl iodide is here accompanied by energy of activation and entropy of activation (log PZ) terms which differ considerably from those for the other compounds investigated.

There seems no good reason to believe that the carbon–iodine bond strength in cyclohexyl iodide is substantially greater than in the other alicyclic iodides. Presumably, then, the higher activation energy for the cyclohexyl iodide exchange is associated with the process of rendering coplanar the atoms at the site of reaction, prior to exchange and subsequent inversion. If it is assumed that the height of the energy barrier to be surmounted during exchange remains unaltered from member to member in the series, the greater activation energy may be attributed to the lower potential energy of the cyclohexyl ring initially (1, 7). The present results indicate that the extent of this stabilization of the cyclohexyl ring is about 4 kcal.

The larger entropy term for the cyclohexyl iodide exchange, compared with the values of log PZ for the other exchange reactions, is probably not anomalous. This is indicated by a plot of log PZ against the reciprocal of the number of carbon atoms in the organic iodide undergoing reaction, as in Fig 2. The figure includes results for the analogous exchange reaction with amyl iodide in ethanol (3). In the figure, a straight line has been drawn through the points but it is probable that the range of values involved represents the mid-portion of a sigmoid relation which rises rapidly as $\frac{1}{N}$ approaches zero and drops rapidly to a constant value of about 16 for small values of $\frac{1}{N}$ (3). Greater accuracy than that attained in the present work would be necessary to define the exact form of the relation.

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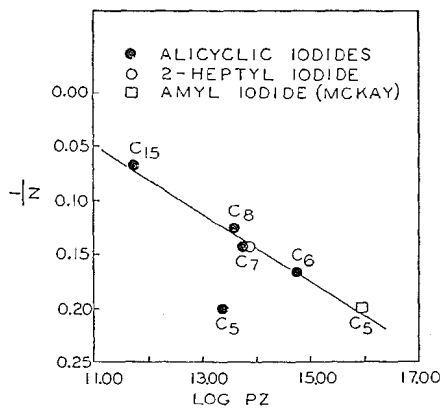

FIG. 2. *Inverse relation between number of carbon atoms and log PZ.*

The inverse relation between log PZ and the number of carbon atoms in the organic iodide may be accounted for if the entropy change associated with activation reflects a change in the number of equivalent constellations (1, 7), and this change has proportionately less effect as the number of possible equivalent constellations increases with increased ring size. The failure of cyclopentyl iodide to conform to the relation in Fig. 2 might be expected, since the cyclopentyl ring is approximately planar in the initial state (Fisher–Hirschfelder model) and relatively little change in it should occur as the atoms at the site of reaction are rendered coplanar during activation prior to exchange.

Acknowledgment

Grateful acknowledgment is made to the Committee on Research, McGill University, for financial assistance in the preparation of this manuscript.

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STUDIES OF RDX AND RELATED COMPOUNDS

III. THE REACTION TO FORM RDX FROM AMMONIUM NITRATE AND FORMALDEHYDE IN ACETIC ANHYDRIDE[1]

By A. Gillies, H. L. Williams, and C. A. Winkler

Abstract

This reaction at 35°C. exhibits a behavior indicative of the presence of an intermediate in the reaction. Reaction of paraformaldehyde and ammonium nitrate in glacial acetic acid resulted in the isolation of hexamine dinitrate. Evidence is presented to indicate that formation of hexamine dinitrate, accompanied by the production of nitric acid, is responsible for the production of RDX in the acetic anhydride system.

Introduction

Kinetic studies of the direct nitrolysis of hexamine with concentrated nitric acids to produce *cyclo*-trimethylenetrinitramine (RDX) have been reported in previous papers from this laboratory (6, 8). The present paper gives some of the results obtained by investigation of an alternative method of preparation involving the interaction of ammonium nitrate and paraformaldehyde in acetic anhydride (4, 7).

Experimental

The procedure, usually, was to place the desired amounts of ammonium nitrate and paraformaldehyde (expressed as moles of formaldehyde) in 125 ml. Erlenmeyer flasks, which were suspended in a thermostat from a shaker oscillating at about 140 cycles per minute. The temperature of the water bath was controlled to within $\pm$ 0.1°C. Acetic anhydride was then added, the time of its addition being taken as zero time for the reaction. The reaction was stopped, after the desired time interval, by the addition of about 20 ml. of water, the flask removed from the thermostat, and the mixture boiled for 15–20 min. After cooling, the flask was filled with water and allowed to stand, usually overnight. Precipitated RDX was collected in a sintered glass crucible, washed with water, dried in an air oven at 90°C. for two to three hours and weighed. In general, the weight of crude RDX was considered to be the yield and was calculated as per cent of the theoretical on a formaldehyde basis.

Results and Discussion

Presence of an Intermediate in the Reaction

RDX was produced only after an induction period, the length of which varied from two to six hours depending on the source of paraformaldehyde, when 0.02 mole paraformaldehyde, 0.04 mole ammonium nitrate, and 5 cc. acetic anhy-

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, with financial assistance from the National Research Council of Canada.

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dride were allowed to react at 35°C. The presence of acetic or trichloracetic acid reduced the induction period somewhat, but neither acid had any appreciable effect on the rate of reaction following the induction period. It appeared from these results that an intermediate was formed during the reaction, the rate of its formation, but not the rate of its conversion to RDX, being influenced by the presence of acetic or trichloracetic acid.

A series of experiments was made in which the various reactants were individually withheld from reaction mixtures at 35°C. for a period equal to the induction period (3.5 hr.), followed by addition of the missing component and further reaction for 3.5 hr. No RDX was produced, hence no intermediate was formed, unless all three reactants were present.

The relative amounts of intermediate present at various times were determined as follows. Seven reaction mixtures, containing 13% acetic acid, were allowed to react for different times, after which they were filtered and six aliquots of each filtrate taken. The RDX content of one of these was determined by immediate dilution, that of the others after further periods of reaction at 35°C. The amounts of intermediate present at various times, expressed in terms of the amount of RDX it was capable of producing, are shown in Fig. 1. The top curve, for example, indicates the amount of intermediate present at the time of filtering, when filtration was made two to six hours after the experiment was started. The second curve from the top gives the amount of intermediate present one half hour after filtration when filtration was made at the same time intervals after start of the experiment; and similarly

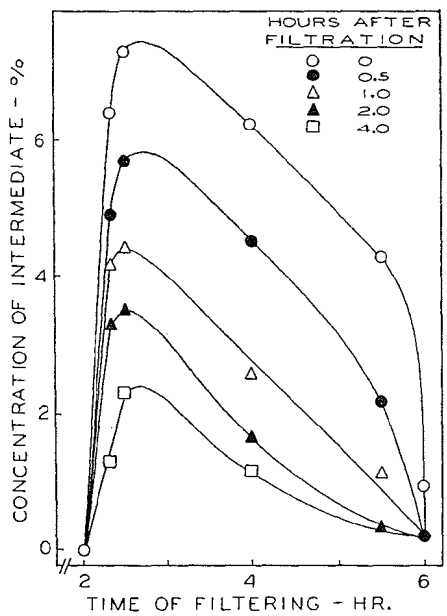

FIG. 1. *Relative amounts of intermediate present at various times.*

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for the other curves. The results show that negligible amounts of intermediate were formed during the first two hours, while the maximum amount was present about 2.5 hr. after the start of the reaction. The RDX yield reached its maximum value at about six hours, after which time the amount of intermediate present was negligible.

The activation energy for conversion of the intermediate to RDX was determined by allowing paraformaldehyde and ammonium nitrate to react to the end of the induction period (2.5 hr.) at 35°C. in 7.5 cc. acetic anhydride containing 13% acetic acid, after which the mixtures were filtered and the filtrates allowed to react further at 25°, 30°, 35°, and 40°C. From initial rates, an activation energy of roughly 18.5 kcal. was obtained.

Using the halochromic compounds of Conant and Hall (3), it was possible to estimate, despite rapid fading of the indicators, that the pH (HAc) of a normal reaction mixture started at about zero but changed to a value of about − 3 as reaction progressed. Comparison with a pH (HAc) value of − 3.2 determined for sulphuric acid (one drop) in acetic acid (5 cc.) containing acetic anhydride gave clear indication that a strong acid, as well as the intermediate discussed above, was formed during reaction.

When paraformaldehyde (0.02 mole) and ammonium nitrate (0.04 mole) were allowed to react in glacial acetic acid (6 cc.) for 11 hr. at 35°C., followed by addition of acetic anhydride (6 cc.) and further reaction for one hour, production of RDX occurred without an induction period following the addition of anhydride. It appeared from this that the intermediate had been formed by reaction of paraformaldehyde and ammonium nitrate in acetic acid. The rate of conversion to RDX of intermediate so formed was increased by the addition of a few drops of sulphuric or perchloric acid, while the yield of RDX obtained was adversely affected by the presence of formaldehyde in excess of a mole ratio of approximately 1.5:1 with ammonium nitrate.

The activation energy for the formation of RDX subsequent to the addition of anhydride to a glacial acetic acid preparation of the intermediate was found to be about 19.5 kcal. Comparison of this value with that recorded previously for conversion, also in acetic acid – acetic anhydride media, of the intermediate present in the filtrates from reaction mixtures suggests that the same substance is involved in the two cases.

When paraformaldehyde and ammonium nitrate reacted at 35°C. in glacial acetic acid, it was observed that the mixture gradually cleared as the paraformaldehyde reacted, until at the end of 2.5 hr. only excess ammonium nitrate remained. An hour later there appeared a dense white precipitate. The excess ammonium nitrate was removed by further reaction with a slight excess of paraformaldehyde, the precipitate filtered off, washed with glacial acetic acid and acetone, and dried in a vacuum desiccator. Elemental analysis gave*: C, 27.4, 27.5; H, 5.3, 5.4; N, 30.7, 30.8%. For hexamine dinitrate, C, 27.1;

*We are indebted to Dr. G. F Wright, University of Toronto, for the analyses.

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H, 5.3; N, 31.6%. The precipitate gave an X-ray powder photograph which showed only the characteristic pattern for hexamine dinitrate. The formation of hexamine by reaction of formaldehyde and ammonia in acidic media has been reported previously by Baur and Ruetschi (2).

Isolation of hexamine dinitrate from the paraformaldehyde – ammonium nitrate reaction in glacial acetic acid, and comparison of the behavior of this system in the presence of acetic anhydride with the characteristics of the reaction to produce RDX from paraformaldehyde, ammonium nitrate, and acetic anhydride, give strong indication that hexamine dinitrate is the intermediate formed during the latter reaction. On this basis, the observed deleterious effect of excess paraformaldehyde on RDX yield may be readily explained, since hexamine is decomposed by formaldehyde in glacial acetic acid at a rate which increases with increased mole ratio of formaldehyde to hexamine (5).

Nitric acid is undoubtedly the strong acid revealed by the Conant – Hall indicators to be formed in the paraformaldehyde – ammonium nitrate – acetic anhydride reaction mixtures. Formation of nitric acid simultaneously with hexamine dinitrate in the reaction mixtures must be assumed to account for the nitrolysis reaction to produce RDX, unless the presence of another intermediate capable of promoting nitrolysis can be demonstrated. Rather exhaustive examination of the system failed to indicate any such alternative agent for nitrolysis.

While one of the functions of acetic anhydride is almost certainly to remove water formed during the initial production of hexamine and nitric acid, and thus maintain the nitric acid concentration at a high level favorable for nitrolysis (7), it seems likely that it also has the role of a "fast" solvent for the reaction. This was revealed by studies in which 6 cc. of various solvents were added to 3 cc. of filtrate obtained from the reaction of ammonium nitrate and paraformaldehyde in acetic acid. The solvent – filtrate mixture was allowed to react with 3 cc. acetic anhydride for 30 min. at 35°C., after which 0.5 gm. hexamine dinitrate was added. The rates of production of RDX, determined in the usual manner, were in the following order for the solvents listed: acetic anhydride $\gg$ propionic anhydride $>$ nitromethane $>$ acetic acid $>$ acetonitrile $>$ benzene $>$ propionic acid $\gg$ dioxane.

Since the present studies gave strong indication that the paraformaldehyde – ammonium nitrate – acetic anhydride reaction to produce RDX consists essentially of the production of hexamine followed by its nitrolysis, investigation of this system was abandoned in favor of studies on the Bachmann reaction (1) in which hexamine and nitric acid are among the starting materials. The results of several studies with the Bachmann system will be reported in subsequent papers.

Acknowledgment

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PREPARATION AND NITRATION OF 1-SUBSTITUTED-2-NITRAMINO-2-IMIDAZOLINES[1]

By A. F. McKay, J. R. G. Bryce, and D. E. Rivington[2]

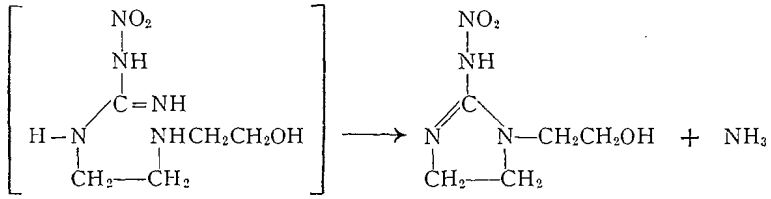
Abstract

A series of 1-substituted-2-nitramino-2-imidazolines have been prepared and nitrated in mixed-acid and nitric acid – acetic anhydride media. These compounds gave the corresponding 1-substituted-2-nitrimino-3-nitroimidazolidines which proved to be quite stable. The hydrolysis products of some of these compounds are described.

The nitration studies (5, 8) on 2-nitramino-2-imidazoline have been extended to 1-substituted-2-nitramino-2-imidazolines. The latter compounds on nitration give a new series of compounds, viz., 1-substituted-2-nitrimino-3-nitroimidazolidines.

The compounds employed in the present investigation were prepared by the addition of 1-amino-3-azabutane, 1-amino-3-azapentane, 1-amino-5-hydroxy-3-azapentane, 1, 5-diamino-3-azapentane, and 1, 8-diamino-3, 6-diazaoctane respectively to N-methyl-N-nitroso-N′-nitroguanidine (4, 6, 7). In all cases, cyclizations occurred to give 1-substituted-2-nitramino-2-imidazolines. The reaction of 1-amino-5-hydroxy-3-azapentane with methylnitroso-nitroguanidine may be represented as follows:

$$HOCH_2CH_2NHCH_2CH_2NH_2 + CH_3N(NO)C(NH)NHNO_2 \longrightarrow$$

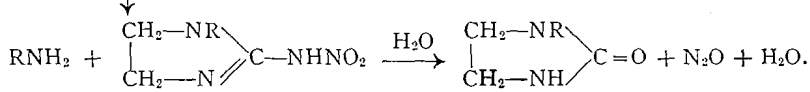


A similar cyclization reaction (B) involving a secondary amino group also explains the formation of 1-aryl-2-imidazolidones (II) from 1-β-arylamino-ethyl-2-aryl-3-nitroguanidines (I) on alkaline hydrolysis (9).

$$RNHCH_2CH_2NHC(NR)NHNO_2 + H_2O \xrightarrow{A} RNHCH_2CH_2NHC(O)NHR$$

I

B



II

R = phenyl, ρ-tolyl, ρ-anisyl or ρ-phenetyl

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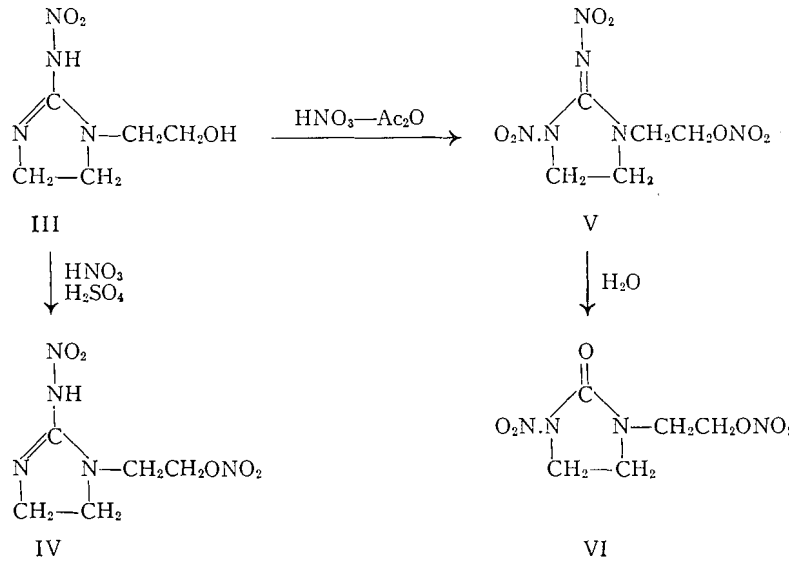
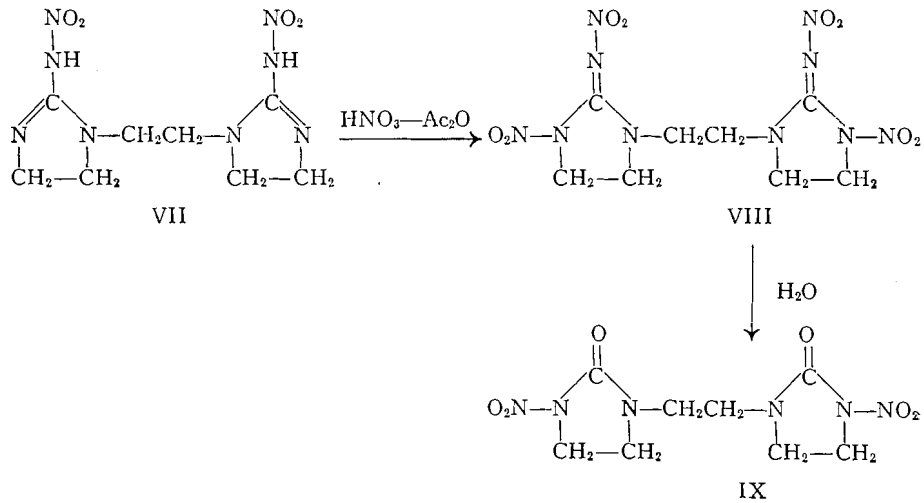
1-β-Hydroxyethyl-2-nitramino-2-imidazoline (III) on treatment with mixed-acid gave 1-β-nitroxyethyl-2-nitramino-2-imidazoline. On the other hand, nitration in acetic anhydride – nitric acid medium gave a 94% yield



of 1-β-nitroxyethyl-2-nitrimino-3-nitroimidazolidine (V). The structure of the latter compound (V) was confirmed by analysis and its hydrolysis in water to 1-β-nitroxyethyl-3-nitro-2-imidazolidone (VI).

Nitration of *bis*-1-(2-nitramino-2-imidazolinyl) ethane (VII) in nitric acid—acetic anhydride medium gave *bis*-1-(2-nitrimino-3-nitroimidazolidinyl) ethane (VIII) in 84–96% yield. This compound (VIII) on boiling with water hydrolyzed to *bis*-1-(3-nitro-2-imidazolidonyl) ethane (IX).



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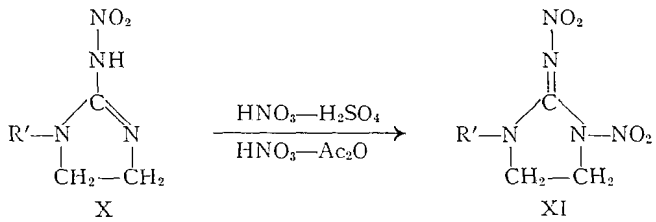
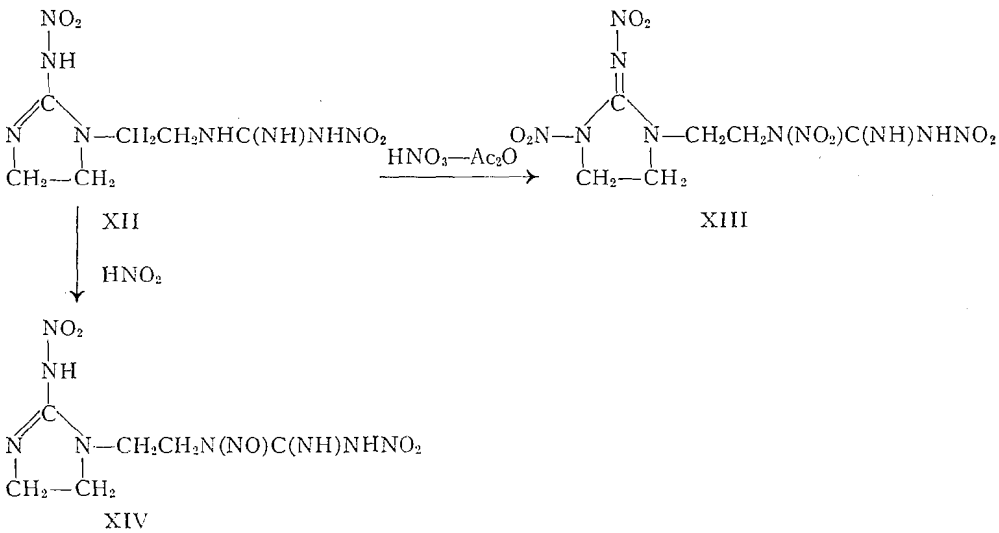
1-Methyl-(X, R′ = Me) and 1-ethyl-2-nitramino-2-imidazoline (X, R′ = Et) behaved differently from the above compounds in that both mixed-acid and nitric acid – acetic anhydride media gave the corresponding 1-alkyl-2-nitrimino-3-nitroimidazolidines (XI).



X XI

R′ = methyl or ethyl

1-β-Nitroguanylaminoethyl-2-nitramino-2-imidazoline (XII) on treatment with absolute nitric acid – acetic anhydride yields besides 1-(N-nitroguanyl-N-nitro-β-aminoethyl)-2-nitrimino-3-nitroimidazolidine (XIII) another compound as yet unidentified. This is the second example in which an additional nitro group has been introduced into a linear substituted nitroguanidine structure. The first one to be described (6) was N-β-nitroxyethyl-N-nitro-N′-nitroguanidine. On nitrosation, 1-β-nitroguanylaminoethyl-2-nitramino-2-imidazoline (XII) yields 1-(N-nitroguanyl-N-nitroso-β-aminoethyl)-2-nitramino-2-imidazoline (XIV). The position of the nitroso group was verified by treating with benzylamine when a 75% yield of benzylnitroguanidine was obtained. If the nitroso group had been present on the ring nitrogen, more highly substituted nitroguanidines would have been obtained (9).



XIV

All the above 1-substituted-2-nitramino-2-imidazolines give stable nitrimine compounds. When there is no substituent present in position 1, the 2-nitramino-2-imidazolines on nitration with excess nitric acid in the presence of

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acetic anhydride are converted into the corresponding 1, 3-dinitro-2-imidazolidones (5, 8), the nitramino group of position 2 being eliminated as N_2O.

The Franchimont test (2) for nitramines has proved very useful in the study of the derivatives of nitroguanidine. Some of these compounds and the color developed with dimethylaniline and diethylaniline are listed in Table I.

TABLE I

Franchimont nitramine test

Compound	Diethyl aniline	Dimethyl aniline
Methylnitroguanidine (6)	Light green	Negative
Allylnitroguanidine (3)	"	"
Cyclohexylnitroguanidine (3)	"	"
p-Tolylnitroguanidine (3)	Negative	Pink
m-Tolylnitroguanidine (3)	"	"
o-Tolylnitroguanidine (3)	Green	"
2, 4-Dimethylphenylnitroguanidine (3)	Green	"
p-tert. Amylphenylnitroguanidine (3)	Negative	Pink
dl-α-Phenylethylnitroguanidine (3)	Green	Negative
Phenylnitroguanidine (3)	Negative	Pink
1-β-Nitroxyethyl-2-nitrimino-3-nitroimidazolidine	Deep green	Deep green
1-Methyl-2-nitrimino-3-nitroimidazolidine	Green (fades)	Pink
1-Ethyl-2-nitrimino-3-nitroimidazolidine	"	"
1-Methyl-2-nitramino-2-imidazoline	Pink	"
1-Ethyl-2-nitramino-2-imidazoline	"	"
1-β-Hydroxyethyl-2-nitramino-2-imidazoline	"	"
1-*p*-Anisyl-2-nitramino-2-imidazoline (9)	"	"
1, 3-Dinitro-4-methyl-2-hexahydropyrimidone (4)	Deep green	Deep green
2, 6-Dinitro-2, 6-diazacycloheptanone-1 (7)	"	"
2-Nitramino-5-nitroxy-2-tetrahydropyrimidine (4)	"	"

These data show the differences to be expected with the two reagents. A summary of the behavior of several types of nitramines in the Franchimont test, which is based on the observations employing more than 60 compounds, is presented in Table II. The procedure used in these tests, along with further observations, is described in an earlier paper (3).

TABLE II

Franchimont color test

Class of compounds	Dimethyl aniline	Diethyl aniline
1. N-alkyl-N′-nitroguanidines	Negative	Pale green
2. N-Aralkyl-N′-nitroguanidines	Negative	Pale green
3. N-Aryl-N′-nitroguanidines	Pink	Negative or pale green
4. 2-Nitramino-2-imidazolines[1]	Pink	Pink
5. 1, 3-Dinitro-1, 3-diaza-2-cycloalkanones	Deep green	Deep green
6. 1-Nitro-2-amino-2-imidazolines	"	"

[1]*Nitroxy derivatives, e.g., 1-β-nitroxyethyl-2-nitramino-2-imidazoline, give deep green colors with both dimethyl and diethylaniline.*

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Experimental*

N-Methyl- and N-Ethylethylenediamine

N-Methyl- and N-ethylethylenediamine were prepared by the method of Aspinall (1) in 10 and 20% yields respectively.

1-*Methyl*-2-*nitramino*-2-*imidazoline*

Eleven and one-half grams (0.156 mole) of N-methylethylenediamine was added to a suspension of 23.2 gm. (0.157 mole) of methylnitrosonitroguanidine in 45 cc. of water. The temperature of the reaction mixture was maintained at 22–25°C. during the addition of the amine, which required 20 min. The clear solution was boiled for seven minutes and then placed in an evaporating dish. After most of the water had evaporated, a pale yellow oil remained. This oil yielded white flat needlelike crystals on standing overnight in the refrigerator. These crystals were filtered from the oil and washed with water. An equal volume of water was added to the oily filtrate and the solution was boiled for five minutes. An additional 1.1 gm. of product was obtained by repeating the above procedure. The total yield of product melting at 110–113°C. was 8.2 gm. (36.2%). One crystallization from absolute ethanol (2.42 cc. per gm.) raised the melting point to 115–116°C. Calc. for $C_4H_8N_4O_2$: C, 33.32; H, 5.52; N, 38.9%. Found: C, 33.26; H, 5.64; N, 38.30%.

1-*Ethyl*-2-*nitramino*-2-*imidazoline*

When 11.3 gm. (0.068 mole) of methylnitrosonitroguanidine was treated with 5.7 gm. (0.065 mole) of N-ethylethylenediamine under the conditions described above, 4.2 gm. (40.8% of theory) of crude product was obtained. The melting point of the product was raised from 78–83°C. to 86.5°C. by one crystallization from absolute ethanol (1.9 cc. per gm.). Calc. for $C_5H_{10}N_4O_2$: C, 37.95; H, 6.32; N, 35.4%. Found: C, 38.15; H, 6.18; N, 35.12%.

1-*β-Hydroxyethyl*-2-*nitramino*-2-*imidazoline*

1-Amino-5-hydroxy-3-azapentane (18.7 gm.; 0.18 mole) was added portionwise with stirring to a suspension of 25 gm. (0.17 mole) of N-methyl-N-nitroso-N′-nitroguanidine in 50 cc. of water. During the addition of the amine, which required 35 min. the temperature was held at 20–22°C. The clear solution was then evaporated on a hot-plate to one-half its original volume and placed in the refrigerator overnight. The crystals were removed by filtration and washed with 95% ethanol. On evaporation of the filtrate to 1/3 its original volume and cooling, a second crop of crystals was obtained. The total yield of product (m.p. 129–131.5°C.) was 12.6 gm. (42%). After crystallization from 95% ethanol, the melting point was 131.5–132°C. Calc. for $C_5H_{10}N_4O_3$: C, 34.5; H, 5.75; N, 32.15%. Found: C, 34.6; H, 5.57; N, 32.02%.

**All melting points are uncorrected.*

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1-β-Nitroguanylaminoethyl-2-nitramino-2-imidazoline

1, 5-Diamino-3-azapentane added to two mole equivalents of methylnitrosonitroguanidine under the conditions described above for 1-β-hydroxyethyl-2-nitramino-2-imidazoline gave a 45% yield of 1-β-nitroguanylaminoethyl-2-nitramino-2-imidazoline (m.p. 195–197°C. with decomposition). One crystallization from water (30 cc. per gm.) gave crystals melting at 197°C. with decomposition. Calc. for $C_6H_{12}N_8O_4$: C, 27.69; H, 4.61; N, 43.09%. Found: C, 27.69; H, 4.81; N, 43.06%.

Bis-1-(2-nitramino-2-imidazolinyl) ethane

The reaction of 1, 8-diamino-3, 6-diazaöctane with 2 mole equivalents of methylnitrosonitroguanidine as described above gave a 43.4% yield of *bis*-1-(2-nitramino-2-imidazolinyl) ethane melting at 300–301°C. with decomposition. Calc. for $C_8H_{14}N_8O_4$: C, 33.6; H, 4.90; N, 39.1%. Found: C, 33.6; H, 5.06; N, 38.7%.

1-β-Nitroxyethyl-2-nitramino-2-imidazoline

1-β-Hydroxyethyl-2-nitramino-2-imidazoline (930 mgm.; 0.0053 mole) was added to a solution of 2.1 cc. (0.06 mole) of absolute nitric acid in 3.2 cc. (0.06 mole) of sulphuric acid (sp. gr. 1.84) at −5°C. The reaction mixture was stirred at this temperature for 20 min. after which the clear solution was poured onto ice. A crystalline product separated which was filtered off and washed with water. It melted at 110–115°C., yield 855 mgm. (73.8%). One crystallization from methanol (11.8 cc. per gm.) raised the melting point to 114.8–115.2°C. Calc. for $C_5H_9N_5O_5$: C, 27.4; H, 4.11; N, 31.95%. Found: C, 27.8; H, 4.17; N, 31.92%.

1-β-Nitroxyethyl-2-nitrimino-3-nitroimidazolidine

A solution of 9.24 cc. (0.22 mole) of absolute nitric acid in 20.6 cc. (0.22 mole) of acetic anhydride was prepared at 0°C. To this solution 3.88 gm. (0.022 mole) of 1-β-hydroxyethyl-2-nitramino-2-imidazoline was added portionwise over a period of five minutes. The temperature of the reaction mixture was maintained at 34°C. for a period of 25 min. and then the contents of the flask was poured onto ice (50 gm.), the crystals recovered by filtration and washed with water. The product melted at 114.5–115.5°C. with decomposition, yield 5.55 gm. (94.2%). One crystallization from methanol (61.9 cc. per gm.) raised the melting point to 115–116°C. with decomposition. Calc. for $C_5H_8N_6O_7$: C, 22.71; H, 3.04; N, 31.8%. Found: C, 22.85; H, 3.16; N, 31.3%.

1-β-Nitroxyethyl-2-nitrimino-3-nitroimidazolidine combined violently with phenylhydrazine giving a partially charred mass. The reaction in methanol gave first a deep green color similar to the Franchimont nitramine test (2) with dimethylaniline and then gas was evolved and the solution turned red. All attempts to obtain a crystalline product were unsuccessful.

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1-β-Nitroxyethyl-3-nitro-2-imidazolidone

One gram (0.0038 mole) of 1-β-nitroxyethyl-2-nitrimino-3-nitroimidazolidine in 20 cc. of water was refluxed for one and a half hours. On cooling to room temperature, a crystalline solid separated. These crystals (m.p. 101–102°C.) were filtered off and washed with water, yield 485 mgm. (58.3%). The melting point remained unchanged after one crystallization from water (34 cc. per gm.). Calc. for $C_5H_8N_4O_6$: C, 27.26; H, 3.64; N, 25.40%. Found: C, 27.60; H, 3.65; N, 25.30%.

Bis-1-(2-nitrimino-3-nitroimidazolidinyl) ethane

Nitration of *bis*-1-(2-nitramino-2-imidazolinyl) ethane under the conditions described above for the preparation of 1-β-nitroxyethyl-2-nitrimino-3-nitroimidazolidine with the exception that the reaction temperature was maintained at 50–56°C. gave a 96% yield of *bis*-1-(2-nitrimino-3-nitroimidazolidinyl) ethane (m.p. 177–178°C. with decomposition). This product was insoluble in all organic solvents and water. On solution in hot 70% nitric acid and dilution with water no water insoluble material separated. Another run was carried out at 40°C. in the presence of 1/20 mole equivalent of zinc chloride. Under the latter conditions an 84% yield of the nitrimino compound was obtained melting at 180–181°C. with decomposition. Calc. for $C_8H_{12}N_{10}O_8$: C, 25.55; H, 3.19; N, 37.24%. Found: C, 25.85; H, 3.26; N, 37.0%.

Bis-1-(3-nitro-2-imidazolidonyl) ethane

Bis-1-(2-nitrimino-3-nitroimidazolidinyl) ethane (990 mgm.; 0.0026 mole) in 40 cc. of water was refluxed for three hours. After cooling to room temperature the crystals were filtered off and washed with water. The product melted at 242–243°C. with decomposition. Since this compound was practically insoluble in all solvents tried, it was analyzed without further purification. Calc. for $C_8H_{12}N_6O_6$: C, 33.33; H, 4.17; N, 29.15%. Found: C, 33.31; H, 4.19; N, 29.03%.

1-Methyl-2-nitramino-3-nitroimidazolidine

A. *Acetic Anhydride - Nitric Acid Nitration*

The nitrating solution was prepared by adding 6.0 gm. (0.143 mole) of absolute nitric acid to 13.3 cc. (0.143 mole) of acetic anhydride at 0°C. Two grams (0.014 mole) of 1-methyl-2-nitramino-2-imidazoline was added over a period of five minutes. Then the temperature of the stirred reaction mixture was raised to 32°C. and maintained at this level for 25 min. The reaction mixture was poured onto ice and the white solid removed by filtration and washed with water, yield 2.16 gm. (91% of theory). The melting point of 167–168°C. with decomposition was raised to 169–170°C. with decomposition after one crystallization from absolute methanol (270 cc. per gm.). Calc. for $C_4H_7N_5O_4$: C, 25.38; H, 3.70; N, 37.0%. Found: C, 25.27; H, 4.01; N, 36.75%.

B. *Mixed-acid Nitration*

A solution of 5.5 cc. (0.16 mole) of absolute nitric acid in 8.4 cc. (0.16 mole) of sulphuric acid (sp. gr. 1.84) was cooled to −5°C. and 2.0 gm. (0.014 mole) of 1-methyl-2-nitramino-2-imidazoline was added within five minutes. The reaction mixture was stirred at −5°C. for 20 min. and then poured onto ice. The white solid was removed by filtration and washed with water, yield 0.46 gm. (17.5% of theory). After crystallizing from methanol the melting point was raised from 165–168°C. to 169–170°C., with decomposition. This product did not depress the melting point of 1-methyl-2-nitrimino-3-nitroimidazolidine (m.p. 169–170°C. with dec.) prepared from the nitric acid – acetic anhydride nitration of 1-methyl-2-nitramino-2-imidazoline.

1-*Ethyl-2-nitrimino-3-nitroimidazolidine*

1-Ethyl-2-nitramino-2-imidazoline (1 gm.; 0.0064 mole) was nitrated under the conditions described in method A above for the preparation of 1-methyl-2-nitrimino-3-nitroimidazolidine. The yield was 1.1 gm. or 86% of theory. The crude product melted at 136–137°C. with decomposition. This melting point was raised to 137–138°C. with decomposition by one crystallization from absolute methanol (121 cc. per gm.). Calc. for $C_5H_9N_5O_4$: C, 29.55; H, 4.43; N, 34.5%. Found: C, 29.71; H, 4.68; N, 34.0%.

Mixed-acid nitration of 1-ethyl-2-nitramino-2-imidazoline as above gave a 28% yield of 1-ethyl-2-nitrimino-3-nitroimidazolidine melting at 137–138°C. with decomposition alone and on admixture with an authentic sample of 1-ethyl-2-nitrimino-3-nitroimidazolidine.

1-(*N-nitroguanyl-N-nitro-β-aminoethyl*)-2-*nitrimino-3-nitroimidazolidine*

To a solution of 16.1 cc. (0.384 mole) of absolute nitric acid in 36.1 cc. (0.384 mole) of acetic anhydride was added 10.0 gm. (0.0384 mole) of 1-β-nitroguanylaminoethyl-2-nitramino-2-imidazoline over a period of six minutes. During the addition period the temperature rose from 0 to 26.8°C. and a colorless gas was evolved. This mixture was allowed to come to room temperature, after which it was poured onto 100 gm. of ice. The solid was recovered by filtration, washed with water and air dried, yield 7.9 gm. The melting point of 134–139°C. with decomposition of the crude product was raised to constant value of 161–162°C. with decomposition by one crystallization from absolute methanol (100 cc. per gm.), yield 2.09 gm. (16.0%). Calc. for $C_6H_{10}N_{10}O_8$: C, 20.58; H, 2.85; N, 40.00%. Found: C, 20.30; H, 3.00; N, 39.52%.

On evaporation of the filtrate from the above crystallization a second compound (1.24 gm.) was obtained which melted at 180.5–181.5°C. with decomposition. The latter compound has not been identified at present.

1-(*N-Nitroguanyl-N-nitroso-β-aminoethyl*)-2-*nitramino-2-imidazoline*

1-β-Nitroguanylaminoethyl-2-nitramino-2-imidazoline (2.5 gm.; 0.0096 mole) was dissolved in 15 cc. of nitric acid (sp. gr. 1.42) and 15 cc. of water added.

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The clear solution was maintained at 8–10°C., while 1.75 gm. (0.026 mole) of sodium nitrite in 10 cc. of water was added over a period of 10 min. Then the solution was stirred while the temperature was allowed to rise to 18°C. and a yellow crystalline precipitate formed. The yellow nitrosamine was washed with water and methanol (20 cc.) after filtration. It melted at 176°C. with decomposition, yield 1.54 gm. (55.6%). Calc. for $C_6H_{11}N_9O_5$: C, 25.29; H, 3.82; N, 42.85%. Found: C, 25.21; H, 3.72; N, 42.88%.

A sample of 1-(N-nitroguanyl-N-nitroso-β-aminoethyl)-2-nitramino-2-imidazoline on treatment with benzylamine under the conditions employed with the nitrosamines of this series (4, 6) gave a 75% yield of benzylnitroguanidine (m.p. 182–183°C.).

Acknowledgment

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PREPARATION OF SUBSTITUTED NITROGUANIDINES AND THE CYCLIZATION OF N-γ-NITROXYBUTYL-N′-NITROGUANIDINE[1]

By A. F. McKay and H. P. Thomas

Abstract

Several new substituted nitroguanidines were prepared by the reaction of amines with N-methyl-N-nitroso-N′-nitroguanidine. N-γ-Nitroxybutyl-N′-nitroguanidine was cyclized to 1-nitro-2-amino-6-methyl-Δ^2-tetrahydropyrimidinium nitrate by refluxing in water.

A further series of nitroguanidine derivatives have been prepared by the reaction of primary amines with N-methyl-N-nitroso-N′-nitroguanidine (3, 6). These are listed in Table I.

The compounds possessing structure I were insoluble in the common organic solvents and water. They did not nitrosate under the usual conditions (3, 5, 6). Generally these compounds were recovered unchanged from the nitrosating medium on dilution with water.

$$O_2NNHC(NH)NH(CH_2)_nNHC(NH)NHNO_2 \qquad I$$

$$n = 2 - 4$$

The diaminotoluenes combined with only one equivalent of N-methyl-N-nitroso-N′-nitroguanidine to give N-aminomethylphenyl-N′-nitroguanidines. This would be expected from the previous observation that the rate of reaction in aqueous ethanol is directly proportional to the K_b of the amine (3). The second amino group would have a much lower basicity constant and a much lower rate of reaction. This posed the problem of determining the position of the amino group involved in the above reaction.

The observation was made previously (8) that N-*o*-methylphenyl-N′-nitroguanidine as well as other phenyl nitroguanidine derivatives having a methyl group ortho to the attachment of the nitroguanyl group gave a green color in the Franchimont test (1) using diethylaniline. The nitroguanyl derivatives of 2,4-diaminotoluene and 2,5-diaminotoluene gave no green color, so it was assumed that the positions of the nitroguanyl group were 4 and 5 respectively. This was confirmed experimentally by diazotization of the free amino group of the 2,4-diaminotoluene derivative (II). The diazonium chloride (III) was converted to the salt of 1, 5-naphthalene disulphonic acid by the method of Hodgson and Marsden (2). Then the crystalline double salt was suspended in ethanol and zinc dust added. At the end of the reaction a 10% yield of N-*p*-methylphenyl-N′-nitroguanidine (IV) was

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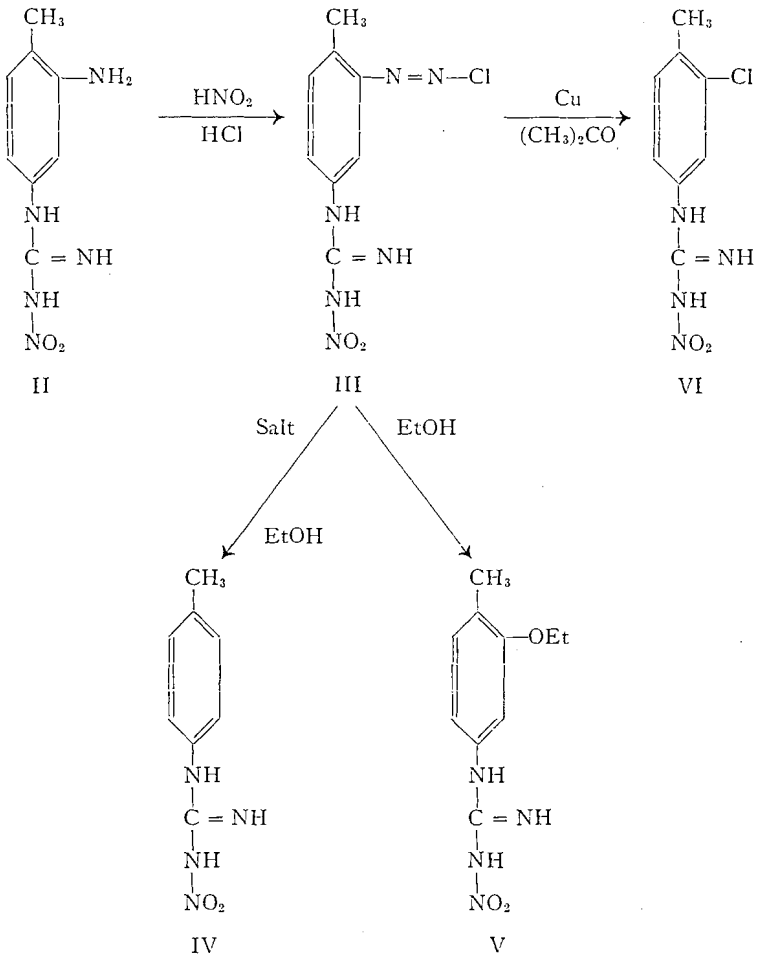
TABLE I

SUBSTITUTED NITROGUANIDINES

Compound	M.p., °C.(a)	Yield, %	Analyses, %					
			Calc. C	Found C	Calc. H	Found H	Calc. N	Found N
N-*p*-Hydroxyphenyl-N′-nitroguanidine	236	90.0	42.8	43.02	4.08	4.19	28.58	28.61
N-*m*-Hydroxyphenyl-N′-nitroguanidine	177–178	66.5	42.8	43.09	4.08	4.00	28.58	28.10
N-*p*-Diethylaminophenyl-N′-nitroguanidine	196	79.7	52.6	52.57	6.77	6.59	27.90	28.21
N-4-Amino-3-methylphenyl-N′-nitroguanidine	201–202	83.0	45.8	46.03	5.30	5.35	33.45	33.12
N-3-Amino-4-methylphenyl-N′-nitroguanidine	178–179.5	81.2	45.8	45.92	5.30	5.33	33.45	33.55
1, 2-Di-(nitroguanylamino) ethane*	248–248.5	75.3	20.5	20.76	4.27	4.38	47.83	47.36
1, 3-Di-(nitroguanylamino)propane*	234–235	77.5	24.2	23.90	4.84	5.08	45.14	44.80
1, 3-Di-(nitroguanylamino)butane*	230	16.0	27.47	27.40	5.38	5.57	42.75	42.65
1, 4-Di-(nitroguanylamino)butane**	>265	25.0	27.47	27.44	5.38	5.80	—	—

a. All compounds melted with decomposition.
* *Prepared by D. E. Rivington, Queen's University, Kingston, Ontario.*
** *This compound was obtained as a by-product in the preparation of 2-nitramino-1, 3-diazacycloheptene-2* (4).

obtained. This verified the above conclusion that the compound derived from the reaction of 2,4-diaminotoluene with N-methyl-N-nitroso-N′-nitroguanidine was N-3-amino-4-methylphenyl-N′-nitroguanidine (II). It was concluded also that with 2,5-diaminotoluene, the 5-amino group was the one involved in the reaction with methylnitrosonitroguanidine.



During the investigation of methods for removal of the free amino group in N-3-amino-4-methylphenyl-N′-nitroguanidine (II) the diazonium chloride (III) was heated with ethanol and with copper in acetone. In the former case N-3-ethoxy-4-methylphenyl-N′-nitroguanidine (V) was obtained. In the latter case with copper in acetone a normal Gattermann reaction occurred yielding the corresponding N-3-chloro-4-methylphenyl-N′-nitroguanidine (VI).

It was demonstrated recently (5) that certain N-β-substituted ethyl-N′-nitroguanidines cyclized on heating to give heterocyclics having two ring nitrogens. Therefore we were interested in extending these observations to

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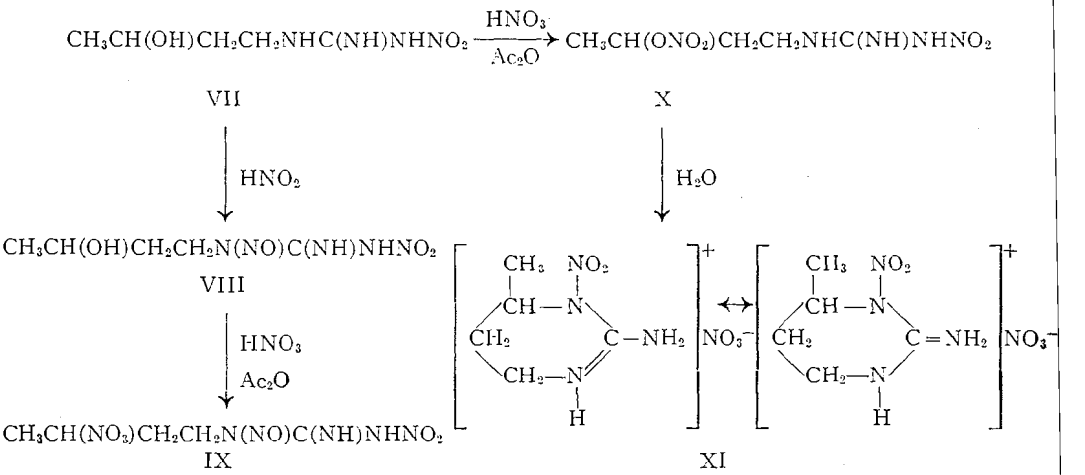
include the N-γ-substituted propyl-N′-nitroguanidines. The starting material, N-γ-hydroxybutyl-N′-nitroguanidine (VII), was obtained as an oil by adding N-methyl-N-nitroso-N′-nitroguanidine to an aqueous solution of 1-amino-3-hydroxybutane. The oily product was characterized by converting



it to N-γ-hydroxybutyl-N-nitroso-N′-nitroguanidine (VIII) for analyses. This latter product on nitration in absolute nitric acid – acetic anhydride medium gave N-γ-nitroxybutyl-N-nitroso-N′-nitroguanidine (IX). After characterization, the original oil (VII) was nitrated in nitric acid – acetic anhydride medium to yield N-γ-nitroxybutyl-N′-nitroguanidine (X). On refluxing this compound (X) in water it cyclized to 1-nitro-2-amino-6-methyl-Δ^2-tetrahydropyrimidinium nitrate (XI) in 72% yield. The cyclized product (XI) gave a positive test (10) for nitrate ion with Nitron and a crystalline picrate. Thus the rearrangement discovered (5) with N-β-substituted ethyl-N′-nitroguanidine also occurs with N-γ-nitroxybutyl-N′nitroguanidine (X).

Experimental*

Substituted Nitroguanidines

The substituted nitroguanidines described in this paper were prepared by adding 3 mole equivalents of the amine to 1 mole equivalent of N-methyl-N-nitroso-N′-nitroguanidine in 50% aqueous ethanol as previously described (3). These compounds are tabulated in Table I.

1, 2-Di-(nitroguanylamino)ethane and Homologues

1, 2-Di-(nitroguanylamino)ethane and homologues were prepared by adding 1 mole equivalent of amine to 2 mole equivalents of N-methyl-N-nitroso-N′-nitroguanidine in methanol as described above. The products were insoluble in all common solvents and were purified by extraction with 95% ethanol or water. The final products are described in Table I.

**All melting points are uncorrected.*

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1, 4-*Di-(nitroguanylamino)butane*

When 2-nitramino-1, 3-diazacycloheptene-2 was prepared by the method of McKay and Wright (7) from 0.038 mole of nitroguanidine and 0.04 mole of 1, 4-diaminobutane dihydrochloride, 4 gm. of a crude product melting at 200–201°C. with decomposition was obtained. This product has now been separated into two constituents by extraction with 200 cc. of acetone. The acetone extract contained 1.8 gm. (29.6%) of 2-nitramino-1, 3-diazacycloheptene-2 (m.p. 219–220°C. with decomposition). The acetone insoluble portion (1.5 gm.; 25%) did not melt below 265°C.; instead, it charred. It proved to be the linear 1, 4-di-(nitroguanylamino)butane (cf. Table I).

Deamination of N-3-Amino-4-methylphenyl-N′-nitroguanidine

The diazonium chloride of 4.0 gm. (0.02 mole) of N-3-amino-4-methylphenyl-N′-nitroguanidine was prepared by the method of Wallingford and Krueger (9), omitting the sodium hydroxide treatment. It was then converted to the 1, 5-naphthalene disulphonic-acid salt by the method of Hodgson and Marsden (2). The crystalline salt (6.9 gm.) was added to 50 cc. of ethanol and stirred mechanically at room temperature while 1.3 gm. of zinc dust was added portionwise. The stirring was continued for 11 hr., after which the precipitate was removed by filtration and the filtrate evaporated to 5 cc. A gummy product (0.67 gm.) was obtained which melted at 157°C. after one crystallization from ethanol, yield 0.26 gm. (10%). After several crystallizations from ethanol the product melted at 164°C. and it did not depress the melting point of an authentic sample of N-*p*-methylphenyl-N′-nitroguanidine (m.p. 165–166°C.).

N-3-Ethoxy-4-methylphenyl-N′-nitroguanidine

A sample of N-3-diazonium chloride-4-methylphenyl-N′-nitroguanidine prepared from 2 gm. (0.01 mole) of N-3-amino-4-methylphenyl-N′-nitroguanidine as described above was stirred with 100 cc. of ethanol at 45°C. for two hours. The solution was concentrated to a volume of 50 cc. and the precipitate removed by filtration. This precipitate was washed with ether, leaving a residue of 0.6 gm. (25%) which melted at 170–180°C. Two crystallizations from ethanol raised the melting point of the N-3-ethoxy-4-methylphenyl-N′-nitroguanidine to 185. 5–186°C. Calc. for $C_{10}H_{14}N_4O_3$: C, 50.50; H, 5.92; N, 23.52%. Found: C, 50.55; H, 6.14; N, 23.71%.

N-3-Chloro-4-methylphenyl-N′-nitroguanidine

N-3-Diazonium chloride-4-methylphenyl-N′-nitroguanidine, prepared by the above procedure from 2 gm. (0.01 mole) of N-3-amino-4-methylphenyl-N′-nitroguanidine, was added to 50 cc. of acetone. A half gram of copper precipitated from copper sulphate solution with zinc was added and the suspension stirred for seven hours at room temperature. The insoluble portion was filtered off and washed with ether. This precipitate was refluxed with 50 cc. of ethanol and the copper removed by filtration. On evaporation of the

ethanol solution 0.7 gm. (32%) of N-3-chloro-4-methylphenyl-N′-nitroguanidine (m.p. 167–169°C.) was obtained. The melting point was raised to 170.5–172°C. after three crystallizations from ethanol. Calc. for $C_8H_9ClN_4O_2$: C, 42.03; H, 3.97; N, 24.52%. Found: C, 41.90; H, 4.40; N, 24.84%.

N-γ-Hydroxybutyl-N′-nitroguanidine

1-Amino-3-hydroxybutane (8.9 gm.; 0.1 mole) was dissolved in 50 cc. of water and 7.0 gm. (0.05 mole) of N-methyl-N-nitroso-N′-nitroguanidine was added portionwise while the temperature was held at 15–20°C. After gassing had ceased, the solution was evaporated to dryness, leaving 19.2 gm. of oil which still contained some water. A portion of the oil was nitrosated in the usual manner (3, 5, 6) to give a 50% yield of yellow crystalline nitroso compound melting at 99.5–100°C. with decomposition. Calc. for $C_5H_{11}N_5O_4$: C, 29.3; H, 5.33; N, 34.2%. Found: C, 29.01, H, 5.14; N, 33.92%.

In order to further identify this product, N-γ-hydroxybutyl-N-nitroso-N′-nitroguanidine (0.47 gm.; 0.003 mole) was nitrated as previously described (8) with nitric acid – acetic anhydride solution to give 0.4 gm. (70%) of N-γ-nitroxybutyl-N-nitroso-N′-nitroguanidine (m.p. 86–87°C. with decomposition). Three crystallizations from ethanol raised the melting point to 88–89°C. with decomposition. Calc. for $C_5H_{10}N_6O_6$: C, 24.00; H, 4.05; N, 33.55%. Found: C, 24.01; H, 4.14; N, 33.13%.

N-γ-Nitroxybutyl-N′-nitroguanidine

The oily N-γ-hydroxybutyl-N′-nitroguanidine (9.2 gm.) was nitrated with 10 mole equivalents of nitric acid in acetic anhydride at 5–10°C. for 45 min., and the product recovered in the usual manner (8). A yield of 51% based on the original N-methyl-N-nitroso-N′-nitroguanidine used in the preparation of N-γ-hydroxybutyl-N′-nitroguanidine was obtained. The actual yield from the nitration would be higher than this. The melting point of 123.5–126°C. of the crude was raised to 125–126°C. by crystallizing from water. Calc. for $C_5H_{11}N_5O_5$: C, 27.37; H, 5.01; N, 31.75%. Found: C, 27.38; H, 5.40; N, 31.66%.

1-*Nitro*-2-*amino*-6-*methyl*-Δ^2-*tetrahydropyrimidinium nitrate*

One gram (0.045 mole) of N-γ-nitroxybutyl-N′nitroguanidine was refluxed in water for one-half hour. The solution was evaporated to 1 cc. and 10 cc. of absolute ethanol was added. This procedure gave 0.72 gm. (72%) of product which gave a positive secondary nitramine test (1) and a positive test for nitrate ion using Nitron (10). The product melted at 115°C. Calc. for $C_5H_{11}N_5O_5$: C, 27.37; H, 5.01; N, 31.75%. Found: C, 27.04; H, 4.81; N, 31.05%.

A 0.35 gm. (0.0015 mole) sample of the cyclized product was dissolved in 2 cc. of water and a saturated aqueous picric acid solution added. A yellow crystalline picrate (0.6 gm.; 87%) separated immediately. The crude picrate melted at 166–173°C. This melting point was raised to 175–176°C. by two crystallizations from water. Calc. for $C_{11}H_{13}N_7O_9$: C, 34.01; H, 3.36; N, 25.35%. Found: C, 33.80; H, 3.18; N, 25.22%.

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THE ULTRAVIOLET ABSORPTION SPECTRA OF SEVERAL DEHYDRATION AND OXIDATION DERIVATIVES OF CHOLESTEROL[1]

By R. H. Cox[2, 3] and E. Y. Spencer

Abstract

Certain dehydration and oxidation products of cholesterol were prepared for subsequent animal experimentation. The ultraviolet absorption spectra of those derivatives possessing two or more conjugate chromophores were determined spectrophotometrically over the wave length range of 220 mμ to 350 mμ. The relative coincidence of the experimental λ_{max} and ϵ_{max} values of cholestadiene-3, 5 and of the enol acetate of cholesten-4-one-3 is offered as support for a 3, 5-diene structure for the latter steroid in particular and for enol esters of 4,5-unsaturated 3-ketosteroids in general.

Introduction

The ultraviolet absorption spectra of certain dehydration and oxidation derivatives of cholesterol were determined in preparation for fractionation studies on the heated egg yolk and heated cholesterol diets used by Altschul (1) to produce experimental arteriosclerosis and also sclerosis of muscle and nerve fiber in the rabbit. A particular attempt was made to locate maxima and minima in regions of low absorption which might aid in the positive identification of derivatives of cholesterol which might be formed during the heating of the experimental diets. The reliability of Beer's law in the ultraviolet was also investigated in connection with possible quantitative studies. The results of animal experimentation with several of the steroids considered in this investigation have been reported elsewhere (2, 6).

Experimental

Cholesterilene (Cholestadiene-3, 5) and Dicholesteryl Ether

Cholesterol was dehydrated by heating with an equal weight of anhydrous copper sulphate, according to the method of Mauthner and Suida (15), to give the intramolecular dehydration product, cholesterilene (cholestadiene-3, 5) in 66% yield. Repeated recrystallization of the crude material from absolute ethanol yielded colorless needles, m.p. 79–80° C., $[\alpha]_D$ − 89.7°, ϵ_{max} = 18.450 at 235 mμ. Two repetitions of this dehydration procedure resulted in yields of cholesterilene equivalent to 62% and 68% of the theoretical. The rest of the starting material was converted in every case to the intramolecular dehydration product, dicholesteryl ether. Purification of the ether by recrystallization from benzene–ethanol gave a colorless product melting from 196° to 199°C. $[\alpha]_D$ − 39.0°.

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[1] *Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.*

[2] *Present address: Faculty of Pharmacy, University of British Columbia, Vancouver, B.C.*

[3] *This work was done during the tenure of a Life Insurance Medical Research Fund Student Fellowship.*

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Cholesterol was also dehydrated using an equal weight of potassium hydrogen sulphate, as suggested by Montignie (18), and gave approximately the same ratio of cholesterilene to dicholesteryl ether as that obtained in the copper sulphate dehydration. However, when the weight of potassium hydrogen sulphate was five times that of cholesterol, the ratio of cholesterilene to dicholesteryl ether was reversed, which confirmed the earlier findings (18).

Cholesteryl Acetate

Cholesteryl acetate was prepared in quantitative yield by treating cholesterol with excess acetic anhydride under reflux. The ester, after repeated recrystallization from absolute ethanol, was obtained as crystalline needles, m.p. 115–116°C., $[\alpha]_D$ − 43.8°.

7-Ketocholesteryl Acetate

7-Ketocholesteryl acetate was prepared by chromic acid oxidation of cholesteryl acetate in acetic acid solution at 55°C., according to the procedure of Windaus, Lettre and Schenck (26). The faintly greenish oxidation product, melting from 154° to 156°C., was obtained in a yield of 28% of the theoretical. Several recrystallizations from ethanol – diethyl ether gave long, colorless needles melting at 158–159°C., $[\alpha]_D$ − 103.2°. A further small amount of crude product was obtained by extracting the mother liquor with diethyl ether after the addition of sodium chloride solution. Additional oxidation runs carried out as before gave yields of purified 7-ketocholesteryl acetate ranging from 25% to 32% of the theoretical.

Subsequently, it was found that lowering the reaction temperature from 55°C. to 40°C., together with reducing by 50% the quantity of distilled water employed in the original procedure to dissolve the oxidizing agent, raised the yield of 7-ketocholesteryl acetate to 35–40%, an increase of roughly 10% over that reported by Windaus *et al.* This compares with a yield of 33% recently reported by Fieser *et al.* (10) using a strictly anhydrous medium.

7-Ketocholesterol

7-Ketocholesterol acetate was saponified at room temperature by suspension in 80% methanol containing a slight excess of potassium carbonate for a period of five to six days. The crude 7-ketocholesterol, obtained in approximately quantitative yield, was recrystallized several times from diethyl ether–ethanol and was obtained as colorless needles melting at 169–170°C., $[\alpha]_D$ − 103.8°. ϵ_{max} = 14.450 at 236 mμ.

When saponification was carried out more rapidly by refluxing for several hours in 80% methanol containing a slight excess of either potassium carbonate or potassium hydroxide, lower yields of a crude, somewhat brownish product were obtained. Purification of this crude saponification product proved difficult and resulted in a further appreciable loss of material. The smaller yields

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of a more crude 7-ketocholesterol obtained when more drastic conditions were employed is attributed to the general sensitivity to alkali of an α, β-unsaturated carbonyl system.

7-Ketocholesterilene (7-Ketocholestadiene-3, 5)

7-Ketocholesterilene was prepared from 7-ketocholesteryl acetate according to the method of Stavely and Bergmann (24) in 95% yield. Three recrystallizations of the reaction product from absolute ethanol gave needles melting at 111–112°C., $[\alpha]_D$ − 314°, ϵ_{max} = 23,300 at 278 mμ.

Epimeric 7-Hydroxycholesterols

7-Ketocholesterol was reduced according to the general method of Meerwein and Schmidt (16) using isopropanol as hydrogen donor and aluminum isopropylate as catalyst. The crude, crystalline reduction product, recovered in 65% of the theoretical yield, melted gradually from 130° to 150°C., a melting point range in agreement with that cited by Buser (5), and gave the expected Lifschutz (14) color reaction. No attempt was made to resolve the crude mixture of α and β epimers. Subsequent ultraviolet absorption studies on this product revealed a small selective absorption in the region of 235 mμ, indicating the presence of some unreduced 7-ketocholesterol. Similar incomplete reduction was subsequently observed by Spencer and Lambert (22) with the Meerwein procedure, but these workers eventually obtained almost quantitative conversion to the diol by employing a lithium aluminum hydride reduction procedure. These observations are in agreement with the recent work of Fieser *et al.* (10), who employed the latter reduction procedure but isolated the reaction product as the dibenzoate.

Cholestenone (Cholesten-4-one-3)

The general method of Oppenauer (19) was followed, but the more readily prepared aluminum isopropylate was substituted for aluminum tertiary butylate as catalyst for the reaction. The yield of almost colorless cholestenone, m.p. 77–79°C., was 76% of the theoretical. Repeated recrystallization from ethanol–diethyl ether gave material melting at 80-81°C., $[\alpha]_D$ + 88.0°, ϵ_{max} = 15,725 at 240 mμ.

In subsequent oxidations, additional modifications were introduced into the original Oppenauer procedure; in particular, these changes were designed to avoid the troublesome emulsions often encountered in the washing of the benzene extracts and to eliminate the time-consuming problem of bringing about crystallization of the oxidation product. After the oxidation step had been carried out according to the original instructions, the procedure was modified as follows.

Distilled water (slightly more than 3 moles per mole of catalyst) was added to the still warm contents of the reaction vessel to bring about hydrolysis of the aluminum alkoxide catalyst, and stirring was continued for an additional

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30 min. The aluminum hydroxide gel so formed was removed from the cold reaction mixture by centrifuging, and the solution of sterol obtained by decantation was concentrated under vacuum (20 mm.) to a yellowish oil. This residue was dissolved in diethyl ether and the ethereal solution was washed with 10% sulphuric acid to remove remaining traces of aluminum hydroxide and then with distilled water until the washings were neutral to litmus. The ethereal solution was then dried over anhydrous sodium sulphate and concentrated under a stream of dry air; gentle rubbing of the oil precipitate of cholestenone as it formed brought about immediate crystallization. When practically all of the diethyl ether had been removed by evaporation, ethanol was added and the mixture was refrigerated for several hours. The almost colorless precipitate was collected by suction filtration and washed thoroughly with ice-cold ethanol to remove residual mesityl oxide. The product was then dried under vacuum to remove final traces of mesityl oxide and was recrystallized as before.

Cholestenone Enol Acetate

Cholestenone was treated with excess acetyl chloride under reflux for 10 hr. The temperature of reflux assisted in the rapid elimination of hydrogen chloride formed in the reaction and hence prevented the transformation of the enol ester into an enol chloride (20). The brownish needles which precipitated when the reaction solution was cooled were washed with cold ethanol and recrystallized several times from ethanol–diethyl ether to give long, colorless needles melting at 80-81°C., $[\alpha]_D -$ 92.0, ϵ_{max} = 19,600 at 235 mμ.

Melting Points

All melting points reported have been corrected against reliable standards.

Optical Rotation Measurements

All specific rotatory values cited for the above cholesterol derivatives were determined at room temperature, which varied from 20°C. to 25°C., with the Rudolph No. 127 precision polarimeter, using a macro-tube 2 dm. in length. Chloroform, purified by refluxing with and distilling from anhydrous calcium chloride, was used as the solvent. The concentrations of the steroids under investigation varied, but were usually of the order of 1–2%. For the sodium "D" line, the wave length used for all rotation measurements, monochromator and slit width settings gave an isolated band width of 9.5 mμ.

Ultraviolet Spectrophotometry

Spectral determinations were made over a wave length range of 220 mμ to 350 mμ with the Beckman DU quartz spectrophotometer. Density readings were never further apart than 4 mμ, while in regions where the optical density was changing rapidly the interval was reduced to 2 mμ, and in the immediate neighborhood of maxima and minima to 1 mμ. The absorption cells were of silica, each having a thickness of 1.001 cm. In every case, concentrations of

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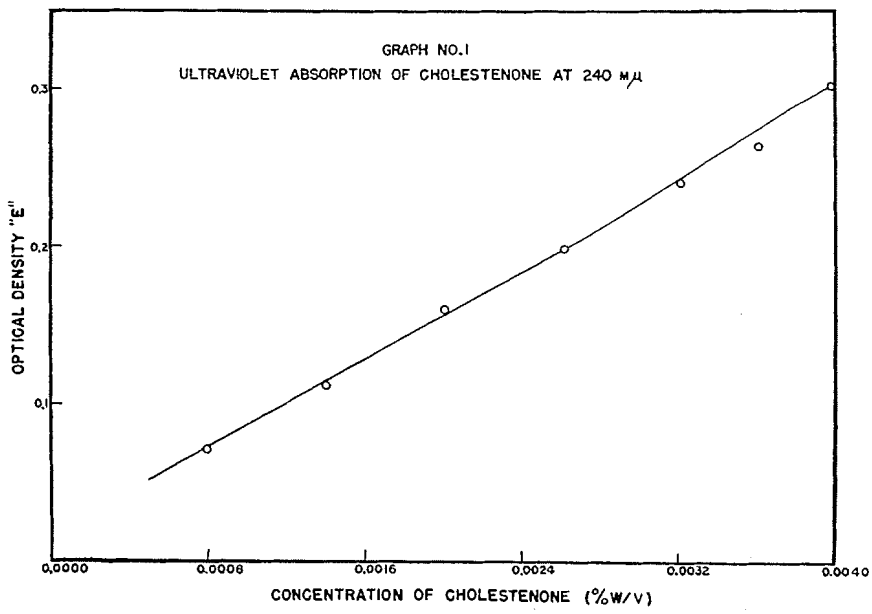
0.1%, 0.01%, and 0.001% of each compound were employed; the stronger concentrations were examined in regions of lower absorption in an attempt to find weak maxima and minima not discernible when concentrations low enough to permit total determination of the curve were used.

A commercial grade of absolute ethanol was found by spectral tests to be satisfactory as a solvent without special purification. In some cases it was necessary, because of the limited solubility in ethanol, to dissolve the sample in a small amount of diethyl ether and then dilute the ether solution to the desired volume with ethanol. The final concentration of ether was never greater than 2% and was of the order of 0.02% in the weakest (0.001%) steroid solutions. In all cases, the reference liquid used as a blank in the spectrophotometer was identical with the solvent of the solution under test, each component being taken from the same batch.

Ultraviolet Absorption Results and Discussion

Validity of Beer's Law

It now appears generally accepted that Beer's law always holds for dilute solutions and that the deviations sometimes encountered are due to a change in the absorbing species with concentration. Graph No. 1 shows that Beer's law is obeyed within the limits of experimental error with ethanolic solutions of cholestenone over the approximate concentration range of 0.001% to 0.005%. (Absorption values were measured at the λ_{max} 240 mμ). However, when the steroid concentration was increased by a further factor of 20 (i.e., to 0.1%), the absorption increased by only a fraction of this factor. This "falling-off" of the ϵ_{max} value which accompanies an increase in concentration was addition-



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ally noted during spectral curve determinations, when concentrations of 0.001%, 0.01%, and 0.1% were employed with each steroid investigated. It was also noted that the extrapolated curve failed to pass through the origin.

Spectral Absorption Measurements

Experimental values of molecular extinction coefficients reported for all maxima and minima have been calculated from spectral absorption curves determined for the steroids under investigation. Where the order of magnitude was large ($\epsilon > 1000$), calculations were based upon absorption curves determined using concentrations of 0.001% steroid; on the other hand, where $\epsilon < 1000$, calculations were made from absorption values for solutions of 0.1% concentration. Although this policy introduces the variation of ϵ_{max} with concentration change seen experimentally, no adjustment for concentration effect was attempted because of the lesser importance, in a quantitative sense, of maxima and minima in regions of low absorption. The spectral band widths reported for individual maxima and minima were calculated from the observed slit-width and the calibration chart accompanying the spectrophotometer.

For comparison purposes, λ_{max} and ϵ_{max} values for the steroids under investigation have also been cited from the literature.

α, β-Unsaturated Ketones

It was early noted (3, 17) that α, β-unsaturated ketones have characteristic spectra. An isolated carbonyl group gives a low intensity band (ϵ = 10–100) near 275 mμ, while an ethylenic group gives a high intensity band ($\epsilon = 10^4$) near 195 mμ. When these two groups are conjugated, producing an α, β-unsaturated carbonyl compound, the two bands, referred to as K and R bands following Burawoy's (4) terminology, occur at longer wave lengths.

Band	Wave length	Intensity
K band	220-260 mμ	10^4
R band	310-330 mμ	10^2

Since the R band is of such low intensity, most attention is focused on the K band.

Cholestenone (Cholesten-4-one-3)

	Experimental values		Spectral band width (mμ)	Literature values		Ref.
	λ_{max} (mμ)	ϵ_{max}		λ_{max} (mμ)	ϵ_{max}	
Maximum	240	15,725	2.1	242	16,300	(13)
Plateau	312	120	2.9	312	76	(13)
				285	55	(13)

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Cholestenone, having an α, β-unsaturated ketonic grouping in ring A was found to have a λ_{max} at 240 mμ (K band) and a plateau on the absorption curve at 312 mμ (suggestive of the R band). Good agreement is seen with available literature values.

7-Ketocholesterol

	Experimental values		Spectral band width (mμ)	Literature values		Ref.
	λ_{max} (mμ)	ϵ_{max}		λ_{max} (mμ)	ϵ_{max}	
Maxima	236	14,450	2.0	238	12,500	(27)
	329	50	3.3			
Minimum	284	20	2.4			

7-Ketocholesterol, having an α, β-unsaturated ketonic grouping in ring B, showed a strong selective absorption maximum at 236 mμ (K band) and a weak absorption maximum at 329 mμ (possibly the R band), the latter previously unreported. Fair agreement is seen between the values of λ_{max} and ϵ_{max} determined in this investigation for the K band, and those previously reported.

α, β: γ, δ-Diunsaturated Ketones

Acyclic triply conjugated systems involving two ethylenic and one ether group usually absorb maximally between 240 and 265 mμ, λ_{max} being little affected by the arrangement of the chromophores. The absorption of triple isocyclic systems is similar to that of the corresponding acyclic systems, with bands situated at somewhat higher wave lengths (about 20 mμ) than in analogous acyclic compounds, provided that all three chromophores are not in the same ring (9). Examples of three conjugated isocyclic chromophores are almost wholly confined to the steroid series.

7-Ketocholesterilene (7-Ketocholestadiene-3, 5)

	Experimental values		Spectral band width (mμ)	Literature values		Ref.
	λ_{max} (mμ)	ϵ_{max}		λ_{max} (mμ)	ϵ_{max}	
Maximum	278	23,300	2.2	280	23,300	(27)
Shoulder	336	150	3.4			

A comparison of the absorption spectrum of 7-ketocholesterilene with that of the α, β-unsaturated ketone 7-ketocholesterol readily illustrates the appreciable increase in λ_{max} and ϵ_{max} which accompanies the introduction of an additional conjugated unsaturation. The shoulder on the absorption curve seen at 336 mμ suggests that this may be the new position of the R band on addition of the third conjugated chromophere. The ϵ_{max} value for 7-ketocholesterilene determined at 278 mμ (K band) is in excellent agreement with the previous value reported in the literature. The fact that our experimental λ_{max} values

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for 7-ketocholesterilene and for 7-ketocholesterol are 2 mμ lower than those reported by Wintersteiner and Bergstrom (27) suggests a linear difference of 2 mμ in the wave length calibrations of the respective spectrophotometers employed.

Conjugated Dienes

Cyclic conjugated dienes fall into two broad groups ,i.e., homoannular dienes, with the conjugated unsaturations in the same ring, which absorb in the region of 260–285 mμ and heteroannular dienes, with the conjugated unsaturations in different rings, which absorb in the region of 230–250 mμ (9). Both cholesterilene and the enol acetate of cholestenone are considered members of the latter group.

Cholesterilene (Cholestadiene–3, 5)

	Experimental values		Spectral band width (mμ)
	λ_{max} (mμ)	ϵ_{max}	
Maxima	235	18,450	2.0
	229	17,300	2.0
Minimum	231	17,000	2.0
Shoulder	243	12,050	2.1

Cholesterilene was originally assigned the structure of cholestadiene–2, 5 by Heilbron (11), but the high absorption of cholesterilene in the ultraviolet is now considered indicative of a conjugated system. The maxima reported at 249, 304, and 312 mμ in its absorption spectrum (12) were later not confirmed; instead, maxima at 229, 235, and 244 mμ (21, 23) and at 235 and 245 mμ (7) have been reported. In the present investigation, maxima were observed at 229 mμ, and at 235 mμ, and a shoulder was found on the curve at 243 mμ (see Graph No. 2); the experimentally determined ϵ_{max} values were of the same order of magnitude as those cited in the literature.

Cholestenone Enol Acetate (Cholesta–3, 5–dien–3yl Acetate)

	Experimental values		Spectral band width (mμ)
	λ_{max} (mμ)	ϵ_{max}	
Maximum	235	20,400	2.0
Plateaux	231	19,600	2.0
	312	130	2.9

In addition to the main absorption maximum at 235 mμ, transient plateaux were observed on the spectral curve for cholestenone enol acetate in the neighborhood of 231 mμ and 312 mμ. The ϵ_{max} value at 235 mμ is in agreement with that determined by Westphal (25), but the corresponding λ_{max} reported by this worker was that of 240 mμ.

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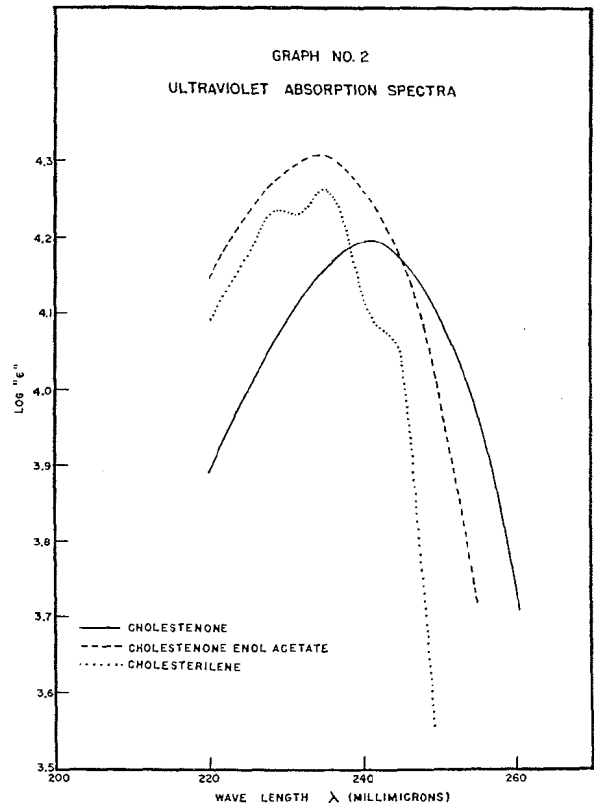
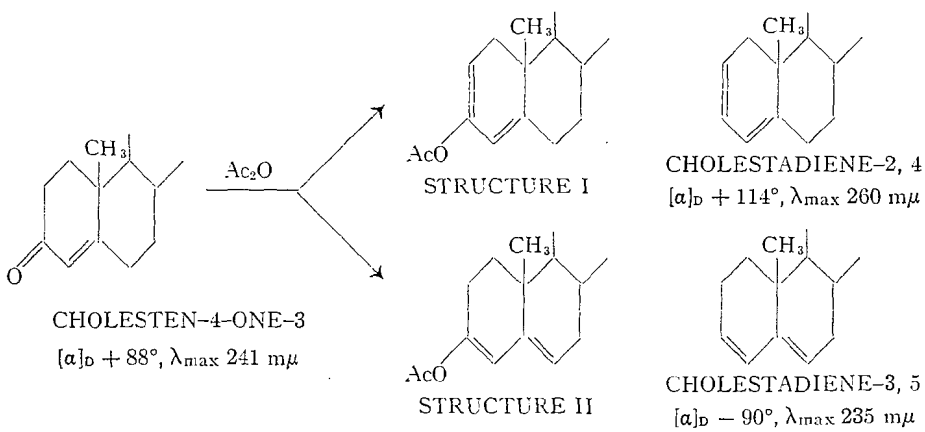


Two possible structures have been proposed for 3-enol esters of 4, 5-unsaturated 3-ketosteroids in general, and hence for the enol acetate of cholestenone in particular. These are shown diagrammatically below, together with the structures and certain physical constants of the corresponding known cholestadienes and also of cholestenone itself.



CHOLESTEN-4-ONE-3
$[\alpha]_D + 88°$, λ_{max} 241 mμ

CHOLESTADIENE-2, 4
$[\alpha]_D + 114°$, λ_{max} 260 mμ

CHOLESTADIENE-3, 5
$[\alpha]_D - 90°$, λ_{max} 235 mμ

FIG. 1.

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Since the specific optical rotation was seen to change from + 88° to − 92° (i.e., to approximately the same negative value as that determined for cholestadiene–3, 5),while the rotation of cholestadiene–2, 4, with a diene structure analogous to that of structure I, is markedly positive, Structure II is suggested for the enol acetate. Similar support has already been offered for Structure II by Westphal (25), based upon optical rotation values differing slightly in magnitude from those reported by us.

Wesphal further supported this postulated shift of the homoannular 2, 4–diene system to the heteroannular 3, 5–diene type by comparing the respective ultraviolet absorption spectra of these steroids. He interpreted the λ_{max} of the enol acetate at 240 mμ as that characteristic of a 3, 5–diene system, since cholestadiene–3, 5 absorbs maximally at 235 mμ and cholestadiene–2, 4 at 260 mμ. However, Westphal's λ_{max} at 240 mμ is somewhat higher than that (about 235 mμ) calculated empirically for this compound by Fieser (9) and others, and in addition is at the same wave length as that of the unesterified parent ketone cholestenone.

In the present investigation, a definite shift in the λ_{max} from 240 mμ to 235 mμ (i.e., to the λ_{max} of cholestadiene–3, 5) was observed upon acetylation of cholestenone. The strict coincidence of the λ_{max} value of cholestenone enol acetate with that of cholestadiene–3, 5, and hence with the empirically calculated value, is considered as supporting more strongly Westphal's postulate of a 3, 5–diene structure. (The authors, in the light of their experimental findings, question Woodward's (28) empirical calculations which predicted a λ_{max} for cholestenone enol acetate about 5 mμ higher than that for cholestadiene–3, 5.) The comparison of the absorption spectra of cholestenone, cholestenone enol acetate, and cholestadiene–3, 5 (cholesterilene) made in Graph No. 2 readily illustrates the shift in λ_{max} on acetylation and the coincidence of the λ_{max} values of the last two steroids. Good agreement is also seen between the λ_{max} values of the last two compounds.

Acknowledgments

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BIOCHEMISTRY OF THE USTILAGINALES

II. ISOLATION AND PARTIAL CHARACTERIZATION OF USTILAGIC ACID[1]

By R. U. Lemieux, J. A. Thorn, Carol Brice, and R. H. Haskins

Abstract

The needlelike crystals which form in aerated submerged cultures of the corn smut *Ustilago zeae* (PRL-119) were found to be a D-glucolipid, m.p. 146-7°C., $[\alpha]_D^{23}+7°$ (pyridine), which contained one carboxyl group, two ester groups, at least two terminal methyl groups, and two D-glucose residues per mole. On the basis of elementary analyses, neutralization equivalent, and molecular weight estimations, the molecular formula of the material isolated was approximately $C_{37}H_{62-6}O_{17}$. The substance was not shown to be chemically homogeneous. Conditions used in culturing the fungus in stirred fermentors to produce the crystalline metabolic product, which was termed "ustilagic acid", are described, and a procedure for the isolation of the material is given.

Haskins (1) has shown that the corn smut *Ustilago zeae* (PRL-119) can dissimilate carbohydrates rapidly in aerated submerged cultures with the production of a substance which precipitated in the culture mixture in the form of long needlelike crystals. Since the culture mixture displayed pronounced antibiotic activity (1), our interest in the chemical nature of the substance was aroused.

The conditions used for the cultivation of the fungus and the production of the material investigated in this work are described in the experimental section. A culture medium containing D-glucose, urea, corn steep liquor, and mineral salts buffered by calcium carbonate was used. The fungus was grown successfully in 30-liter stainless steel fermentors.

Tests showed the crystalline material which was deposited in the culture medium to be readily soluble in methanol, pyridine, 2,3-butanediol, and 1,2-propanediol, only sparingly soluble in ethanol, butanol, and acetone, and insoluble in water, glycerol, ethyl acetate, diethyl ether, benzene, and petroleum ether. These remarkable solubility properties indicated that the substance was moderately polar in chemical nature and provided means for its separation from the other culture solids.

The isolation of the crystalline material was effected under the following mild conditions which would be expected in no way to alter the chemical nature of the substance. The culture solids were collected by filtration and pressed as dry as possible. The moist filter cake was extracted with methanol to remove the crystalline material and the methanolic extract was added to twice its volume of ether. The resulting solution, after clarification, was poured into double its

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volume of water. On standing overnight at 0°C., the mixture yielded a white flocculent precipitate which was collected by filtration and washed with water, then ether. The dried product varied in color from white to a light tinge of yellow. The yields of this crude product varied from 3 to 4.5 gm. per liter of culture medium.

In the above procedure, the ether was added to solubilize the substantial amounts of fatlike substances which were formed in the culture mixture. Although the crystalline material was insoluble in ether, a methanolic solution of the substance tolerated the addition of large amounts of ether without causing precipitation. This solubility property was found useful for the removal of the ash-producing substances which contaminated certain of the crude preparations. On the addition of water to a dilute ether–methanol solution of the substance, precipitation was slow and the product often was essentially crystalline. In many experiments, the portion of the product which precipitated in the ether phase appeared thoroughly crystalline and the crystalline samples used for some of the characterization work were isolated from this phase.

The material dissolved in 5% sodium bicarbonate solution to yield a soaplike solution. A sharp end point was observed on titration of a methanolic solution of the substance with aqueous alkali and phenolphthalein indicator. Purified samples exhibited neutralization equivalents of 777 ± 7. Since the material contained only carbon, hydrogen, and oxygen, it was concluded that it contained a carboxyl group. It is proposed that the acidic substance, isolated from cultures of *Ustilago zeae* in the manner described which showed the following physical and chemical properties, be designated as "ustilagic acid."

The molecular weight found for a crystalline sample of ustilagic acid was of the same magnitude as the neutralization equivalent. Elementary analyses thus indicated a molecular formula of approximately $C_{37}H_{62-6}O_{17}$. However, the substance was not shown to be chemically homogeneous.

The high oxygen content of ustilagic acid suggested the presence of carbohydrate residues, and methyl-α-D-glucopyranoside was readily isolated from the product of the methanolysis of the material. Estimation of the sugar content as D-glucose by the anthrone colorimetric method (3) showed the presence of sugar equivalent to two D-glucose residues per mole of ustilagic acid.

Ustilagic acid possessed alkali-labile groups, and treatment with excess 0.02 *N* sodium hydroxide at room temperature revealed a saponification equivalent one-half the neutralization equivalent. It was therefore apparent that ustilagic acid possessed two ester groups per mole. Terminal methyl group estimation by chromic oxide oxidation (2) indicated the presence of at least two CH_3–C groups per mole of ustilagic acid.

The 12 oxygen atoms which would reside in two D-glucose residues and the four oxygen atoms in the carboxyl and the two acyl groups accounted for all but one of the oxygen atoms in the approximate molecular formula. $C_{37}H_{62-6}O_{17}$.

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It was thus apparent that the remainder of the substance was essentially hydrocarbon in chemical nature and that ustilagic acid was a D-glucolipid.

Crystalline ustilagic acid samples melted at temperatures which varied from 144° to 147°C. The crystalline sample herein reported melted at 146–147°C. and was weakly dextrorotatory, specific rotation +7°, in pyridine.

Experimental

Production of Ustilagic Acid

The ustilagic acid used throughout the present work was produced by the aerobic fermentation of cerelose by the corn-smut fungus *Ustilago zeae* (PRL-119) (1). The medium used contained, in tap water, 1.0 gm. potassium dihydrogen phosphate, 0.6 gm. corn steep liquor, 0.6 gm. urea, 50 gm. cerelose (D-glucose monohydrate) and 1.7 gm. calcium carbonate, per liter.

The fermentations were carried out in 9-liter stirred aerated bottles each containing 4 liters of broth, and in 30-liter stainless steel fermentors, similar to the apparatus described by Rivett, Johnson, and Peterson (5), each containing 15 liters of fermentation broth. The fermentors containing the culture medium were autoclaved for the minimum time necessary to ensure sterilization and then cooled to about 30°C. in a water bath. A sterilized slurry of the calcium carbonate in an aqueous solution of the urea was added aseptically to the cooled medium.

The culture medium was inoculated with 5% (volume per volume) of shake-flask culture mixture of the smut fungus grown for four days at 30°C. on a rotary shaker.

The fermenting culture mixtures were stirred in the range of 400–600 r.p.m. at 30°C., and aerated with approximately 0.27 liter of sterile air per liter of mixture per minute. Excessive foaming was controlled by the aseptic addition of sterile lard oil, about 20 ml. being required for each 15-liter fermentation. The fermentations in the 9-liter bottles were completed in five to six days, those in the 30-liter stainless steel fermentors in two to four days. The fermented broth was allowed to stand for 12 to 24 hours before isolation of ustilagic acid was begun.

Isolation of Ustilagic Acid

The culture solids were collected on a large Büchner funnel or with a laboratory model "Sparkler" filter press with 2% by weight of Johns-Manville Celite No. 545 as filter aid. The solids could also be collected conveniently in a basket centrifuge lined with cloth and a thin layer of shredded asbestos. In each case, the filter cake was pressed as dry as possible and stirred vigorously for about one hour with 250 ml. of methanol for each liter of fermentation broth filtered. The insoluble materials were collected by filtration and the filtrate was poured into twice its volume of diethyl ether. The small amount

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of gelatinous precipitate which formed was removed by filtration and the filtrate was diluted with twice its volume of water. On standing overnight at 0°C., the mixture deposited a white flocculent precipitate, the material which we have termed "ustilagic acid". The substance was somewhat gelatinous and it was most conveniently collected by gravity filtration with hard filter paper. After washing with water, the material was triturated with ether several times. Usually, the composition of the dried product was essentially that of further purified samples. In some cases, however, the material contained appreciable ash largely derived from calcium. The salts responsible for this ash content were removed by dissolving the dry crude ustilagic acid in 20 parts of warm methanol and diluting the resulting solution with twice its volume of diethyl ether. The precipitate which formed immediately was removed by filtration and the ustilagic acid in the filtrate was reprecipitated by the addition of water in the manner described for the isolation of ustilagic acid.

The crude ustilagic acid samples were amorphous white to faintly yellow powdery solids. The purified preparations were colorless, both as solids or in methanolic solution. In many experiments, the portion of the ustilagic acid which had precipitated and remained in the ether phase of the precipitation medium was in the form of clusters of long needlelike crystals of the same appearance as the crystals observed in the culture mixture. The crystalline samples used for the characterization of ustilagic acid were obtained by the mechanical separation of this portion of the precipitate. Most successful fermentations yielded 3 to 4.5 gm. of crude ustilagic acid per liter of fermentation broth.

When the crude ustilagic acid showed a detectable ash content, the neutralization equivalent was higher but the saponification equivalent was essentially that of ash-free samples. This result indicated that the crude sample was composed of a mixture of free and neutralized ustilagic acid.

Partial Characterization of Ustilagic Acid

Table I lists the results of physical and chemical tests which are typical of those obtained for both crystalline and amorphous samples of ustilagic acid. Some of the analytical methods used are described below. The analytical results given in Table I are the average of duplicate estimations with the precision ordinarily expected for the various methods of analysis.

Neutralization and Saponification Equivalents of Ustilagic Acid

A weighed sample of ustilagic acid, about 35 mgm., was dissolved in 5 ml. of pure methanol in a 50 ml. glass-stoppered Erlenmeyer flask. The solution was cooled to near 0°C. in ice-water and slowly titrated to phenolphthalein end point with standard 0.01 *N* sodium hydroxide. The neutralization equivalent was calculated from the amount of alkali necessary to yield an indicator coloration which was stable for 15 sec. Exactly 10 ml. aliquots of 0.02 *N* sodium hydroxide was then added to the neutralized ustilagic acid solution and to 5 ml.

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TABLE I

PARTIAL CHARACTERIZATION OF USTILAGIC ACID

	Ustilagic acid sample		Calc. for $C_{37}H_{62-6}O_{17}$ as $C_{20}H_{33-7}O(C_6H_{11}O_5)_2(COO)_2(CH_3)_2COOH$
No.	1	2	–
Physical state	Crystalline	Amorphous	–
Melting point	146–7°C.	–	–
$[\alpha]_D^{23}$ (*c*, 1 in pyridine)	+7°	+7.5°	–
Molecular weight	760	–	779–783
Neutralization equivalent	770	784	779–783
Saponification equivalent	384	392	389.5–391.5
% Glucose liberated on hydrolysis	42	48	46.0– 46.2
% Carbon	56.8	56.5	56.76– 57.04
% Hydrogen	8.2	8.5	8.04– 8.50
Terminal methyl as % acetyl	11.9	11.3	11.0–

of the methanol. The latter solution served as reagent blank. After standing for 24 hr. at room temperature, the alkali in each solution was determined by titration with 0.01 *N* hydrochloric acid. For accurate estimations the titration must not cause the precipitation of ustilagic acid, and a clear solution must result. This was facilitated by heating the solution to about 60°C. before titration. The difference between the blank titration and the titration of the ustilagic acid solution was taken as the volume of the standard hydrochloric acid solution equivalent to the ester groups in the sample.

The D-*Glucose Content of Ustilagic Acid*

Ustilagic acid, 400 mgm., was heated at 100°C. in a sealed tube with 10 ml. of 5% hydrogen chloride in methanol for 16 hr. The resulting solution was poured into 50 ml. of water and the precipitate which formed was removed by filtration. The chemical nature of this neutral precipitate will be described in the next paper of this series. It contained no carbohydrate, as shown by the anthrone test. The filtrate was neutralized with silver carbonate and the silver salts removed by filtration. The silver ions in the filtrate were removed as silver sulphide and the resulting aqueous solution was reduced *in vacuo* to a thick sirup which soon crystallized. The crystals were washed with ethanol and recrystallized from ethanol to yield 66 mgm. of material, m.p. 165–6°C., $[\alpha]_D^{20}$+ 158° (*c*, 0.8 in water); and this melting point was not depressed by admixture with authentic methyl-α-D-glucopyranoside, m.p. 165.5–166°C., $[\alpha]_D^{25}$+159° (*c*, 1 in water). A sample of the material was acetylated with acetic anhydride and sodium acetate to yield a derivative, m.p. 101–2°C., $[\alpha]_D^{22}$+ 131° (*c*, 0.9 in chloroform), which did not depress the melting point of methyl tetraacetyl-α-D-glucopyranoside, m.p. 101–2°C., $[\alpha]_D^{25}$+ 130.5° (*c*, 1 in chloroform). The yield of methyl-α-D-glucopyranoside was 33% of that expected if ustilagic acid contained two glucose residues per mole.

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The isolation of methyl-α-D-glucopyranoside as a methanolysis product of ustilagic acid indicated that the substance was a glucoside and the colorimetric assay for sugar content by the anthrone method (3) was based on glucose. A weighed sample of ustilagic acid, 12 to 15 mgm., was dissolved in 5 ml. of 0.1 *N* sodium hydroxide solution in a 100 ml. volumetric flask. After dilution to 100 ml., 4 ml. aliquots of the solution were added to Coleman Model 6 spectrophotometer cuvettes. Eight milliliter volumes of the anthrone reagent (3) were then rapidly added to each cuvette by means of a syringe pipette and the color was allowed to develop for one-half hour. A standard absorption curve was established by treating solutions which contained known amounts of glucose, varying from 200 to 400γ per 4 ml. volume, in the same manner. The spectrophotometer was set at 100% transmittance with the solution resulting from the addition of 8 ml. of anthrone reagent to 4 ml. of water. The spectrophotometer readings were taken at λ540 and results were interpreted in the usual manner (3).

Determination of the Molecular Weight of Ustilagic Acid

We are indebted to Dr. I. E. Puddington, Division of Chemistry, National Research Council, for the molecular weight estimation on the crystalline ustilagic acid sample. The microtechnique for the accurate determination of molecular weights devised by Dr. Puddington (4) was used with methanol as solvent. The average value of several determinations was 760.

Acknowledgments

We are indebted to Dr. Ping Shu for valuable suggestions and help in establishing conditions for the 15-liter fermentations and to Mr. W. J. G. Cudmore who performed many of the larger scale fermentations and isolations.

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THE BIOCHEMISTRY OF THE USTILAGINALES

III. THE DEGRADATION PRODUCTS AND PROOF OF THE CHEMICAL HETEROGENEITY OF USTILAGIC ACID[1]

By R. U. Lemieux

Abstract

The D-glucolipid designated as ustilagic acid was shown to be a mixture of partially acylated derivatives of a di-D-glucosyl-dihydroxyhexadecanoic acid. The dihydroxyhexadecanoic acid was named "ustilic acid" and its di-D-glucosyl derivative was termed "glucoustilic acid". Alkaline hydrolysis of ustilagic acid yielded glucoustilic acid, acetic acid, *dextro*-β-hydroxy-*n*-caproic acid, *dextro*-β-hydroxy-*n*-caprylic acid and a small amount of *n*-caproic acid. The β-hydroxy-acids were characterized as *dextro*-β-hydroxy-*n*-caprohydrazide, m.p. 131–132°C., $[\alpha]_D$ + 15.9° (water), and *dextro*-β-hydroxy-*n*-caprylhydrazide, m.p. 127–128°C., $[\alpha]_D$ + 12° (water). Ustilic acid, m.p. 114–115°C., $[\alpha]_D$ − 6.3° (methanol), yielded a methyl ester, m.p. 80–81.8°C., $[\alpha]_D$ − 0.2 (chloroform). The methyl ustilate formed a di-phenylurethane derivative, m.p. 76–77°C. The infrared spectra of crystalline and amorphous samples of ustilagic acid are given. The specific rotation of glucoustilic acid, $[\alpha]_D$ − 11° (methanol) was that expected of β-D-glucosides and the infrared spectrum of this substance showed a marked resemblance to that of methyl-β-D-glucopyranoside.

In a previous publication (11) in this series, the production, isolation, and partial characterization of a D-glucolipid, termed ustilagic acid, was described. The material was found to contain one carboxyl group, two ester groups, at least two terminal methyl groups, and probably two D-glucose residues per mole (777 ± 7) and its composition was approximately $C_{37}H_{62-6}O_{17}$. The substance was isolated most readily as an amorphous solid although small amounts of crystalline preparations were obtained. The compositions of the crystalline and amorphous samples were essentially the same.

Forty-one grams of an amorphous preparation of ustilagic acid was saponified and the salts were decomposed by the addition of sulphuric acid. A highly swollen precipitate formed which was collected by filtration and thoroughly washed with cold water. On freeze drying, a white amorphous powder, 74% of the weight of the ustilagic acid hydrolyzed, was obtained. This water-insoluble material was a weak acid with neutralization equivalent 612; hence the yield obtained corresponded to one equivalent per mole of ustilagic acid hydrolyzed. The filtrate and wash waters from the isolation of the above water-insoluble acid were combined and subjected to steam distillation. A steam-volatile acid fraction was obtained which contained one equivalent of acidity per mole of ustilagic acid decomposed. The residue from the steam distillation was extracted with ether to yield an equivalent of steam-nonvolatile acid fraction per mole of ustilagic acid saponified. Thus ustilagic acid on alkaline hydrolysis gave both volatile and nonvolatile water-soluble acids and a water-insoluble acid.

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Methanolysis of the water-insoluble acid yielded 1.44 moles of D-glucose per neutralization equivalent. The D-glucose was isolated in the form of its methyl-α-D- and β-D-glucopyranosides and their acetyl derivatives. The glucosides were separated partially by fractional crystallization and partially by the precipitation of the β-anomer as its potassium acetate complex (14). A neutral, water-insoluble substance was also formed. This material was the methyl ester of a dihydroxyhexadecanoic acid. The acid was obtained in quantitative yield and it was designated "ustilic acid". The methyl ustilate, after several recrystallizations, melted at 80-81.8°C. However, other preparations of this material were obtained which melted at 84-85°C. Hydrolysis of the methyl ester yielded ustilic acid, m.p. 114-115°C., $[\alpha]_D$ −6.3° in methanol. The presence of two alcoholic hydroxyl groups in methyl ustilate was established by the preparation of a di-phenylurethane derivative, m.p. 76-77°C.

The estimation of the glucose content of the water-insoluble acid by the anthrone method (11, 13) showed it to contain two glucose residues per neutralization equivalent. The above described isolation of 1.44 moles of D-glucose per neutralization equivalent showed that the carbohydrate content was probably entirely derived from D-glucose. Elementary analyses of the substance yielded the carbon and hydrogen contents calculated for $(C_6H_{11}O_6)_2(C_{15}H_{29})$-COOH, the molecular formula expected from the nature of the hydrolytic products and the magnitude of the neutralization equivalent. It was thus evident that the water-insoluble acid was a di-D-glucosyl ustilic acid, and the material was given the trivial designation "glucoustilic acid".

The steam-volatile acid fraction was extracted with ether and converted to methyl ester with diazomethane. On solvent removal, most of the ester content was found in the ether distillate. The acid derived from this highly volatile ester displayed the Duclaux numbers of acetic acid, and the mixed melting point of its *p*-bromophenacyl ester with *p*-bromophenacyl acetate showed it to be acetic acid. A small amount of ester boiled between 144 and 154°C. This substance was shown to be methyl *n*-caproate, b.p. 150°C., by conversion to the *p*-bromophenacyl ester. The melting point of the latter substance was not depressed by admixture of *p*-bromophenacyl *n*-caproate. The amount of *n*-caproic acid thus isolated corresponded to only 0.06 mole per mole of ustilagic acid hydrolyzed.

The steam-nonvolatile acid fraction was isolated by extraction and methylated with diazomethane. After solvent removal, an oil remained which was separated into two components by fractional distillation under reduced pressure. The materials boiled at 194-197°C. and about 230°C. with decomposition at atmospheric pressure. Both components were dextrorotatory methyl esters which contained one hydroxyl and one terminal methyl group per saponification equivalent. The lower-boiling ester, $[\alpha]_D$ +28°, yielded a hydrazide, m.p. 131-132°C., $[\alpha]_D$ +15.9°, with the composition expected for $C_6H_{14}N_2O_2$. It was therefore apparent that the substance was derived from a monohydroxyhexanoic acid. The higher boiling ester, $[\alpha]_D$ + 24°, yielded a

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hydrazide, m.p. 127-128°C., $[\alpha]_D$ + 12°. This melting point was depressed to 114-120°C. on admixture with the hydrazide derived from the lower-boiling methyl ester. The composition of the hydrazide corresponded to $C_8H_{18}O_2N_2$, and it was therefore apparent that the substance was derived from a monohydroxyoctanoic acid.

Oxidation of the monohydroxyhexanoic acid yielded *n*-butyric acid. It thus appeared that the substance was an optically active form of β-hydroxy-*n*-caproic acid. Levorotatory β-hydroxy-*n*-caprohydrazide, m.p. 130-131°C., $[\alpha]_D$ − 15.6°, obtained through the phytochemical reduction of β-keto-*n*-caproic acid (9), was shown to be the optical antipode of the hydrazide prepared from the monohydroxyhexanoic acid derived from ustilagic acid. The two hydrazides were mixed in equal amounts and the mixture was recrystallized to yield a substance, with a melting point 105-106°C., which remained unchanged on admixture of DL-β-hydroxy-*n*-caprohydrazide, m.p. 105.5-106°C.

The structure of the monohydroxyoctanoic acid was established in the same manner. The substance was assumed to be an optically active β-hydroxy-*n*-caprylic acid since, on oxidation, it yielded *n*-caproic acid. Levorotatory β-hydroxy-*n*-caprylhydrazide, m.p. 127.5-128°C., $[\alpha]_D$ − 11.4°, was prepared (9) from the β-hydroxy-*n*-caprylic acid obtained on the phytochemical reduction of β-keto-*n*-caprylic acid. The recrystallization of this hydrazide with an equal amount of the hydrazide of the monohydroxyoctanoic acid derived from ustilagic acid yielded a substance with a melting point 104-104.5°C. which remained unchanged on admixture of DL-β-hydroxy-*n*-caprylhydrazide, m.p. 104.2-104.7°C.

The infrared absorption spectra (see Fig. 1) obtained for both crystalline and amorphous samples of ustilagic acid were essentially the same. As would be expected from its chemical composition, ustilagic acid displayed strong absorption at the regions characteristic for carbonyl groups (5.76μ) and hydroxyl groups (2.92μ). Fig. 1 also shows the infrared spectrum obtained for the amorphous glucoustilic acid. This substance also showed absorption in the regions characteristic of the carbonyl and hydroxyl groups. The absorption in the carbonyl group region for glucoustilic acid was less intense, relative to that in the hydroxyl group region, than that found for ustilagic acid. This appears reasonable since glucoustilic acid was obtained by the deacylation of ustilagic acid. Kuhn (7) pointed out that acyl derivatives of sugars showed a strong absorption at 8 to 8.2μ which was characteristic of the ester groups. It is interesting to note that ustilagic acid showed a rather strong absorption band at 8.04 μ which was not present in the spectrum of glucoustilic acid.

The specific rotation of ustilic acid in methanol solution was weakly levorotatory, −6.3°, and that of glucoustilic acid was only slightly higher, −11°. These results can be interpreted (12, p. 375), on the basis of Hudson's Rules of Isorotation (6) to indicate that the D-glucosidic linkages in glucoustilic acid

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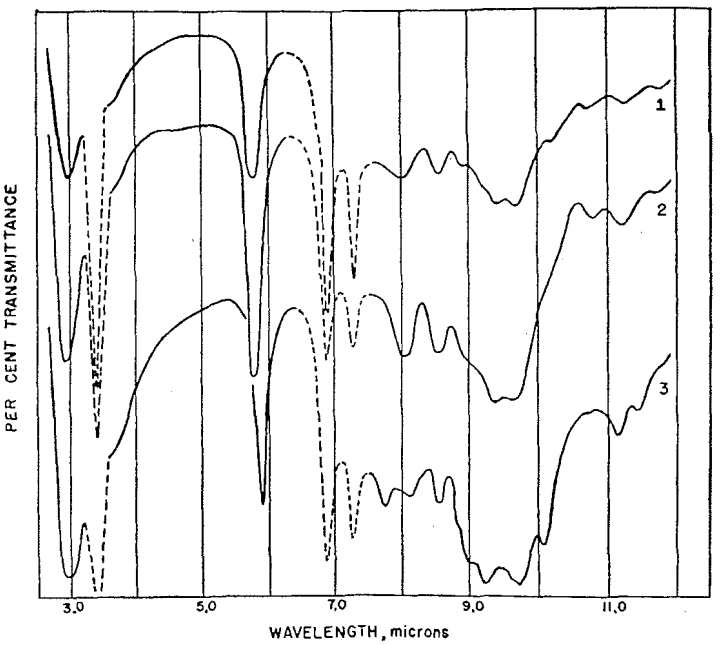
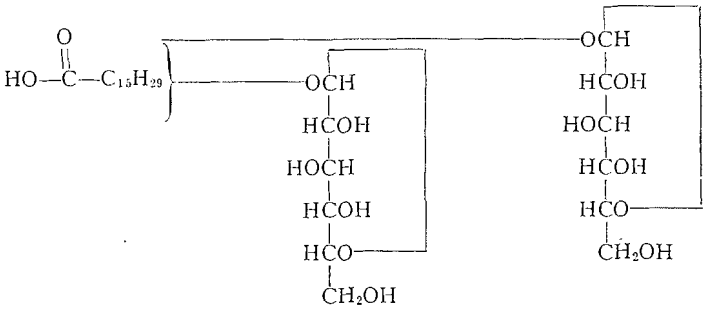


FIG. 1. *Infrared spectra. Curves 1 and 2—The crystalline and amorphous ustilagic acid samples, respectively, previously described (11). Curve 3—Amorphous glucoustilic acid. – – – Nujol absorption bands.*

were of the β-D-configuration. It is noteworthy in this respect that the infrared absorption spectrum of glucoustilic acid, Fig. 1, in the region 7.5 to 12.0 μ was nearly identical to the spectrum published by Kuhn (7) for methyl-β-D-glucopyranoside. This similarity of absorption spectra would not be surprising if glucoustilic acid possessed the structure shown below.



Glucoustilic acid (?)

This inference as to the structure of glucoustilic acid is being verified by conventional methods.

To summarize, the hydrolysis of an amorphous sample of ustilagic acid yielded a substance, designated glucoustilic acid, which, although it was amorphous, appeared to be chemically homogeneous. On this basis, glucousti-

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lic acid was shown to be a di-β-D-glucosyl derivative of a dihydroxyhexadecanoic acid termed "ustilic acid". The further consideration of the structures of these substances is reserved for forthcoming publications in this series. Along with glucoustilic acid, the hydrolysis of ustilagic acid liberated four other acids, acetic acid, *dextro*-β-hydroxy-*n*-caproic acid, *dextro*-β-hydroxy-*n*-caprylic acid, and a small amount of *n*-caproic acid. Since ustilagic acid was found to contain only two ester groups per mole and a total of five different acids were identified as products of its alkaline hydrolysis, it was clear that the substance was a complex, the components of the mixture being made up of glucoustilic acid in combination with an average of two of the lower molecular weight acids per mole. The nature and distribution of the acyl groups in ustilagic acid will form the subject of a forthcoming publication in this series (8).

Experimental

Instrumentation

The infrared spectra were obtained by means of the National Technical Laboratories Model IR-2 infrared spectrometer. This instrument, thermostated at 25 ± 1°C., was calibrated to within 0.02 μ by means of the spectra of carbon dioxide, pyridine, and dioxane (15, p. 92). The transmissions through the sample and sample cell were compared with an empty cell. Nujol mulls (15, p. 93) of the materials were pressed between sodium chloride windows. The spectra represent a combination of the data obtained from recorder tracings and from point-by-point per cent transmission measurements.

All the rotations were determined in a 2 dm. polarimeter tube of about a 2 ml. capacity. The solutions were made up in a 2.5 ml. volumetric flask. All measurements were made at room temperature.

The melting points are uncorrected.

Alkaline Hydrolysis of Ustilagic Acid

Amorphous ustilagic acid, 41.0 gm., was dissolved in 400 ml. of methanol and the solution was refluxed for four hours with 352.2 ml. of 0.577 *N* sodium hydroxide solution. Neutralization of the saponified mixture required 103.8 ml. of 0.484 *N* sulphuric acid solution. Therefore, 153 m.e. of alkali was consumed. The salts of the organic acids were decomposed by the addition of 325 ml. of 0.484 *N* sulphuric acid solution and the mixture was kept at 0°C. for five hours. The heavy deposit of a highly swollen precipitate was collected by filtration on a large Büchner funnel. The material was washed with cold water then stirred with about 500 ml. of water and transferred back to the filter where it was pressed as dry as possible. This procedure was repeated three times more. The filter cake was pressed free of loosely held water, then frozen and dried by lyophilization. The product, after further drying *in vacuo* over calcium chloride for three days, weighed 30.5 gm. The fine, white amorphous powder, designated as glucoustilic acid, was soluble in alkali,

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methanol, and pyridine, very sparingly soluble in water or ethanol, and insoluble in ether, chloroform, ethyl acetate, and benzene. Calc. for $(C_6H_{11}O_6)_2$ $C_{15}H_{29}COOH$: C, 54.89; H, 8.56; glucose, 58.7%; neutralization equiv., 612.7. Found: C, 54.61; H, 8.57; glucose, 58.5, 62.0%; neutralization equiv., 610, 612 (11). Oxidation in 30% chromium trioxide (10) yielded no steam-volatile acid. The yield of this substance, glucoustilic acid, $[\alpha]_D$ − 11° (*c*, 0.75 in methanol), $[\alpha]_D$ − 8.9° (*c*, 0.82 in 0.1 *N* sodium hydroxide), corresponded to 49.8 m.e. of acid.

The filtrate and wash waters from the above isolation were combined and concentrated by distillation at atmospheric pressure to about 500 ml. and the steam-volatile acids which remained in the residue were removed by continuing the distillation with steam. The distillation was stopped after steam-volatile acidity equivalent to 94.2 ml. of 0.577 *N* sodium hydroxide, 54.3 m.e., had passed into the distillate. At this point the vapors contained only a trace of acidity. The salts of the steam volatile acids were isolated by evaporation of the neutralized distillate.

Of the 153 m.e. of free or potential acidity in the ustilagic acid sample, 49.8 m.e. was isolated as glucoustilic acid and 54.3 m.e. was found to be derived from steam-volatile acid. The 48.9 m.e. of acid unaccounted for was in the residue from the steam distillation. This was shown by a separate experiment. Ustilagic acid, 1.94 gm., consumed 7.28 m.e. of base. Acidification and steam distillation of the filtrate from the removal of the glucoustilic acid precipitate yielded 2.42 m.e. of steam-volatile acid, and ether extraction of the residue yielded 2.32 m.e. of steam-nonvolatile, water-soluble, ether-extractable acid. This acid fraction was isolated from the residue of the steam distillation in the main experiment by continuous extraction with ether for 18 hr.

Methanolysis of Glucoustilic Acid

Glucoustilic acid, 20.0 gm., was heated under reflux with 250 ml. of 5% methanolic hydrogen chloride for 19 hr. The reaction mixture was poured into ice-water and the aqueous mixture was extracted four times with chloroform. The combined chloroform extracts were washed twice with water. The water extracts were combined and neutralized with 35 gm. of silver carbonate. The insoluble silver salts were removed by filtration and the dissolved silver ions were precipitated with hydrogen sulphide. The clear, colorless filtrate was evaporated *in vacuo* to a thick sirup which soon began to crystallize. The dry material was dissolved in 50 ml. of boiling methanol and the solution, on standing in the cold, deposited 5.33 gm. of a crystalline material, m.p. 165–166° C., $[\alpha]_D$ + 158° (*c*, 0.8 in water). The melting point was not depressed on admixture with an authentic sample of methyl-α-D-glucopyranoside, m.p. 165.5–166°C., $[\alpha]_D$ + 159° (*c*, 1 in water). The mother liquors were concentrated at room temperature to 15 ml. and this solution on cooling deposited 2.9 gm. of crystals, m.p. 137–150°C., which were recrystallized from 10 ml. of

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methanol to yield 1.25 gm. of methyl-α-D-glucopyranoside, m.p. 165–166°C., $[\alpha]_D$ + 156° (*c*, 1.2 in water). The mother liquors from the above crystallizations were combined and evaporated to dryness. The dry sirup was dissolved in 11 ml. of dry ethanol, and 4 gm. of potassium acetate in 22 ml. of dry ethanol was added. The crystalline potassium acetate complex (14) which precipitated was washed twice with ethanol, twice with acetone, and dried. The yield was 3.79 gm. of a substance with m.p. 175–178°C., and $[\alpha]_D$ − 11.1° (*c*, 0.8 in water). The material was suspended in 30 ml. of acetic anhydride and heated on the steam bath for two hours. The reaction mixture was poured into crushed ice, and the mixture thoroughly stirred and left overnight at 4°C. The aqueous mixture was extracted with chloroform three times, the combined chloroform extracts were washed with water and dried, and the chloroform was removed by aeration. The resulting semicrystalline sirup was dissolved in a little hot ethanol and the solution was allowed to stand overnight in the cold. There was deposited 3.87 gm. of a white crystalline material, m.p. 104–105°C., $[\alpha]_D$ − 18° (*c*, 1.2 in chloroform). The melting point was not depressed by admixture with authentic methyl tetraacetyl-β-D-glucopyranoside. The mother liquors from the isolation of the potassium acetate complex were dried *in vacuo* to a semicrystalline sirup. This material was heated on the steam bath for two hours with 20 ml. of acetic anhydride. The sirupy acetyl derivative was isolated as described above. The dry yellow sirup was dissolved in a little ethanol and the solution was seeded with a few small crystals of methyl tetraacetyl-α-D-glucopyranoside. After standing overnight at 4°C., the crystals which had deposited were gathered by filtration and washed with ethanol. The yield was 1.00 gm. of material, m.p. 93–100°C. Recrystallization from ether–Skellysolve C mixture yielded 0.86 gm. of a substance, m.p. 101–101.5°C., $[\alpha]_D$ + 132° (*c*, 0.74 in chloroform), the melting point of which was not depressed by admixture of methyl tetraacetyl-α-D-glucopyranoside, m.p. 101–102°C. There was thus isolated from 20 gm. of glucoustilic acid 8.45 gm. of D-glucose in the form of essentially pure derivatives or 1.44 moles of the sugar per mole of glucoustilic acid.

The chloroform extract of the methanolysis mixture was dried over sodium sulphate and concentrated on the steam bath to a yellow oil which crystallized on cooling. The crystalline mass was ground to powder and thoroughly dried *in vacuo*. The yield was 9.8 gm. and the crude material melted at 79–81°C. Several recrystallizations from methanol did not raise the melting point above 80–81.8°C., $[\alpha]_D$ − 0.2 in chloroform. Calc. for $C_{17}H_{34}O_4$: C, 67.53; H, 11.33%; mol. wt., 302.4; sapon. equiv., 302.4. Found: C, 67.50; H, 11.47%; mol. wt. (Rast), 328; sapon. equiv., 300, 304. The yield of crude methyl ustilate was nearly quantitative.

Saponification of methyl ustilate and decomposition of the salt gave ustilic acid. After recrystallization from dioxane followed by two recrystallizations from 75% ethanol, the free acid melted at 114–115°C. with $[\alpha]_D$ − 6.3° (*c*, 1.1 in methanol). Calc. for $C_{16}H_{32}O_4$: C, 66.64; H, 11.19%; neutralization equiv., 288.4. Found: C, 66.52; H, 11.22%; neutralization equiv., 288, 289.

Methyl ustilate, 150 mgm., was heated at 100°C. with about 200 mgm. of phenylisocyanate and a drop of pyridine for 15 min. On cooling, the solution hardened to a crystalline mass which was washed with Skellysolve C. The material was treated with boiling Skellysolve C and the insoluble substances were removed by filtration. On cooling the filtrate, an oil separated which soon crystallized. After recrystallization from ether – Skellysolve C, the material melted at 76–77°C. Calc. for $C_{31}H_{44}O_6N_2$: C, 68.85; H, 8.20; N, 5.18%. Found: C, 68.95; H, 8.28; N, 5.15, 5.13%.

Characterization of the Steam-volatile Acids

The sodium salts of the steam-volatile acids (see above) were dissolved in 125 ml. of 0.5 *N* sulphuric acid and the solution was extracted continuously with ether for 24 hr. The ether extract was dried over sodium sulphate and treated with an excess of an ethereal solution of diazomethane. The ether was removed by rather rapid distillation through a Widmer fractionating column. Only a small amount of a yellow oil boiled above 100°C. Nearly all of this liquid distilled between 144° and 154°C. to yield 0.34 gm. of a methyl ester. The ester was saponified to yield a sodium salt which was treated with an alcoholic solution of *p*-bromophenacyl bromide. The product after two recrystallizations from ethanol melted at 70–71°C. and this melting point was unchanged on mixing with an authentic sample of *p*-bromophenacyl *n*-caproate, m.p. 71–72°C. Methyl *n*-caproate boils at 150°C. The ether distillate was refluxed for six hours with 60 ml. of 0.6 *N* sodium hydroxide. Titration of the resulting mixture showed that nearly all of the alkali was neutralized. The neutral solution was evaporated to dryness and the salts were dissolved in 75 ml. of 0.5 *N* sulphuric acid. The resulting solution was steam distilled until all volatile acids were recovered in the distillate. The first 115 ml. of distillate was kept for the determination of Duclaux numbers. Titration of a 10 ml. aliquot of this fraction required 17.50 ml. of 0.1 *N* sodium hydroxide. A 100 ml. aliquot was then distilled in the standard manner for the determination of Duclaux numbers (16, p. 120). The Duclaux numbers listed (16, p. 121) for acetic acid are 6.8, 7.1, and 7.4 and the corresponding numbers found were 6.0, 6.9, and 7.3. The combined distillates were neutralized and evaporated to the sodium salt. Treatment of the salt with *p*-bromophenacyl bromide yielded a *p*-bromophenacyl ester which after one recrystallization from ethanol melted at 84–85°C. The mixed melting point with an authentic sample of *p*-bromophenacyl acetate, m.p. 84–85°C., was 84–85°C.

Separation of the Steam-nonvolatile Acids.

The ether extract of the water-soluble, steam-nonvolatile acid fraction (see above) was dried over sodium sulphate and treated with an excess of diazomethane. The ether was removed by distillation to yield 6.5 gm. of a neutral yellow oil, sapon. equiv. 156, n_D^{25} 1.429. Fractional distillation (1) at 1 mm. pressure of 5.04 gm. of the material separated it into two components. The lower-boiling ester, sapon. equiv. 146, $[\alpha]_D$ + 28° (*c*, 0.86 in chloroform), n_D^{25} 1.427, boiled at 194–197°C. at 710 mm. in the Emich (3) micro boiling point determination and comprised 60–70% of the mixture. The higher

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boiling ester, sapon. equiv. 168, $[\alpha]_D$ + 24° (*c*, 0.85 in chloroform), n_D^{25} 1.433, boiled (3) at about 230°C. with decomposition at 710 mm. Analysis showed each component to contain one hydroxyl group and one terminal methyl group (10) per saponification equivalent. The magnitude of the boiling points found for these substances required their molecular weights to be equal to their saponification equivalents. The proofs of the structures of the two esters are described separately below.

Characterization of dextro-Methyl β-hydroxy-n-caproate

The lower-boiling ester (see above), 0.292 gm., was dissolved in 12 ml. of water which contained 1.2 gm. of sodium hydroxide. To the solution, cooled in ice-water, was added dropwise 1.62 gm. of bromine. After standing at room temperature overnight, the solution was heated at 100°C. for 15 min., acidified with sulphuric acid and decolorized with sodium bisulphite. The solution was steam distilled to yield 150 ml. of distillate, which was treated with an excess of silver sulphate, and the volatile acids were removed by steam distillation. The distillate was neutralized and evaporated to the sodium salts, 2.2 m.e. The salts were decomposed by the addition of hydrochloric acid and portions of the resulting solution were subjected to partition chromatography under the conditions to be described in a forthcoming publication (8). The first acid found in the percolate appeared at the position characteristic of *n*-butyric acid. The zones for this acid from five such chromatograms were combined, neutralized and the resulting solution was evaporated to dryness to yield 0.18 m.e. of sodium salt. The salt in 2 ml. of water was heated with 50 mgm. of *p*-phenylphenacyl bromide in 3 ml. of ethanol for two hours. The substance which crystallized on cooling melted at 81.5–82°C. after one recrystallization from ethanol. This melting point was unchanged on admixture of an authentic sample of *p*-phenylphenacyl *n*-butyrate, m.p. 81.5–82°C.

The methyl ester, 381 mgm., was heated on the steam bath with 0.38 ml. of hydrazine hydrate for a half hour. Ethanol, 0.5 ml., was then added and the solution was refluxed for two hours. On cooling, the solution deposited crystals which were washed with cold ethanol. The yield was 312 mgm. of material, m.p. 129–131°C. Recrystallization from ethanol yielded pure material, m.p. 131–132°C., $[\alpha]_D$ + 15.9° (*c*, 0.75 in water). Calc. for $C_6H_{14}N_2O_2$: C, 49.29; H, 9.65%. Found: C, 49.25, 49.13; H, 9.89, 9.77%.

α, β-Hexenoic acid (2), 5 gm., was heated with boiling 10% aqueous alkali, 350 ml., for 33 hr. The resulting solution was treated with an excess of hydrochloric acid and freed of steam-volatile acids by steam distillation. The residue was extracted with ether to remove the steam-nonvolatile β-hydroxy-*n*-caproic acid (5). The ether extract was treated with an excess of diazomethane, and 1.65 gm. of methyl DL-β-hydroxy-*n*-caproate was obtained by distillation. The substance yielded a hydrazide, m.p. 105.5–106°C. which was purified by recrystallization from ethanol. Calc. for $C_6H_{14}O_2N_2$: C, 49.29; H, 9.65%. Found: C, 49.20, 49.14; H, 9.51, 9.68%.

The above described hydrazide, m.p. 131–132°C., $[\alpha]_D$ + 15.9°, obtained from the monohydroxyhexanoic acid derived from ustilagic acid, 10.65 mgm.,

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was mixed with 10.65 mgm. of levorotatory hydrazide of β-hydroxy-*n*-caproic acid, m.p. 130–131°C., $[\alpha]_D$ − 15.6° (*c*, 0.9 in water) (9). The mixture was dissolved in the minimum amount of boiling ethanol and the crystalline material which separated on cooling was collected by filtration and dried. The yield was 18.6 mgm. or 87% of a substance, m.p. 105–106°C., $[\alpha]_D$ 0° (*c*, 0.5 in water). This melting point was unchanged on admixture of the above described DL-β-hydroxy-*n*-caprohydrazide.

The optically active β-hydroxy-*n*-caproic acid derived from ustilagic acid was not isolated in pure form; however, a chloroform solution of the substance was dextrorotatory, $[\alpha]_D$ + 30° (*c*, 2 in chloroform).

Characterization of dextro-Methyl β-Hydroxy-n-caprylate

The higher-boiling ester (see above), 0.336 gm., was dissolved in 12 ml. of water and 1.2 gm. of sodium hydroxide. Bromine, 1.62 gm., was added dropwise to the ice-cold solution. After standing at room temperature for four and one-half hours, the mixture was heated for 15 min. on the steam bath. The sodium salts of the steam volatile acids formed under these conditions were isolated as described above for the lower-boiling ester. The salts, 1.3 m.e., were dissolved in 1.5 ml. of *N* hydrochloric acid and the solution was diluted to 5 ml. The solution was turbid and possessed a strong odor similar to that of *n*-caproic acid. Partition chromatography (8) of 0.5 ml. aliquots of the mixture showed it to contain an acid fraction which passed through the chromatographic column almost as rapidly as the developing phase. Several chromatograms yielded 0.38 m.e. of this acid fraction which was converted to the sodium salt. The salt was treated with 103 mgm. of *p*-phenylphenacyl bromide in aqueous ethanol to yield an ester which melted at 61–63°C. after two recrystallizations from ethanol. This material with *p*-phenylphenacyl *n*-caproate, m.p. 65°C., yielded a mixture which melted at 62–65°C.

The ester, 407 mgm., was heated on the steam bath for a half hour with 0.41 ml. of hydrazine hydrate. Ethanol, 0.5 ml., was added and the solution was refluxed for two hours. On cooling, the solution deposited a precipitate which, after washing with ethanol and drying, weighed 248 mgm. and melted at 124-127°C. Recrystallization from ethanol yielded pure material, m.p. 127–128°C., $[\alpha]_D$ + 12° (*c*, 1.1 in water). Calc. for $C_8H_{18}O_2N_2$: C, 55.16; H, 10.41%. Found: C, 54.80, 54.74; H, 10.32, 10.43%. The melting point was depressed to 114–120°C. on admixture of the hydrazide derived from the lower-boiling ester.

Ethyl β-keto-*n*-caprylate (17), 10 gm., prepared from *n*-caproyl chloride and ethyl acetoacetate under conditions which paralleled the preparation of ethyl β-keto-*n*-caproate (4), was dissolved in 25 ml. of ethanol. The solution was cooled to about 0°C. and 127 ml. of 0.456 *N* potassium hydroxide solution was added dropwise with vigorous stirring. The stirring was continued for two hours and the solution was left at room temperature overnight. To the solution, cooled in ice-water, powdered 3% sodium amalgam, 150 gm., was added, about 5 gm. at a time, with vigorous mechanical stirring. The pH of the mixture was kept between 7 and 9 by the addition of 0.1 *N* hydrochloric

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acid. After the sodium appeared completely reacted, the aqueous phase, clarified by filtration, was concentrated *in vacuo* to about 100 ml. and made strongly acid by the addition of 25 ml. of concentrated hydrochloric acid. The unreacted β-keto-*n*-caprylic acid which separated as an oil soon crystallized on cooling to 0°C. and it was removed by filtration. The clear filtrate was extracted continuously with ether for 18 hr. The ether extract, after drying over sodium sulphate, was treated with an excess of diazomethane. On solvent removal an oil remained which on distillation yielded 1.38 gm. of methyl DL-β-hydroxy-*n*-caprylate, b.p. 110–112°C. at 9 mm., n_D^{25} 1.432. The ester was treated with hydrazine hydrate in the usual manner to yield the hydrazide, m.p. 104.2–104.7°C., which was purified by recrystallization from ethanol. Calc. for $C_8H_{18}O_2N_2$: C, 55.16; H, 10.41%. Found: C, 55.47; H, 10.25%.

The above hydrazide, m.p. 127–128°C., $[\alpha]_D$ + 12°, prepared from the monohydroxyoctanoic acid derived from ustilagic acid, 11.60 mgm., was mixed with 11.65 mgm. of the hydrazide of β-hydroxy-*n*-caprylic acid (9), m.p. 127.5–128°C., $[\alpha]_D$ − 11.4°. The mixture was dissolved in a few drops of boiling ethanol and, on cooling, 14.8 mgm., 64% yield, of crystals was deposited, m.p. 104–104.5°C., $[\alpha]_D$ 0° (*c*, 0.4 in water). The melting point of this substance was unchanged by admixture of the above described DL-β-hydroxy-*n*-caprylhydrazide.

The optically active β-hydroxy-*n*-caprylic acid derived from ustilagic acid was not isolated in the pure form. That the substance is dextrorotatory was shown by the fact that its optical antipode (9) was levorotatory, $[\alpha]_D$ − 21° (*c*, 1.9 in chloroform).

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SYNTHESE DES ACIDES AMINES A PARTIR DE LA RHODANINE[1]

par ROGER GAUDRY et ROBERT A. MCIVOR

Summary

The Gränacher method has been investigated to discover its applicability to the synthesis of a variety of natural amino acids. The procedure has been simplified for phenylalanine and tyrosine, and extended to valine and isoleucine. An unusual product of the oxidation of α-thioketo-β-(*p*-methoxyphenyl)propionic acid is described.

Introduction

La rhodanine a eu plusieurs applications dans les synthèses organiques (20, 23, 24, 25). En 1922, Gränacher *et al.* (21, 22) ont publié une nouvelle synthèse des acides aminés à partir de la rhodanine. Bien qu'ils aient obtenu des rendements élevés, la méthode n'a eu qu'un usage restreint jusqu'à aujourd'hui. Puisque la rhodanine est actuellement un produit commercial, nous avons pensé que cette méthode pourrait être utilisée pour une synthèse pratique de plusieurs acides aminés.

La méthode de Gränacher consiste à condenser une aldéhyde ou une cétone avec la rhodanine (I), et à scinder le produit de condensation (II) avec une solution alcaline, pour obtenir ainsi l'acide α-thionique (V). Ces acides peuvent être transformés en oximes (VI) ou en phénylhydrazones (VII), qu'on peut facilement réduire par plusieurs méthodes pour obtenir les acides aminés correspondants (VIII).

Gränacher a utilisé cette méthode pour préparer la phénylalanine, la furylalanine, l'O-méthyltyrosine, et la pipéronylalanine avec des rendements totaux de 50–58%. De plus, plusieurs acides aminés qui contenaient les radicaux thényles et pyrryles (7, 28) furent ainsi préparés. Cependant, on n'avait pas preparé auparavant d'acides aminés aliphatiques par cette méthode.

On sait depuis longtemps que la rhodanine peut être condensée quantitativement avec les aldéhydes aliphatiques, aromatiques et hétérocycliques, ainsi qu'avec les α-dicétones (21, 22, 23, 31). Andreasch et ses collaborateurs ont préparé des centaines de produits venant de condensations de rhodanine et d'aldéhydes*. Quand nous avons commencé ces recherches, on n'avait pas encore rapporté de condensation entre la rhodanine et des cétones simples, mais plus récemment, deux articles ont paru sur ce sujet (5, 6).

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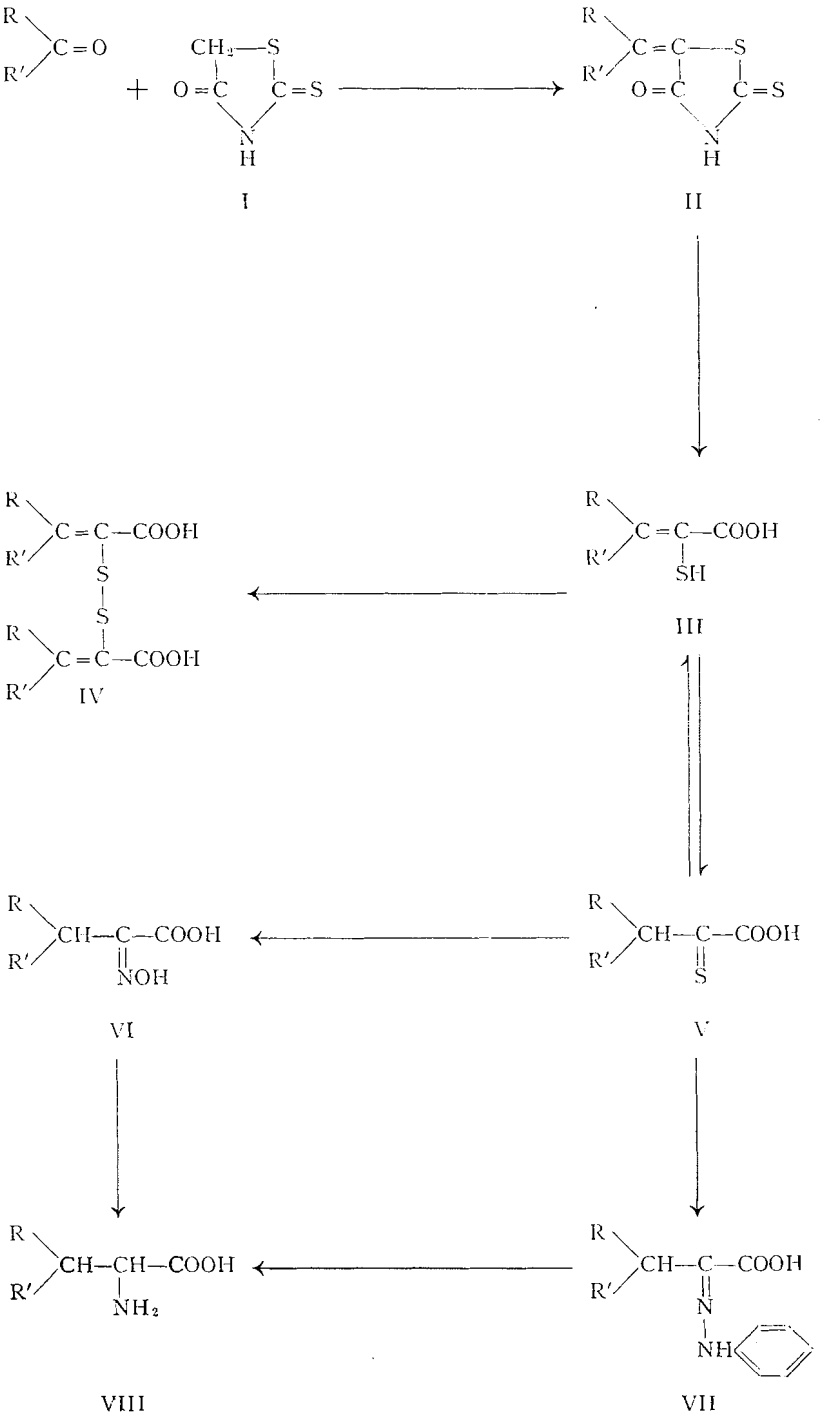
* *Pour une liste complète de ses publications, voir la référence No.* 21.



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Les condensations peuvent être effectuées soit en milieu acide (27), soit en milieu basique (5, 19), mais la condensation en milieu basique a l'avantage de donner un produit moins coloré et plus cristallin, et donne un meilleur rendement avec les cétones aliphatiques.

Il n'est pas possible d'isoler à l'état pur les acides α-thioniques résultant de la scission des produits de condensation de la rhodanine avec les cétones aliphatiques de faibles poids moléculaires. On n'obtient que des huiles qu'il est impossible de distiller. Cependant, en cherchant à préparer l'acide α-thionique à partir de l'isopropylidène rhodanine, nous avons obtenu de petites quantités (5 à 10%), d'un solide qui possède, croyons nous, la formule IV (R et R′ = CH_3). En effet, il a déjà été demontré que la rhodanine donne par réaction avec les alcalis un produit analogue (18). De plus, son point de fusion est beaucoup plus élevé que celui qu'on pourrait s'attendre à trouver pour le monomère. Le composé ne donne d'ailleurs pas de réaction au chlorure ferrique, comme c'est le cas pour les α-thioacides. Si l'on introduit un agent oxydant tel que le chlorure ferrique dans le mélange reactionnel, ou même simplement en y faisant barbotter de l'air, on peut porter le rendement du produit solide à 55%. Il faut ajouter que ce composé vient d'être rapporté dans la littérature (6). On n'en donne pas la structure, mais on y mentionne cependant le fait qu'il se comporte comme un dimère de l'acide α-thionique. Gränacher lui-même a été incapable d'isoler et de caracteriser les acides α-thioniques aliphatiques et personne n'en a jamais preparé les oximes ou les phénylhydrazones. Tous nos essais de précipitation des acides α-thioniques aliphatiques sous forme de sels ont échoué de même que nos tentatives pour en préparer les oximes.

Les oximes des acides α-thioniques aromatiques ont généralment été préparées en solution alcoolique absolue. Elles peuvent cependant l'être plus facilement à partir des acides α-thioniques en solution alcaline aqueuse, en solution alcoolique diluée, ou en solution acétique diluée. La façon la plus convenable de les préparer consiste à ajouter directement du sulfate d'hydroxylamine au mélange qui résulte de la scission du produit de condensation. On peut préparer les phénylhydrazones d'une façon analogue. Ces préparations peuvent être effectuées en grandes quantités, alors qu'il vaut mieux isoler les acides α-thioniques en petites quantités (27).

Bien que nous n'ayons pas réussi à synthétiser les oximes des acides aliphatiques, nous en avons cependant préparé les phénylhydrazones avec de faibles rendements (25 à 30%) par addition de chlorhydrate de phénylhydrazine au mélange obtenu par scission des produits de condensation.* Il est probable qu'on pourrait en augmenter les rendements en ajoutant la phénylhydrazine au moment même où la réaction de scission commence, parce qu'il

*Au cours d'une de ces expériences, nous avons isolé comme sous-produit un solide, fondant à 110°C., insoluble dans les solutions alcalines, et qui semble être, à l'analyse, la phénylhydrazone de la méthyléthylcétone. Ce composé n'est pas rapporté dans la littérature comme étant un solide, peut-être parce qu'on l'obtient généralement sous forme d'un mélange des deux isomères possibles. La phénylhydrazone de l'acétone, qui ne peut exister que sous une seule forme, es taussi un solide.

semble que des quantités appreciables d'acides α-thioniques sont détruites au cours de la réaction.

Gränacher a employé l'amalgame de sodium pour réduire les oximes. Bien que les rendements soient bons, cette méthode n'est pas facilement applicable sur une grande échelle.

Nous avons trouvé que les oximes peuvent être réduites par l'hydrogène à basse pression en présence de nickel Raney W-6 ou W-7 (1) ou encore avec le nickel Raney *in situ*. Dans ce cas, les rendements furent de 30 à 50%. Les oximes peuvent aussi être réduites par la méthode de Feofilaktov (8), ce qui donne des rendements d'environ 10% pour la réduction. La réduction électrolytique est celle qui donne les rendements les plus élevés, soit 75 à 80%.

Des essais de réduction de l'acide α-oximino-β-phénylpropionique avec la poudre de zinc et l'acide acétique de même qu'avec l'étain et l'acide chlorhydrique n'ont pas réussi, bien qu'il soit possible de réduire ainsi l'acide α-oximino-β-(*p*-méthoxyphényl)propionique.

La préparation des phénylhydrazones à partir des acides α-thioniques n'a pas été décrite jusqu'à présent, mais elle est assez facile. Les phénylhydrazones peuvent être facilement réduites chimiquement. Feofilaktov se sert de zinc et d'une solution alcoolique d'acide chlorhydrique à 0°C. pour réduire ces phénylhydrazones. Il a prétendu ainsi obtenir des rendements quantitatifs dans ses publications antérieures (8,9,10,11,12) mais plus récemment (13,14) il donne des rendements de 50 à 60% pour des composés analogues. Nous avons aussi obtenu de bons rendements bruts avec sa méthode, mais le produit n'était pas pur, dû probablement à la formation des indoles ou pseudoindoles correspondants. Après purification les rendements furent de 50 à 60%. Sa méthode est aussi passablement incommode pour les préparations sur une grande échelle. La méthode qui utilise la poudre de zinc et l'acide acétique concentré (mais pas glacial), est plus élégante, mais elle aussi ne donne que des rendements de 50 à 60% pour les phénylhydrazones aromatiques et de 20% pour la phénylhydrazone de l'acide diméthylpyruvique. Il ne semble pas possible de réduire électrolytiquement les phénylhydrazones.

Les points de décomposition de l'acide α-oximino-β-phénylpropionique donnés dans la littérature varient entre 155°C. et 173° à 174°C. (4). Le produit obtenu ordinairement se décompose avec dégagement abondant de gaz à 155°C. (non corrigé); mais dans d'autres préparations nous avons obtenu des produits qui se décomposent à 172°C. et 206°C. Un réarrangement de Beckmann avec l'acide sulfurique sur les isomères qui se décomposent à 172°C. et à 206°C. a donné la phénylacétamide dans les deux cas. Nous croyons maintenant que ces oximes sont capables d'énolisation et qu'ainsi les isomères seraient interconvertibles en solution. De plus, tous les deux pourraient donner la phénylacétamide par déshydratation et décarboxylation, suivie d'hydrolyse. L'isomère qui fond à 155°C. se forme en présence d'un très grand excès d'hydroxylamine, et les autres quand il n'y a qu'un excès de trois

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molécules-grammes d'hydroxylamine. Par traitement des isomères ayant les points de fusions les plus élevés par l'hydroxylamine en solution alcaline, on obtient l'isomère qui fond à 155°C.

Gränacher déclare (21) avoir synthétisé l'acide phénylpyruvique par l'hydrolyse de cette oxime avec la formaldéhyde et l'acide chlorhydrique tandis que Hall, Hynes et Lapworth (26) ont obtenu un rendement de 50% de α-hydroxy-β-phényl-γ-crotonolactone avec les mêmes réactifs en proportion différente. Nous avons répété les expériences des deux, et nous avons trouvé que toutes les deux sont correctes, mais qu'il est difficile de purifier l'acide phénylpyruvique obtenu par la méthode de Gränacher, parce qu'il est contaminé par la lactone. Cette lactone ne se condense pas avec la rhodanine.

Le point de fusion de l'acide α-oximino-β-(*p*-méthoxyphényl)propionique donné dans la littérature est 159°C. (22), tandis que notre produit fond à 199°C. (déc.). Cet isomère donne en solution alcaline avec l'hydroxylamine un autre isomère qui fond à 144°–145°C. (déc.).

Le traitement de l'acide α-thio-β-(*p*-méthoxyphényl)propionique par l'hydroxylamine donne en plus de 50% de l'oxime, environ 20% d'un composé inconnu qui se décompose avec dégagement abondant de gaz à 147.5°–148°C. Ce composé est soluble dans les bases, mais insoluble dans les acides dilués. Par pyrolyse, il se décompose en plusieurs gaz, dont l'ammoniaque et le bioxyde de carbone. Il réduit la liqueur de Fehling à froid, et réagit immédiatement avec le permanganate et l'eau de brome. Il réduit l'acide périodique en l'iode. Une partie demeure inchangée par réaction avec le pentachlorure de phosphore et l'isocyanate de phényle. Les valeurs trouvées pour le poids moléculaire sont les suivantes:

Par l'analyse Kjeldahl (2 atomes d'azote)	245
Par la méthode de Rast (32)	241
Par titrage du groupement carboxyle	238

Par réduction avec l'étain et l'acide chlorhydrique on obtient un dichlorhydrate d'un acide aminé. Il est en effet possible de titrer trois groupements acidiques différents, dont les équivalents chimiques sont: 285, 145 et 90.5. Par dissolution de ce chlorhydrate dans l'éthanol absolu, suivie de l'addition de pyridine, on obtient un précipité d'un monochlorhydrate instable qu'on peut transformer en picrate.

L'oxydation du produit inconnu original par le permanganate de potassium en solution alcaline à 0°C. a donné l'acide α-oximino-β-(*p*-méthoxyphényl)-propionique avec un point de fusion de 144.5°C. Cette oxime fut réduite par l'étain et l'acide chlorhydrique en O-méthyltyrosine, identifiée sous forme de dérivé phényluréidé, p.f. 165° à 166.5°C. (dec.). Le point de fusion ne fut pas abaissé par mélange avec un échantillon authentique.

Nous croyons que ce composé peut être l'acide α,α-dihydroxylamino-β-(*p*-méthoxyphényl)propionique.

Nous n'avons pas réussi à préparer d'acides aminés en traitant directement les produits de condensation des aldéhydes aromatiques avec la rhodanine par l'ammoniaque sous pression, ni même en chauffant les acides α-thioniques avec l'ammoniaque selon la méthode de Galat (16).

La phénylalanine et l'O-méthyltyrosine peuvent ainsi être facilement et rapidement synthétisées en grandes quantités à partir de la rhodanine, par condensation en milieu ammoniacal avec la benzaldéhyde ou l'anisaldéhyde, scission avec la soude caustique, suivie de l'addition de l'hydroxylamine sans isoler l'acide α-thionique, et réduction électrolytique de l'oxime ainsi obtenue. On transforme ensuite l'O-méthyltyrosine en tyrosine par chauffage à reflux avec un mélange d'acide chlorhydrique concentré et d'acide acétique glacial. Quant à la valine et à l'isoleucine, nous avons demontré que leur synthèse est possible par la méthode à la rhodanine, mais elle ne présente qu'un intérêt théorique à cause des faibles rendements des produits intermédiaires.

Partie Expérimentale

Benzalrhodanine (II: R = C_6H_5; R′ = H)

A un mélange de rhodanine (120 g., 0.904 mole) et de chlorure d'ammonium (80 g. dissous dans 160 ml. d'eau chaude), on ajoute une suspension de benzaldéhyde (96 g., 0.904 mole) dans l'ammoniaque à 28% (80 ml.). Après deux ou trois minutes d'agitation, le mélange se solidifie. On le laisse refroidir et on le verse dans trois litres d'eau froide. Par filtration, on obtient 196 g. (98%) d'un précipité jaune orangé, assez pur pour les réactions subséquentes. Par recristallisation de l'alcool aqueux, on obtient des aiguilles jaunes. P.f. 199° à 200°C.* Litt.: 200°C. (30).

On peut préparer la *p*-hydroxybenzalrhodanine et l'anisalrhodanine d'une façon analogue avec des rendements pareils. Mais l'anisalrhodanine forme souvent des masses dures qui renferment de l'anisaldéhyde n'ayant pas réagi.

La *p*-hydroxybenzalrhodanine est une poudre jaune (recristallisée de l'éthanol). P.f. 275° à 285°C. (déc.). Litt.: 260°C. (3), 274°C. (2).

L'anisalrhodanine forme des aiguilles rouges brunâtres (recristallisée de l'éthanol). P.f. 249° à 254°C. (déc.). Litt.: 230° à 242°C. (3), 230° à 232°C. (22).

Les produits de condensation entre la rhodanine et les aldéhydes n'ont pas de points de fusion nets, et le point de fusion peut dépendre de la vitesse avec laquelle on chauffe le capillaire.

Isopropylidène Rhodanine (II: R = R′ = CH_3)

A un mélange de rhodanine (30 g., 0.226 mole) et de chlorure d'ammonium (20 g. dissous dans 40 ml. d'eau chaude), on ajoute une suspension d'acétone (40 ml., 0.454 mole) dans l'ammoniaque à 28% (20 ml.). Le produit de condensation commence parfois à précipiter tout de suite. On chauffe à reflux

* *Les points de fusion ne sont pas corrigés.*

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pendant une heure, et on verse le mélange dans l'eau froide (1500 ml.). Les petits granules jaunes pâles qui se forment sont assez purs pour les réactions subséquentes. Rendement: 33 g. (84%). P.f. 194° à 196°C. Litt.: 196° à 197°C. (5). Calculé pour $C_6H_7NOS_2$: N, 8.09%. Trouvé (Kjeldahl): N, 8.17%.

Quand on prépare ce produit par la méthode de Julian et Sturgis (27), le produit initial fond aux environs de 130°C., mais on peut le purifier par recristallisation de l'éthanol dilué ou de l'acide acétique dilué. Si on le cristallise du benzène ou du toluène, on concentre l'impureté de rhodanine au dépens du produit de condensation.

On peut préparer l'α-méthylpropylidène rhodanine d'une façon semblable. Rendement: 70%. Elle cristallise (de l'éthanol aqueux ou de l'acide acétique aqueux) en granules jaunes. P.f. 122° à 123°C. Litt.: 119° à 120°C. (5). Calculé pour $C_7H_9NOS_2$: N, 7.49%. Trouvé: N, 7.41%.

Acide α-Thio-β-phénylpropionique (V: R = C_6H_5; R′ = H)

On ajoute de la soude caustique à 15% (65 ml., 0.29 mole) à de la benzalrhodanine (12.5 g., 0.057 mole) dans une fiole conique et on chauffe 30 min. sur un bain-marie, suivi par deux minutes d'ébullition. On refroidit à 0°C., et on ajoute *rapidement* de l'acide chlorhydrique à 10% (100 ml.). Un précipité jaune se forme. Après une heure à 0°C., on filtre. Le produit est assez pur pour les réactions subséquentes. Rendement: 10.2 g., (100%). Il cristallise en aiguilles blanches (du toluène). P.f. 127° à 129°C. Litt.: 125° à 129°C. (21).

Les composés suivants furent préparés par une méthode semblable:

Acide α-thio-β-(*p*-hydroxyphényl)propionique. (Porté à ébullition pendant cinq minutes après le chauffage sur le bain-marie, ou encore chauffé à reflux pendant 30 min.). Rendement: 100% d'une poudre blanche ou jaune (recristallisé du toluène). P.f. 176° à 178.5°C. Litt.: 186°C. (2).

Acide α-thio-β-(*p*-méthoxyphényl)propionique. Rendement: 98% de feuilles jaunes (recristallisé du toluène). P.f. 178° à 180°C. Litt.: 178°C. (22).

N.B. Il est conseillé de ne pas scinder à la fois plus de 15 g. de produit de condensation si l'on veut isoler l'acide α-thionique.

Bisulfure de bis(α-Carboxy-β, β-diméthylvinyl-) (IV: R = R′ = CH_3)

A. On ajoute de la soude caustique à 15% (36 g., 0.884 mole dissoute dans 250 ml. d'eau) à de l'isopropylidène rhodanine (40 g., 0.232 mole) dans une fiole conique et on chauffe pendant 30 min. sur un bain-marie, suivi par deux minutes d'ébullition. On refroidit à 0°C., on divise la solution en quatre parties, et on ajoute *rapidement* de l'acide chlorhydrique à 10% (80 ml. pour chaque partie). Des cristaux oranges se forment lentement. Rendement: 1.9 g., (6%). Granules oranges (recristallisés de l'eau). P.f. 172° à 175°C. Calculé pour $C_{10}H_{14}O_4S_2$: COOH, 34.4%; S, 24.4%. Trouvé: COOH, 34.6%, S, 24.2%.

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B. On ajoute de l'isopropylidène rhodanine (17.2 g., 0.1 mole) à une solution de soude caustique à 15% (12 g., 0.3 mole, dissoute dans 56 ml. d'eau). On y fait barbotter de l'air pendant une heure. On acidifie rapidement avec de l'acide chlorhydrique à 1:1 (60 ml.) ce qui provoque la séparation d'une huile jaune. En faisant barbotter de l'air dans le liquide pendant une heure supplementaire, l'huile cristallise en un solide jaune pâle. Rendement: 7.2 g., (55%). P.f. 175° à 184°C.

On peut aussi poursuivre l'oxydation en faisant la scission par la méthode usuelle, suivie par l'addition d'une solution concentrée de chlorure ferrique, goutte à goutte, jusqu'à ce que la coloration rouge du thiocyanate ferrique dure pendant plusieurs minutes. Rendement: 4.2 g. (31%).

Acide α-Oximino-β-phénylpropionique (VI: R = C_6H_5; R′ = H)

On chauffe de la benzalrhodanine (95.3 g., 0.43 mole) avec de la soude caustique à 15% (72 g., 1.81 moles dissoute dans 411 ml. d'eau) pendant 30 min. sur un bain-marie, puis deux minutes à l'ébullition. On ajoute à cette solution chaude, de la soude caustique (36.0 g., 0.91 mole) et une solution aqueuse de sulfate d'hydroxylamine (223 g., 1.36 moles). Il y a un dégagement vigoureux d'acide sulfhydrique. On reporte la solution à l'ébullition pendant deux minutes, et on la laisse refroidir à la glacière. On filtre et on lave le précipité avec de l'acide chlorhydrique dilué. Par acidification du filtrat, on obtient parfois un précipité additionnel. Le premier précipité est généralement l'isomère qui fond à 155°C. (déc.). Le deuxième peut être n'importe quel isomère. Si l'on emploie la moitié de la quantité d'hydroxylamine mentionnée plus haut, l'oxime précipite seulement après acidification, la plupart du temps sous forme d'isomère fondant à 206°C. Après recristallisation de l'éthanol, on obtient 62.8 g. (81%) de cristaux blancs soit en aiguilles, soit en feuilles.

L'isomère qui fond à 155°C. est soluble dans l'eau, l'acétone et l'alcool chaud, peu soluble dans l'alcool froid, très peu soluble dans l'éther, le chloroforme, le dioxane et le benzène. L'isomère qui fond à 206°C. est moins soluble dans l'eau et plus soluble dans les solvants organiques. Calculé pour $C_9H_9NO_3$: N, 7.82%. Trouvé: N, 7.96% (155°C.); 7.23% (172°C.); 7.52% (206°C.).

On peut préparer l'acide α-oximino-β-(*p*-hydroxyphényl)propionique et l'acide α-oximino-β-(*p*-méthoxyphényl)propionique d'une façon analogue, bien qu'il soit conseillé de n'utiliser que la moitié du sulfate d'hydroxylamine.

Acide α-oximino-β-(*p*-hydroxyphényl)propionique. Rendement: 60% de granules bruns, assez purs pour les réactions subséquentes. P.f. 178.5° à 179°C.* (déc.). Calculé pour $C_9H_9NO_4$: N, 7.48%. Trouvé: N, 7.24%.

Avec l'anisalrhodanine et le sulfate d'hydroxylamine en milieu alcalin, on obtient un précipité d'un composé inconnu décrit plus haut avec un rendement de 20%. Il cristallise (de l'éthanol absolu) en aiguilles blanches. P.f. 147.5° à 148°C. (dec.). Après acidification, on obtient l'acide α-oximino-β-(*p*-méthoxy-

**Variable selon la vitesse de chauffage.*

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phényl)propionique avec un rendement de 50%, qui cristallise (de l'éthanol aqueux) en feuilles. P.f. 199°C. (déc.). Litt.: 159°C. (22). Calculé pour $C_{10}H_{11}NO_4$: N, 6.70%. Trouvé: N, 6.98%.

Phénylhydrazone de l'acide phénylpyruvique (VII: R = C_6H_5; R′ = H)

On chauffe de la benzalrhodanine (30 g., 0.136 mole) avec de la soude caustique à 15% (18.2 g., 0.472 mole dissoute dans 104 ml. d'eau). Après que tout est passé en solution, on chauffe sur un bain-marie pendant 30 min. supplémentaires. On porte la solution à l'ébullition pendant deux minutes, et on y ajoute une solution aqueuse de chlorhydrate de phénylhydrazine (17 g., 0.136 mole). Après avoir laissé reposer toute la nuit, on centrifuge (si nécessaire) et on acidifie avec l'acide chlorhydrique en agitant rapidement avec un agitateur mécanique. Par filtration on obtient la phénylhydrazone sous forme d'une poudre jaune-orange. Rendement: 96% brut et 74% pur. Elle cristallise de l'éthanol aqueux en granules jaunes. P.f. 160° à 161°C. Litt.: 160° à 161°C. (33).

On prépare les phénylhydrazones suivantes d'une façon analogue:

Phénylhydrazone de l'acide *p*-hydroxyphénylpyruvique. Rendement: 96% (brut) et 75% (recristallisée de l'éthanol aqueux). Elle cristallise en granules bruns rougeâtres. P.f. 157°C. (déc.). Litt.: 159° à 161°C. (capillaire chauffé lentement) et 167° à 169°C. (déc.) (capillaire chauffé rapidement) (29).

Phénylhydrazone de l'acide *p*-méthoxyphénylpyruvique. Rendement: 100% (brut) et 80% (recristallisée de l'éthanol aqueux). Elle cristallise en aiguilles jaunes pâles. P.f. 141° à 142°C. On peut la séparer en deux isomères par cristallisation fractionnée de l'alcool absolu: un isomère incolore qui fond de 158° à 159°C. et un isomère jaune qui fond à 150°C. Litt.: 158° à 159°C. et 150°C. (13)*.

Phénylhydrazone de l'acide diméthylpyruvique. Rendement: 40% (brut) et 25% (recristallisée de l'éthanol aqueux). Elle cristallise en aiguilles jaunes ou de couleur chamois, très longues et minces. P.f. 143° à 144°C. (déc.). Litt.: 144°C. (12).

Phénylhydrazone de l'acide méthyléthylpyruvique. Rendement: 40-50% (brut) et 20% (recristallisée de l'éthanol aqueux). Elle cristallise en aiguilles jaunes pâles, très longues et soyeuses. P.f. 133.5°C. (déc.). Litt.: 132° à 133°C. (8).

dl-Phénylalanine (VIII: R = C_6H_5; R′ = H)

A. On effectue l'hydrogénation pendant trois heures à la température de la chambre, de l'acide α-oximino-β-phénylpropionique (5 g., 0.028 mole) dissous dans 150 ml. d'eau en présence de nickel Raney W-6 (2 g.) comme catalyseur, à une pression de 2 à 3 atmosphères. On filtre le nickel Raney, on acidifie et on filtre à nouveau. On ajuste le pH à 5.9, on évapore à sec et on ajoute un peu d'eau pour solubiliser les sels inorganiques. Par filtration, on obtient de

* *La cristallisation fractionnée a été faite par le docteur Karl F. Keirstead.*

la phénylalanine. Rendement: 2.0 g., (43%). P.f. 239°C. à 244°C. (capillaire scellé). Litt.: 260° à 270°C. (21). L'hydrogénation ne réussit pas dans l'éthanol ou le dioxane. Calculé pour $C_9H_{11}NO_2$: N, 8.49%. Trouvé: N, 8.30%.

Le dérivé phényluréidé cristallise en aiguilles blanches de l'éthanol aqueux. P.f. 174.5°C. (déc.). Litt.: 169° à 170°C. (17). Le point de fusion ne fut pas abaissé par le mélange avec un échantillon authentique. Calculé pour $C_{16}H_{16}N_2O_3$: N, 9.85%. Trouvé: N, 9.70%.

La réduction de l'acide α-oximino-β-(*p*-hydroxyphényl)propionique par cette méthode donne la *dl*-tyrosine avec un rendement de 20%. P.f. 291° à 293°C. Litt.: 290° à 295°C. (15). Calculé pour $C_9H_{11}NO_3$: N, 7.73%. Trouvé: N, 7.79%.

B. On dissout dans l'eau chaude de l'acide α-oximino-β-phénylpropionique (10 g., 0.056 mole) et on y ajoute de l'alliage de nickel Raney (25 g.). On porte la solution à reflux, et on ajoute de la soude caustique en pastilles une à une (ATTENTION) pendant trois à quatre heures, jusqu'à ce que l'aluminium soit entièrement dissous. On filtre, on ajuste le pH à 7-8 et on enlève l'hydroxide d'aluminium par filtration. On acidifie avec l'acide chlorhydrique concentré et on évapore à sec. On dissout le chlorhydrate de l'acide aminé dans l'éthanol absolu, on filtre les sels inorganiques et on ajoute de la pyridine en léger excès. Après avoir laissé 24-48 h. à la glacière, on filtre. Rendement: 4 g. (44%). P.f. 224° à 228°C. (capillaire scellé).

C. On place dans un ballon muni d'un agitateur mécanique et plongeant dans un bain de glace, une solution d'acide α-oximino-β-phénylpropionique (9 g., 0.05 mole) dans l'éthanol (100 ml.) et du zinc en poudre (9 g.).

On y ajoute, goutte à goutte, pendant trois à quatre heures, une solution d'acide chlorhydrique (15 g., 0.411 mole) dans l'éthanol. On filtre l'excès de zinc s'il en reste, on évapore à sec, on ajoute de l'eau, on évapore de nouveau à sec, on dissout le résidu dans l'eau, et on précipite le zinc avec l'acide sulfhydrique. On acidifie le filtrat avec l'acide chlorhydrique, on évapore à sec, on dissout le résidu dans l'éthanol absolu et on précipite l'acide aminé avec la pyridine.

Rendement: 0.5 g. (6%). P.f. 254° à 260°C. (déc.) (capillaire scellé). Calculé pour $C_9H_{11}NO_2$: N, 8.49%. Trouvé: N, 8.54%.

Si l'on applique la même méthode à la phénylhydrazone de l'acide phénylpyruvique, on obtient un rendement brut de 97%.

D. On porte à reflux pendant 24 h., un mélange d'acide acétique à 75% (150 ml.), de zinc (14 g., 0.24 mole) et de phénylhydrazone d'acide phénylpyruvique (10 g., 0.0394 mole). Pendant ce temps, la solution devient blanche ou limpide. On décante alors de l'excès de zinc, et on évapore à sec. On ajoute 150 ml. d'eau au résidu, on filtre si nécessaire, on précipite le zinc par l'hydrogène sulfuré et on porte à ébullition la solution avant de filtrer. On évapore le filtrat à sec, on ajoute de l'éthanol au résidu, on filtre et on lave avec de

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l'éthanol et de l'eau. Rendement: 3.4 g. (53%). P.f. 236° à 242°C. (capillaire scellé). Calculé pour $C_9H_{11}NO_2$: N, 8.49%. Trouvé: N, 8.48%.

On peut préparer d'une façon analogue:

L'O-méthyltyrosine (de la phénylhydrazone correspondante). Rendement: 58%. P.f. 252°C. à 255°C. (capillaire scellé). Litt.: 262°C. (13). Calculé pour $C_{10}H_{13}NO_3$: N, 7.18%. Trouvé: N, 7.18%.

L'O-méthyltyrosine (de l'oxime correspondante). Rendement: 26%. P.f. 252° à 255°C. Calculé pour $C_{10}H_{13}NO_3$: N, 7.18%. Trouvé: N, 7.16%.

Le dérivé phényluréidé de l'O-méthyltyrosine cristallise de l'éthanol aqueux en feuilles blanches. P.f. 165° à 165.5°C. Calculé pour $C_{17}H_{18}O_4N_2$: N, 8.91%. Trouvé: N, 8.94%.

Le dérivé phényluréidé fut ensuite cyclisé en 3-phényl-5-anisylhydantoine par l'action de l'acide chlorhydrique. Il se forme une poudre blanche de l'éthanol aqueux. P.f. 159° à 160°C. Calculé pour $C_{17}H_{16}O_3N_2$: N, 9.46%. Trouvé: N, 9.54%.

dl-Tyrosine. Rendement: 20%. P.f. 293° à 294°C. (capillaire scellé). Calculé pour $C_9H_{11}NO_3$: N, 7.73%. Trouvé: N, 7.75%.

dl-Valine. Rendement: 20%. P.f. 254°C. (capillaire scellé). Calculé pour $C_5H_{11}NO_2$: N, 12.0%. Trouvé: N, 12.0%.

E. On ajoute de l'acide α-oximino-β-phénylpropionique (10 g., 0.055 mole) à un mélange d'éthanol (100 ml.) et d'acide sulfurique à 15% (60 ml.). La cellule électrolytique consiste en un bécher qui contient du mercure d'une surface de 139 cm.², et servant de cathode. L'anode est un filament de platine placé dans une petite coupe poreuse, suspendue dans la solution. L'anolyte est de l'acide sulfurique à 15%. On refroidit la solution à 0–5°C. et on y fait passer un courant de 3 ampères pendant deux heures. On peut isoler l'acide aminé de la solution soit par précipitation au point isoélectrique, soit par neutralisation exacte avec l'hydroxide de barium, filtration et évaporation du filtrat. Rendement: 6.6 g. (82%).

On peut préparer l'O-méthyltyrosine d'une façon analogue. Rendement: 48%. P.f. 258° à 260°C. Litt.: 262°C. (13). Calculé pour $C_{10}H_{13}NO_3$: N, 7.18%. Trouvé: N, 7.14%.

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CONDUCTANCE MEASUREMENTS IN WATER – NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT VARIOUS TEMPERATURES[1]

By Edward G. Taylor,[2] L. Murray Lyne, and Alan G. Follows

Abstract

Conductance measurements in the system water – nitric acid – nitrogen pentoxide have been made over a range of temperatures. The results are in accordance with the findings of Veley and Manley (12) as regards (1) the presence of a minimum in the specific conductance at about 96% by weight nitric acid (2) the existence of a negative temperature coefficient of specific conductance for solutions rich in nitric acid. As reported by Berl and Saenger (1) the specific conductance of solutions of nitrogen pentoxide in nitric acid at first increases with increasing concentration of the former, ultimately attaining a maximum and then decreasing with further increase in the nitrogen pentoxide content. Some viscosity and density data for nitric acid – nitrogen pentoxide mixtures are included.

Introduction

In recent years the nature of concentrated aqueous solutions of nitric acid has formed the object of many types of experimental investigations. The evidence obtained seems to indicate the presence of nitryl ion(NO_2^+) although it is likely that more complex constituents must be present in order to account for the results thus far observed. The presence of ionic constituents will of course be made evident by conductance measurements. While these alone cannot be expected to elucidate completely this apparently complicated problem it seemed worthwhile to make this type of attack. Furthermore, even allowing for the instability of such systems it is difficult to reconcile the contradictory conductance values reported by various workers.

Veley and Manley (12), on the basis of a carefully planned investigation, reported measurements for 0–100% nitric acid at 0°, 15°, and 30°C. They note the presence of a minimum in the specific conductance at about 96% nitric acid and report a small negative temperature coefficient of conductance for concentrations slightly greater than this value. Hantzsch (5), on the other hand, was unable to confirm the minimum and asserts that at 0°C. the conductance increases steadily as the water content is increased. The work of Berl and Saenger (1), who carried out a rather extensive physicochemical study of the system nitric acid – nitrogen pentoxide and who have reported specific conductances in this system at 18°C. made it clear that a conductance minimum must exist, as Veley and Manley report. The recent publication of

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Chanukvadze (3), including a conductance investigation of the system water – nitric acid from 0° to 40°C. at 10° intervals, presents data for lower concentrations which are considerably at variance with those of other workers. Chanukvadze does not include sufficient data to ascertain the form of the conductance curve in the region of the minimum reported by Veley and Manley.

We have determined the specific conductances of water – nitric acid mixtures (0–100% acid) at 25°C. Our results are in substantial agreement with those calculated from the data given by Veley and Manley (see Fig. 1). We have made conductance measurements with mixtures rich in nitric acid and with nitric acid – nitrogen pentoxide mixtures at 0°, 18°, 25° and 40°C. Where comparison is possible our results are in fairly good agreement with those reported by Veley and Manley and by Berl and Saenger (see Figs. 1, 1A, 2 and 3).

In view of the difficulty of avoiding completely decomposition of the nitric acid we have determined the influence of nitrogen tetroxide on the conductance of the solutions. In addition the effect of water on nitric acid – nitrogen tetroxide mixtures has been investigated.

Some density and viscosity determinations have been made because these were not available.

Experimental

Materials

Anhydrous nitric acid was prepared by the distillation of sodium nitrate with 98% sulphuric acid at a pressure of approximately 30 mm. It was analyzed gravimetrically using Iceland spar by a method almost identical with that described by Masson (11). The chloramine-T method (13) was used to determine nitrogen tetroxide in the nitric acid. The anhydrous acid as distilled always contained less than 0.05% nitrogen tetroxide although the solutions rich in nitrogen pentoxide sometimes contained as much as 0.2% nitrogen tetroxide after standing for several hours at room temperature. Solutions of nitrogen pentoxide in nitric acid were prepared in the usual manner by distilling a mixture of phosphorus pentoxide and anhydrous nitric acid at a pressure of about 35 mm. Usually about one half of the yellowish distillate consisted of a solid phase which went into solution after removal from the freezing bath. These mixtures were analyzed either gravimetrically as mentioned above or volumetrically by the addition of excess standard sodium hydroxide solution followed by back-titration with hydrochloric acid using phenol red as indicator. Nitrogen tetroxide was prepared from lead nitrate in the usual manner and redistilled into weighed ampoules which were then sealed off, leaving a thin glass tip which could be easily broken off inside the conductance cell.

Procedure

In runs at constant temperature a weighed amount of the nitric acid or nitric acid – nitrogen pentoxide mixture was placed in the conductance cell

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and successive additions of water were made from a Lunge weighing pipette. The cell and contents were cooled in ice water before making the additions so as to minimize decomposition. The above method is not suitable for measurements at elevated temperatures because of decomposition, so that fresh samples of a water – nitric acid or of a nitric acid – nitrogen pentoxide mixture of known composition were placed in the cell for each measurement. Additional experiments were made in which a solution of known composition was placed in the cell and the temperature raised from 0° to 30°C., the conductance being measured at 5° intervals.

In the addition of nitrogen tetroxide to the cell it was found that this substance is so readily soluble in nitric acid mixtures that little loss occurs when the tip of the ampoule is broken off. Density measurements were made using a 25 ml. volumetric flask as a pycnometer. The viscosities were measured in an Ostwald viscometer for which the time of flow of water at 25°C. was about 120 sec. The densities and viscosities are precise to about $\pm 1\%$.

Electrical Measurements

The cells consisted of 250 ml. Erlenmeyer flasks to the bottoms of which were sealed long tubes carrying small platinized electrodes. The cell constants varied between 16 and 60; such high values were necessary because of the high conductances encountered. Electrically controlled oil thermostats (temperatures constant to $\pm 0.02°$) were used for most of the measurements while for those at 0°C. and for those in which the temperature was changed continuously from 0° to 30°C. a water thermostat was employed.

The resistances were measured by means of a direct reading a-c. bridge constructed according to the principles laid down by Jones and Josephs (8). Measurements were made at different frequencies so that polarization effects could be detected and the appropriate corrections applied if necessary (7).

Results

In Table I are presented the specific conductances (x) of water – nitric acid – nitrogen pentoxide mixtures whose compositions are expressed in mole % total nitrogen pentoxide. The results of 12 separate runs are included together with 16 values obtained on individual nitric acid – nitrogen pentoxide mixtures. The results shown in Table I are plotted in Figs. 1 and 1A together with data calculated from the results of Veley and Manley and of Chanukvadze. In Table II are presented the conductances of water – nitric acid mixtures at 0°C., the results being plotted in Fig. 2 in which the data of Hantzsch and of Chanukvadze are included for comparison. In Table III are presented the conductances of water – nitric acid – nitrogen pentoxide mixtures at 18°C.: the results are plotted in Fig. 3, which shows also data published by Veley and Manley and by Berl and Saenger. In Table IV are recorded the conductances of water – nitric acid – nitrogen pentoxide mixtures at 40°C., the values being plotted in Fig. 4. Table V gives the results of experiments in which the conductances of various single water – nitric acid – nitrogen pentoxide mixtures

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were measured at one or more temperatures; the data are plotted in Fig. 5 and the composition of each mixture is recorded on the plots. In Table VI are presented the densities ($D_4^{25°}$) and viscosities of various nitric acid-nitrogen pentoxide mixtures, the values, along with some for water – nitric acid mixtures taken from the literature, being plotted in Fig. 6. In Tables

TABLE I

THE CONDUCTANCE OF WATER – NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT 25°C.

Mole % N_2O_5	$10^2\kappa$	Mole % N_2O_5	$10^2\kappa$
0.03347	1.480	28.27	17.93
0.1049	4.449	32.23	10.45
0.3504	14.00	38.57	4.111
0.8851	32.06	43.63	1.836
1.520	49.15	50.15	3.952
1.486	48.93	41.94	2.284
2.055	60.52	44.51	1.557
2.950	73.32	45.57	1.450
3.825	80.99	46.35	1.473
4.014	81.90	47.14	1.604
4.138	82.72	48.48	2.169
4.306	83.28	48.96	2.508
4.484	83.94	49.47	2.925
4.628	84.50	50.00	3.744
4.226	83.38	50.35	3.366
5.119	85.80	51.42	5.918
5.786	86.22	52.72	10.64
6.913	84.74	54.07	14.25
8.088	81.60		
9.370	77.68	54.86	15.38
11.35	70.95	56.50	16.78
		57.56	16.67
8.619	80.10	58.43	16.27
10.31	74.57	59.54	15.72
12.00	68.98		
14.52	61.23	55.47	16.07
16.60	54.76	57.77	16.94
		60.00	16.16
11.08	71.92		
14.91	59.13		
18.46	48.50		
20.00	43.52	51.06	6.320
		51.61	7.650
12.96	65.76	51.97	9.450
13.85	62.95	52.72	11.99
15.75	57.23	53.29	13.13
17.33	52.31		
20.34	42.34	53.87	14.23
23.54	31.51	53.87	14.27
		54.86	15.75
21.11	39.58	56.71	16.71
23.34	31.87	57.34	16.84
26.51	21.95		
45.57	1.393	57.34	16.84
49.47	3.318	58.43	16.68
		58.43	16.73
		59.09	16.32
		61.39	15.39
		61.39	14.90

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TABLE II

THE CONDUCTANCE OF WATER – NITRIC ACID MIXTURES AT 0°C.

Mole % N_2O_5	10^2x
49.84	3.368
48.45	2.118
46.35	1.390
44.36	1.302
42.63	1.578
40.34	2.241
36.47	4.084
31.28	8.513

TABLE III

THE CONDUCTANCES OF WATER – NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT 18°C.

Mole % N_2O_5	10^2x	Mole % N_2O_5	10^2x
50.16	3.358	50.01	3.703
47.65	1.674	49.81	3.102
46.32	1.403	48.96	2.473
45.70	1.386	48.65	2.314
45.24	1.400	48.10	1.928
43.64	1.651	46.80	1.509
39.40	3.338	45.59	1.400
		44.36	1.497
		41.81	2.192
		40.75	2.602
59.54	14.11	54.07	13.30
58.43	14.69	52.72	9.995
57.56	15.17	51.42	5.711
56.50	15.42	50.35	3.379
54.86	14.26		

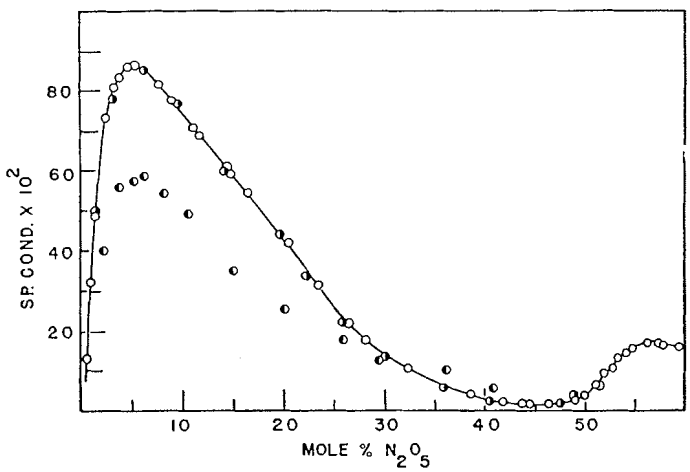

FIG. 1. *The conductance of water – nitric acid – nitrogen pentoxide mixtures at 25°C.* ⊙ *Present investigation;* ◑ *Veley and Manley (interpolated);* ◐ *Chanukvadze (interpolated).*

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VII and VIII are presented results showing the effect of nitrogen tetroxide on the conductance of anhydrous nitric acid and on that of a nitric acid – nitrogen pentoxide mixture respectively; the results are illustrated graphically in Fig. 7. Tables IX and X give the results of adding water to nitric acid and to nitric acid – nitrogen pentoxide mixture respectively, both containing given amounts of nitrogen tetroxide; the data are plotted in Fig. 8.

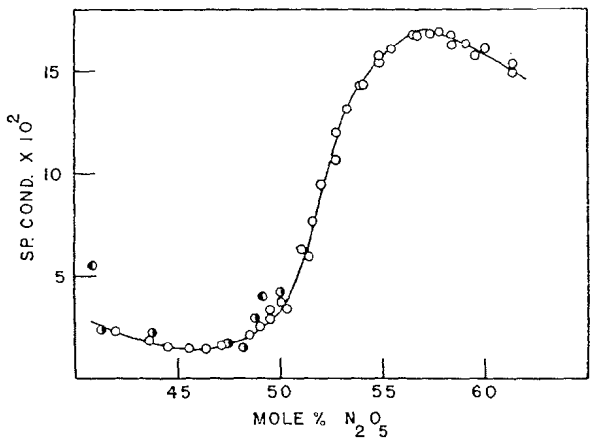

FIG. 1A. *The conductance of water – nitric acid – nitrogen pentoxide mixtures (large scale plot of region rich in nitrogen pentoxide) at 25°C.* ⊙ *Present investigation;* ◑ *Veley and Manley (interpolated);* ◐ *Chanukvadze (interpolated).*

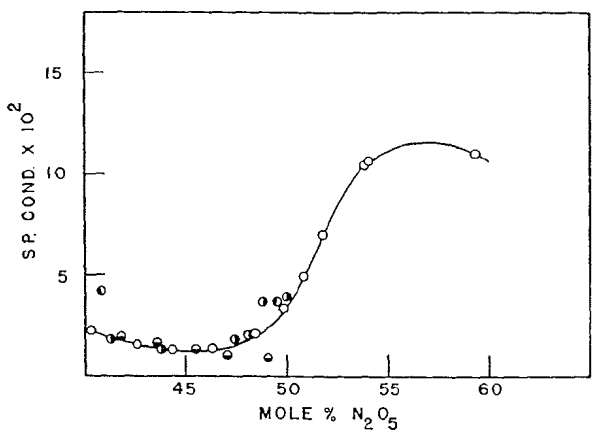

FIG. 2. *The conductance of water – nitric acid – nitrogen pentoxide mixtures at 0°C.* ⊙ *Present investigation;* ◑ *Veley and Manley;* ◐ *Chanukvadze;* ◒ *Hantzsch.*

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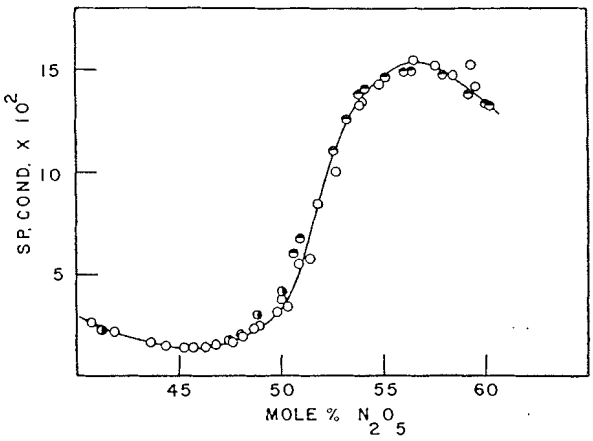

FIG. 3. *The conductance of water – nitric acid – nitrogen pentoxide mixtures at 18°C.* ⊙ *Present investigation;* ◑ *Veley and Manley (interpolated);* ◓ *Berl and Saenger.*

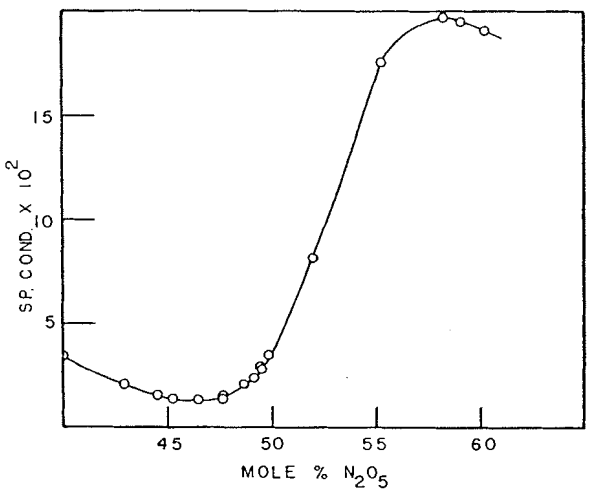

FIG. 4. *The conductance of water – nitric acid – nitrogen pentoxide mixtures at 40°C.*

TABLE IV

THE CONDUCTANCE OF WATER – NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT 40°C.

Mole % N_2O_5	$10^2\kappa$	Mole % N_2O_5	$10^2\kappa$
60.22	19.11	49.84	3.453
59.09	19.54	49.48	2.944
58.21	19.73	48.62	2.042
55.26	17.58	47.64	1.555
51.97	8.166	46.48	1.332
		45.26	1.375
49.97	3.462	44.50	1.544
49.47	2.778	42.89	2.058
49.12	2.330	40.06	3.439
47.63	1.560		

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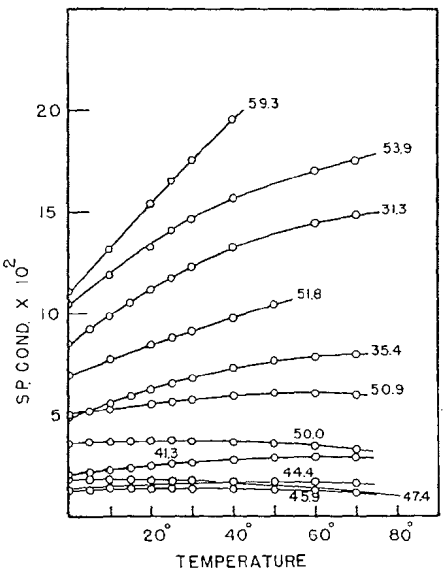

FIG. 5. *The variation of conductance with temperature for various water – nitric acid – nitrogen pentoxide mixtures.*

TABLE V

THE CONDUCTANCE OF WATER – NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT VARIOUS TEMPERATURES

Mole % N_2O_5	31.28	35.44	41.26	44.36	45.88	47.44
Temperature, °C.	Specific conductance × 10^2					
0	8.513	4.840	2.020	1.360	1.288	1.789
5	9.212	5.187	2.150	1.418	1.295	1.778
10	9.835	5.560	2.269	1.470	1.311	1.765
15	10.55	5.918	2.380	1.520	1.322	1.745
20	11.19	6.250	2.485	1.562	1.328	1.720
25	11.74	6.552	2.578	1.596	1.330	1.686
30	12.30	6.813	2.659	1.623	1.328	1.652
40	13.25	7.323	2.796	1.671	1.313	1.579
50		7.637	2.865	1.683	1.282	1.483
60	14.47	7.892	2.910	1.672	1.248	1.395
70	14.80	7.962	2.884	1.638	1.190	1.26

Mole % N_2O_5	50.00	50.86	51.79	53.87	54.07	59.32
Temperature, °C.	Specific conductance × 10^2					
0	3.558	4.931	6.986	10.47	10.63	11.05
5	3.615	—	—	—	—	—
10	3.653	5.262	7.735	11.90	12.15	13.11
15	3.678	—	—	—	—	—
20	3.701	5.551	8.482	13.29	13.63	15.34
25	3.704	5.674	8.840	14.10	14.36	16.51
30	3.690	5.766	9.132	14.63	14.99	17.54
40	3.638	5.952	9.770	15.69	16.22	19.5
50	3.541	6.075	—	—	—	—
60	3.419	6.070	10.47	17.02	17.49	—
70	3.240	5.968	—	17.5	—	—

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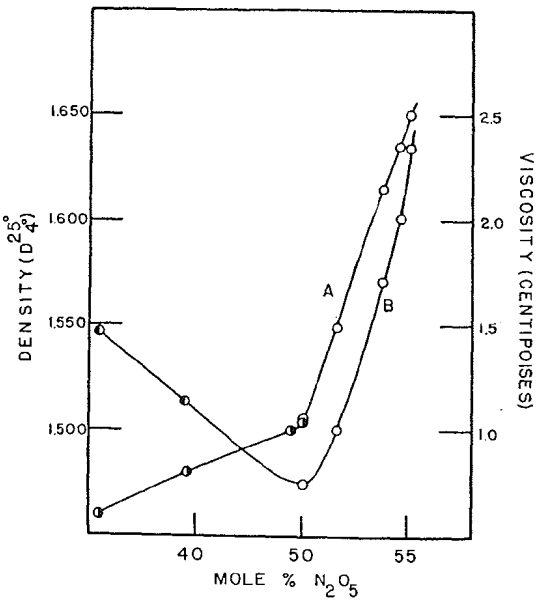

FIG. 6. *The density and viscosity of water – nitric acid – nitrogen pentoxide mixtures at 25°C. Curve A: Densities (left hand scale);* ⊙ *present investigation;* ◑ *interpolated from data given in International Critical Tables (6). Curve B: Viscosities (right hand scale);* ⊙ *present investigation;* ◐ *Bingham and Stone (2).*

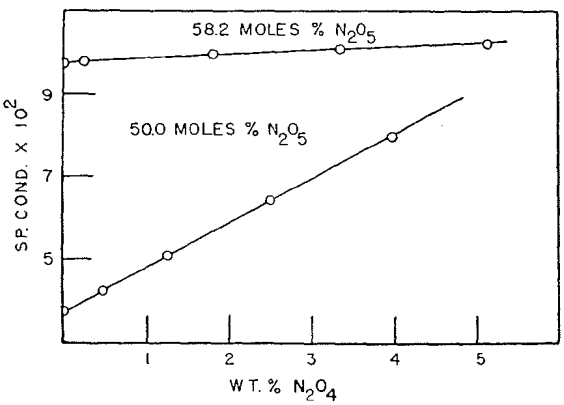

FIG. 7. *The effect of nitrogen tetroxide on the conductance of nitric acid – nitrogen pentoxide mixtures at 25°C.*

TABLE VI

DENSITIES AND VISCOSITIES OF NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT 25°C.

Mole % N_2O_5	Density (d_4^{25})	Viscosity, centipoises
60.2	1.65	2.35
59.1	1.64	2.02
57.6	1.62	1.71
53.3	1.55	1.01
50.2	1.51	0.745

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TABLE VII

THE CONDUCTANCE OF NITROGEN TETROXIDE IN ANHYDROUS NITRIC ACID AT 25°C.

Weight % N_2O_4	10^2x
0.00	3.735
0.469	4.231
1.260	5.098
2.500	6.428
3.986	7.958

TABLE VIII

THE CONDUCTANCE OF NITROGEN TETROXIDE IN A NITRIC ACID – NITROGEN PENTOXIDE MIXTURE CONTAINING 58.43 MOLE % N_2O_5 AT 25°C.

Weight % N_2O_4	10^2x
0.00	16.73
0.251	16.78
1.81	16.93
3.35	17.07
5.14	17.19

TABLE IX

THE EFFECT OF ADDING WATER TO ANHYDROUS NITRIC ACID CONTAINING 4.38% BY WEIGHT OF NITROGEN TETROXIDE AT 25°C.

Weight % H_2O	10^2x
0.00	7.889
0.643	7.088
1.617	6.452
2.785	6.260
3.79	6.32
5.19	6.63
7.15	7.46

TABLE X

THE EFFECT OF ADDING WATER TO NITRIC ACID – NITROGEN PENTOXIDE (58.4 MOLE % N_2O_5) CONTAINING 5.14% NITROGEN TETROXIDE AT 25°C.

Weight % H_2O	10^2x
0.00	17.25
1.122	17.81
2.234	15.80
3.670	10.14
5.67	8.863
7.72	8.715
10.71	9.515
15.41	13.28

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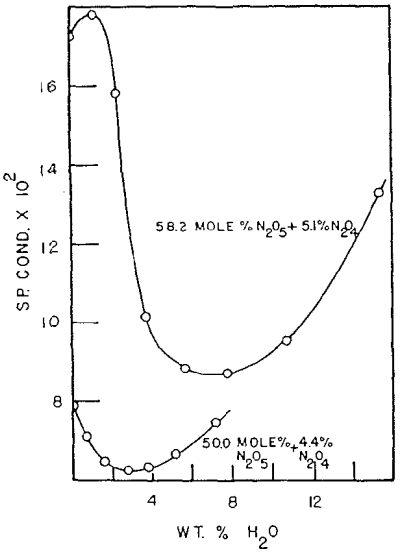

FIG. 8. *The effect of water on the conductance of nitric acid – nitrogen pentoxide – nitrogen tetroxide mixtures at 25°C.*

Discussion

It appears, in accordance with the earlier findings of Veley and Manley and of Berl and Saenger, that the variation of the specific conductance of water – nitric acid – nitrogen pentoxide mixtures with composition is fairly complex. The form of the curve (Fig. 1) is not unlike that for water – sulphuric acid – sulphur trioxide systems (10) although the sulphur system shows a somewhat more complicated behavior, probably because of a more complex ionization of the acid. The conductance maximum observed at about 30% by weight nitric acid (5.5 mole % N_2O_5) is in the same region of weight concentration as those found for other aqueous systems, in which its occurrence has been attributed to ionic hydration phenomena (4). The decrease in the conductance following the initial maximum must be due in part to an increase in viscosity for at 25°C. the viscosity–concentration curve for water – nitric acid passes through a maximum at approximately 70% nitric acid (20 mole % N_2O_5). However, large interionic forces are undoubtedly responsible for the major portion of the decrease. Calculation shows that the equivalent conductance falls to a value of about 0.6 at the minimum following which it rises to about 1.6 at 100% nitric acid. It thus appears that at approximately 97.5% nitric acid (46 mole % N_2O_5) some highly conducting species must be forming in appreciable quantity. That no sharp break is evident in the conductance curve at 100% nitric acid seems to indicate that the newly formed ionic species may be closely related to nitrogen pentoxide. In conformity with recent ideas (9) it is not unlikely that the nitryl ion (NO_2^+) is involved. From this it is but a short step to the assumption that nitrogen pentoxide may ionize thus:

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$$

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On this basis, calculations of the equivalent conductance at 25°C. of nitrogen pentoxide in anhydrous nitric acid as the solvent yield values of from 40 to 50 mhos (the solvent conductance being subtracted from the total conductance to get the true specific conductance of the nitrogen pentoxide) for concentrations of from 0.4 to 3.6 equivalents per liter. These values are not unreasonable although it is realized that the treatment is somewhat arbitrary especially in view of the high solvent conductance.

The effect of temperature on the conductance of various water – nitric acid – nitrogen pentoxide mixtures (Fig. 5) is of considerable interest in throwing light on the nature of the system in the neighborhood of the minimum (45.9 mole % nitrogen pentoxide).

It is striking that for concentrations around this point the conductance varies little with temperature while on either side of the minimum the variation is appreciable. Perhaps a more illustrative picture of the situation is given by Fig. 9 in which the temperature coefficients of specific conductance

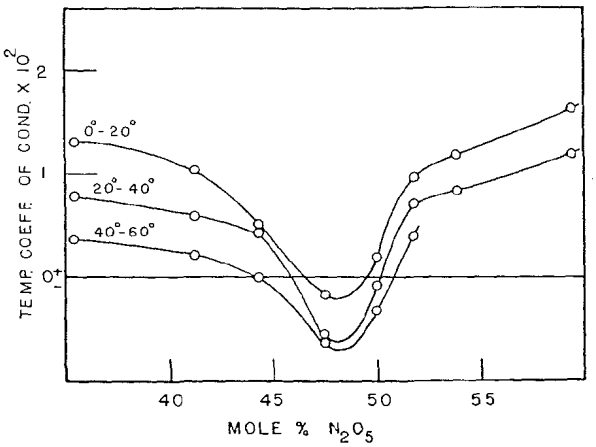

FIG. 9. *The temperature coefficients of conductance* $(1/\kappa \cdot \Delta\kappa/\Delta t)$ *of various water – nitric acid – nitrogen pentoxide mixtures.*

$(1/\kappa \cdot \Delta\kappa/\Delta T)$ have been plotted against mole % nitrogen pentoxide. Here it is clearly brought out that approximately between the minimum in the conductance curve and 100% nitric acid the conductance decreases with increasing temperature. It is in this range we have concluded that some new conducting species is being formed in quantity. Presumably the effect of raising the temperature is to oppose this change, which is probably concerned in some manner with the presence of water. The following simple equilibria may be relevant:

$$\begin{array}{c} B \\ NO_2OH \rightleftharpoons NO_2^+ + OH^- \\ + \\ A \\ NO_3^- + H_3O^+ \rightleftharpoons H_2O \end{array}$$

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We may conjecture that the nitric acid molecule possesses a dual character; the pure acid ionizes as in B, while, upon addition of water, equilibrium A comes into play. The effect of temperature on these two equilibria, the one involving a simple ionization and the other an ionization following a reaction with water, might well be expected to be complex. Some information on this point could doubtless be obtained by an investigation of ultraviolet, infrared, and Raman spectra at different temperatures. In all probability the system we are dealing with between the minimum in the conductance curve and 100% nitric acid consists essentially of equilibrium B and it is well known that the degree of ionization of weak electrolytes may be decreased by increasing temperature. In addition it is probable that equilibrium A is shifted towards the left with increasing temperature since it may be seen from Figs. 1A, 2, 3, and 4 that a slight shift in the conductance minimum from 45 mole % to 46.5 mole % nitrogen pentoxide occurs between 0° and 40°C.

For solutions of nitrogen pentoxide in nitric acid we can expect a positive temperature coefficient of conductance. The conductance maximum which appears at 57 mole % nitrogen pentoxide is doubtless due in large measure to the appreciable increase in the viscosity (Fig. 6).

The chemical instability of systems rich in nitrogen pentoxide prompted us to investigate the influence of nitrogen tetroxide on the conductance property. Fig. 7 shows that for anhydrous nitric acid the conductance is a linear function of the weight % nitrogen tetroxide, at least, for low concentrations of the latter. The effect on the conductance is large, 1/10% nitrogen tetroxide raising the conductance from 3.73×10^{-2} to 3.8×10^{-2}. Since water may also be present we have determined the influence of water on the conductance of anhydrous nitric acid containing nitrogen tetroxide. It should be noted that owing to the opposite effects of nitrogen tetroxide and water on the conductance, a conductimetric analysis of water – nitric acid mixtures (using, say, Fig. 1A) may be in error, owing to mutual cancellation of the effects of such impurities. In Fig. 7 it is shown that the effect of nitrogen tetroxide on the conductance of nitric acid – nitrogen pentoxide mixtures rich in the latter is comparatively small. This fact is fortunate, since it is in these mixtures that small amounts of nitrogen tetroxide are unavoidably present.

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CONDUCTANCE OF AMMONIUM NITRATE IN WATER – NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT VARIOUS TEMPERATURES[1]

By Edward G. Taylor,[2] Charles A. N. Baker, and L. Murray Lyne

Abstract

Conductance measurements have been made with ammonium nitrate in water – nitric acid – nitrogen pentoxide mixtures at various temperatures and over a wide range of concentrations. For all solutions except those rich in nitrogen pentoxide the variation of the specific conductance with the concentration of ammonium nitrate is similar to that observed for many electrolytes in a variety of solvents. With nitrogen-pentoxide-rich solvents however the specific conductance of ammonium nitrate is observed to decrease with increasing salt concentration. This is regarded as indicative of an interaction between the salt and one or more of the components of the nitric acid – nitrogen pentoxide system. The variation of conductance with temperature is normal in all cases. It is shown that ammonium nitrate confers a considerable degree of thermal stability on anhydrous nitric acid.

Introduction

In connection with certain physicochemical studies of various components of the Cyclonite reaction mixture it appeared of interest to carry out conductance measurements with ammonium nitrate in nitric acid and related mixtures. The first reported conductance measurements with this salt in nitric acid (99.4%) were made by Bouty (1) who showed that at 0°C. the solutions were comparatively good conductors. Results are also given for sodium, potassium, rubidium, and thallous nitrates. However, the few data recorded are for relatively low concentrations, although Bouty does remark that as the proportion of alkali metal nitrate is increased the conductance at first increases rapidly, attains a maximum, and then decreases. At the maximum and beyond, the solutions are quite viscous. More recently, Jander and Wendt (2) measured the conductances of several inorganic nitrates in anhydrous nitric acid but here again the measurements have been confined to relatively dilute solutions.

We have measured (1) the conductance of ammonium nitrate in various water – nitric acid – nitrogen pentoxide mixtures at 25°C., (2) the conductance of ammonium nitrate in 100% nitric acid at 25°, 40°, 50°, 60°, and 70°C. It has been shown that, if conductance is any criterion, concentrated solutions of ammonium nitrate are extremely stable as compared with the pure acid.

[1] *Manuscript received in original form November 3, 1950, and, as revised February 14, 1951. Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario. The contents of this paper has been extracted from theses submitted by Charles A. N. Baker (1945) and by L. Murray Lyne (1946) to Queen's University in partial fulfillment of the requirements for the degrees of Master of Science. Our thanks are due to the Associate Committee on Explosives of the National Research Council of Canada for financial assistance.*

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Experimental

The ammonium nitrate was of reagent grade and was powdered and dried *in vacuo* over phosphorus pentoxide before use. The salt was added to the cell from a weighed stoppered glass bottle. Otherwise the experimental details are the same as those described in an earlier paper (4). It was noted that while heat evolution occurred during the solution of ammonium nitrate in 100% nitric acid or lesser concentrations of the latter, heat absorption took place when ammonium nitrate was added to nitric acid containing free nitrogen pentoxide. When the ammonium nitrate content was high and when mixtures rich in nitrogen pentoxide were studied, sufficient gassing (nitrogen tetroxide) occurred at the electrodes to make resistance readings difficult. This is the reason for failure to extend our measurements to high concentrations of ammonium nitrate in nitric acid containing large amounts of free nitrogen pentoxide. It was further noted that if the nitric acid used was slightly yellow, the addition of ammonium nitrate resulted in the production of a colorless solution. When these solutions were kept for as long as three days in the cell, small bubbles of gas formed in the electrode chamber, yet the conductance of the solution remained virtually unchanged over the entire period (care was of course taken to ensure that no bubbles remained in the electrode chamber during a resistance measurement). Certain solutions of high ammonium nitrate content failed to wet the glass walls of the cell properly. We believe, in spite of these possible sources of error, that our results are precise to ± 1 or 2% or better.

Results

In Table I are presented the specific conductance (κ-in mhos) and mole % concentration of ammonium nitrate in various water – nitric acid mixtures at 25°C. The results have been plotted in Figs. 1 and 2. Table II gives data showing the effect of nitrogen tetroxide on the specific conductance of am-

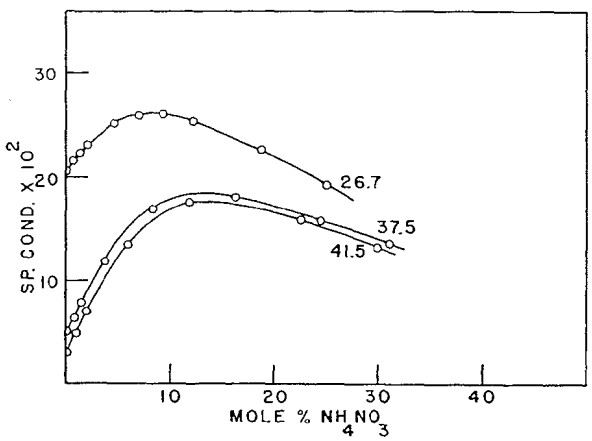

FIG. 1. *The conductance of ammonium nitrate in water-nitric acid mixtures at 25° (on this and other figures the values refer to the mole % total nitrogen pentoxide of the solvent).*

monium nitrate in 100% nitric acid at 25°C.; the data are plotted in Fig. 2 (Curve *A*).

In Table III are presented the specific conductance (κ) for ammonium nitrate in 100% nitric acid at various temperatures: these data are shown graphically in Fig. 3. Table IV gives the results of heating under reflux a concentrated solution of ammonium nitrate in 100% nitric acid for successive one hour periods at three temperatures. In Table V are presented the specific

TABLE I

THE CONDUCTANCE OF AMMONIUM NITRATE IN VARIOUS WATER – NITRIC ACID MIXTURES AT 25°C.

Mole % NH_4NO_3	$10^2\kappa$	Mole % NH_4NO_3	$10^2\kappa$
A. 26.6 mole % N_2O_5		*B. 37.48 mole % N_2O_5*	
0.000	20.54	0.000	5.090
0.644	21.50	0.6619	6.408
1.283	22.25	1.368	7.842
1.977	23.04	3.595	11.87
4.475	25.10	8.280	16.84
6.945	25.96	16.33	18.06
9.293	26.04	24.41	15.85
12.20	25.39	31.04	13.61
18.67	22.75		
24.97	19.25		
C. 41.53 mole % N_2O_5		*D. 44.95 mole % N_2O_5*	
0.000	3.019	0.000	1.527
0.8621	4.920	1.545	5.330
1.844	7.102	3.400	9.377
5.845	13.46	9.570	16.57
11.82	17.55	15.81	17.68
22.55	15.94	23.96	15.30
29.97	13.35	31.97	12.27
E. 50.00 mole % N_2O_5			
0.000	3.865	0.000	3.730
0.7973	5.743	1.204	6.146
1.620	7.129	2.582	8.830
4.627	12.41	5.452	13.46
9.883	17.74	10.51	18.10
16.41	18.73	19.98	17.76
22.22	16.75	29.00	13.79
31.48	12.72	36.68	10.68
38.84	10.00	43.27	8.566
49.30	7.078		
0.000	3.300	25.88	15.17
31.08	12.90	34.14	11.64
34.07	11.79	39.53	9.683
37.24	10.56	44.88	8.066
41.73	9.080		
45.58	7.968		
48.82	7.109		

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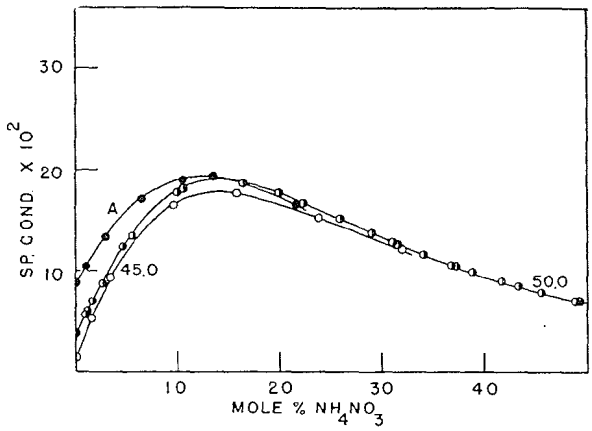

FIG. 2. *The conductance of ammonium nitrate in water – nitric acid mixtures at 25°C.; Curve A is for a 50 mole % total nitrogen pentoxide solvent containing 5.0% by weight of nitrogen tetroxide.*

TABLE II

CONDUCTANCE OF AMMONIUM NITRATE IN 100% NITRIC ACID CONTAINING 5.00% BY WEIGHT OF NITROGEN TETROXIDE AT 25°C.

Mole % NH_4NO_3	$10^2\kappa$
0.000	8.940
0.9474	10.48
2.901	13.35
6.448	17.11
10.45	18.98
13.39	19.28
16.47	18.68
21.59	16.73

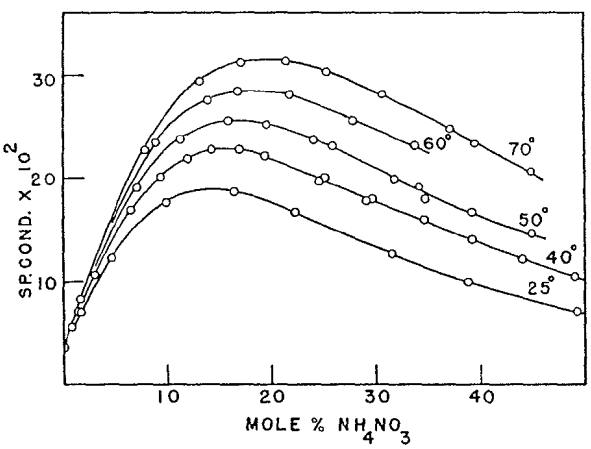

FIG. 3. *The conductance of ammonium nitrate in anhydrous nitric acid at various temperatures.*

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conductance of ammonium nitrate in nitric acid – nitrogen pentoxide mixtures at 25°C.; the results are plotted in Figs. 4 and 5. Finally in Table VI are recorded density and viscosity data for two solutions of ammonium nitrate in nitric acid – nitrogen pentoxide mixtures at 25°C.

TABLE III

CONDUCTANCE OF AMMONIUM NITRATE IN 100% NITRIC ACID AT VARIOUS TEMPERATURES

Mole % NH_4NO_3	$10^2\kappa$	Mole % NH_4NO_3	$10^2\kappa$
A. Temperature, 40°C.			
0.000	3.732	0.000	3.868
0.7744	5.616	25.11	20.12
2.965	10.74	29.74	18.11
6.474	16.93	34.48	16.02
9.263	20.15	39.18	14.01
11.95	21.89	44.00	12.24
14.21	22.65	49.06	10.57
16.90	22.71	54.13	9.75
19.35	22.18		
24.55	19.73		
29.14	17.80		
B. Temperature, 50°C.			
0.000	3.332	25.88	23.18
1.378	7.026	34.14	19.22
7.077	19.05	39.06	16.79
11.23	23.68	44.88	14.66
15.88	25.51		
19.58	25.16		
24.07	23.65		
31.72	19.88		
34.59	18.02		
C. Temperature, 60°C.			
0.000	3.481		
1.631	8.347		
8.915	23.38		
13.85	27.46		
16.78	28.44		
21.71	28.13		
27.83	25.52		
33.71	23.18		
D. Temperature, 70°C.			
0.000	3.397	39.50	23.35
1.369	7.588	44.88	20.62
7.927	22.67		
13.10	29.26		
17.07	31.07		
21.39	31.27		
25.28	30.27		
30.59	28.06		
37.13	24.78		

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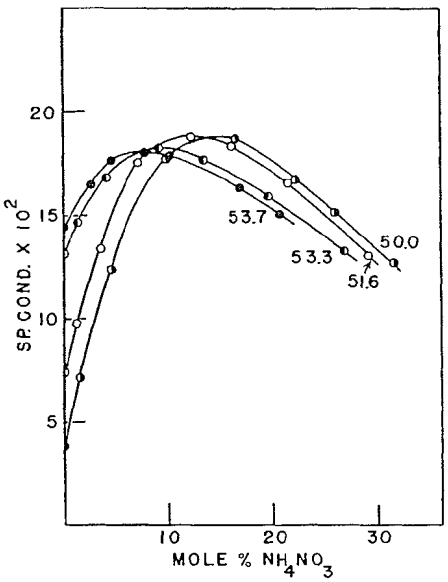

FIG. 4. *The conductance of ammonium nitrate in nitric acid – nitrogen pentoxide mixtures at 25°C.*

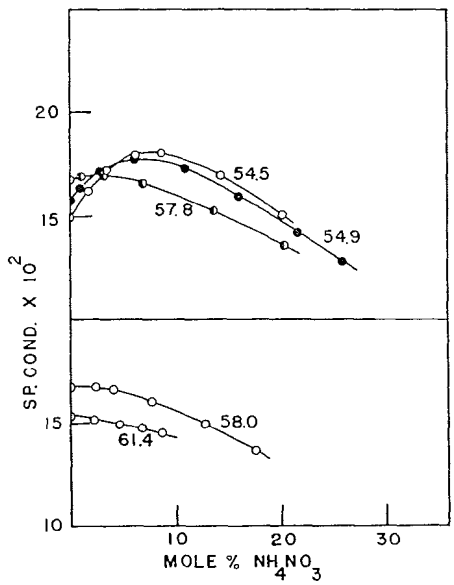

FIG. 5. *The conductance of ammonium nitrate in nitric acid – nitrogen pentoxide mixtures at 25°C.*

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TABLE IV

CONDUCTANCE OF A SOLUTION OF AMMONIUM NITRATE (34.03 mole %) IN 100% NITRIC ACID, BEFORE AND AFTER HEATING UNDER REFLUX FOR ONE HOUR

Temperature of heating, °C.	Initial conductance (25°C.) $10^2\kappa$	Final conductance (25°C.) $10^2\kappa$
60	12.45	12.59
80	12.59	12.62
100	12.62	12.60

TABLE V

CONDUCTANCE OF AMMONIUM NITRATE IN NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT 25°C.

Mole % NH_4NO_3	$10^2\kappa$	Mole % NH_4NO_3	$10^2\kappa$
A. 51.61 mole % N_2O_5		*B. 53.3 mole % N_2O_5*	
0.000	7.370	0.000	13.13
1.258	9.713	1.400	14.68
3.600	13.38	4.184	16.83
8.139	17.55	9.151	18.28
12.34	18.73	13.53	17.73
16.12	18.33	19.57	15.94
21.42	16.57	26.82	13.31
29.11	13.08		
C. 53.68 mole % N_2O_5		*D. 54.46 mole % N_2O_5*	
0.000	14.41	0.000	14.90
2.681	16.48	1.715	16.20
4.597	17.62	3.512	17.21
7.862	18.02	6.231	17.91
10.17	17.93	8.684	18.02
16.85	16.32	14.30	16.98
20.72	15.08	20.17	15.06
E. 54.86 mole % N_2O_5		*F. 57.78 mole % N_2O_5*	
0.000	15.75	0.000	16.76
0.9543	16.34	0.9459	16.92
2.795	17.13	3.143	16.98
6.149	17.73	6.870	16.60
10.98	17.33	13.56	15.24
16.04	15.98	20.28	13.60
21.59	14.20		
25.86	12.84		
G. 58.0 mole % N_2O_5		*H. 61.4 mole % N_2O_5*	
0.000	16.73	0.000	15.35
2.334	16.74	2.100	15.15
4.036	16.61	4.525	14.93
7.688	16.04	6.694	14.73
12.58	14.96	8.734	14.53
17.51	13.67		

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TABLE VI

DENSITIES AND VISCOSITIES OF SOLUTIONS OF AMMONIUM NITRATE IN NITRIC ACID – NITROGEN PENTOXIDE MIXTURES AT 25°C.

Mole % N_2O_5	Mole % NH_4NO_3	Density (d^{25}_4)	Viscosity (centipoises)
53.68	0.000	1.558	1.060
53.68	20.72	1.580	4.27
58.00	0.000	1.620	1.553
58.00	17.08	1.594	3.88

Discussion

Figs. 1, 2, and 3 show that ammonium nitrate is a normal electrolyte over the concentration and temperature ranges we have investigated. The usual maximum appears in the conductance–concentration curves, and it may be noted that it is shifted towards higher concentrations of ammonium nitrate as the temperature is increased. Undoubtedly the increasing viscosity is an important factor in causing this behavior. Calculation of the equivalent conductance of ammonium nitrate in anhydrous nitric acid at 25°C. gives values of 85 mhos at about 0.2 *N* and 76 mhos at about 1.3 *N*. Owing to the high solvent conductance it seems pointless to explore these values further but it may be remarked that such values are quite reasonable in comparison with those found in water for the same salt.

The effect of ammonium nitrate in stabilizing nitric acid towards the action of heat is remarkable (see Table IV).

As seen from Figs. 4 and 5, the presence of free nitrogen pentoxide in the nitric acid exerts an appreciable effect on the conductance increment due to added ammonium nitrate. The increased viscosity (Table VI) may be partly responsible for the large diminution in the extent to which ammonium nitrate raises the conductance of nitric acid – nitrogen pentoxide mixtures. It is however difficult to understand why the conductance of a solution containing 61.4 mole % nitrogen pentoxide falls almost continuously as ammonium nitrate is added (See Fig. 5). Possibly a repression of the ionization of the free nitrogen pentoxide is partly responsible for the effects observed. The formation of molecular nitrogen pentoxide may be the reason for the extreme instability noted for these systems. The apparent stabilization of 100% nitric acid by ammonium nitrate may be explained thus:

$$\begin{array}{ccc} HNO_3 & \rightleftharpoons & N_2O_5 + H_2O \\ & & \uparrow\downarrow \\ & & NO_2^+ + NO_3^- \end{array}$$

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At any rate it seems plausible that these two phenomena are somehow related although it must be admitted that in the absence of additional data these hypotheses are largely speculative.*

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* *One of the referees has suggested the following as the mode of interaction of ammonium nitrate with the nitric acid – nitrogen pentoxide system*:

$$NH_4NO_3 + NO_2^+ + NO_3^- \cdot \rightarrow [NH_3.NO_2]^+ + NO_3^- + HNO_3$$

The $[NH_3 \cdot NO_2]^+$ *ion is suggested as the ammono analogue of the nitracidium ion. We had previously envisaged such an interaction but, because of the similarity in the ultraviolet absorption spectra of potassium and ammonium nitrates in anhydrous nitric acid (3) and because the conductance curves for the two salts are quite similar (5), we had decided that the ammonium ion offered no specific interaction possibilities. However, because of the specificity of ammonium nitrate in the Cyclonite reaction mixture such a suggestion is certainly plausible in the absence of further information.*

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SOME FREEZING POINT AND CONDUCTANCE MEASUREMENTS IN THE SYSTEM NITRIC ACID – ACETIC ACID[1]

By Edward G. Taylor[2] and Alan G. Follows

Abstract

An independent investigation of the phase diagram for the solid–liquid system nitric acid – acetic acid has confirmed the findings of Miskidzh'yan and Trifonov (4), namely, that a 1 : 1 molecular compound exists. Conductance measurements at 0°, 25°, and 40°C. have been made for the same system. It does not appear possible to predict compound formation from the conductance measurements alone. A preliminary investigation of the liquid–vapor equilibrium for the system nitric acid – acetic acid indicates the existence of a maximum boiling azeotrope. Diacetylorthonitric acid—$(CH_3COO)_2N(OH)_3$—discovered by Pictet and Genequand (8) is, in all probability, identical with this binary azeotrope. Some molecular weight measurements tend to confirm this view.

Introduction

The investigation of the properties of nitric acid – acetic acid systems is of importance in connection with nitration processes. To this end Briner, Susz, and Favarger (1) carried out Raman spectra, viscosity, and freezing point measurements in this system. From their results they concluded the existence of a loose addition compound composed of one molecule of each acid. A detailed solid–liquid phase diagram cannot be drawn on the basis of the sketchy data (see Fig. 1) reported and it was deemed desirable to obtain more points for this purpose. In addition we decided to measure the conductances of nitric acid – acetic acid mixtures over a wide range of concentrations at 0°, 25°, and 40°C. Subsequent to the completion of the present investigation Miskidzh'yan and Trifonov in 1947 (4) (6) and Naumova in 1949 (7) reported density, viscosity, conductance, and freezing point measurements for this system. Miskidzh'yan and Trifonov report a rather large change in conductance with time, and some of their data together with those of Naumova differ from ours (see Figs. 2 and 3). While we have noticed a change of conductance with time, it is small—averaging about 0.2% per hour—and in view of the time taken for a run we estimate our precision to be ± 1% or better. Furthermore, almost all of our points obtained in independent runs lie on the same smooth curve for the same temperature. We have therefore reported our conductance data for 0° and 25°C. as well as those at 40°C. for which no data are available. In determining the freezing point curve for the nitric acid – acetic acid system we have found that the results reported by Briner *et al.* differ somewhat from ours, which are in excellent agreement with those obtained by Miskidzh'yan and Trifonov.

[1] *Manuscript received in original form November 3, 1950, and, as revised February 14, 1951. Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario. The contents of this paper has been extracted from a thesis submitted by Alan G. Follows in 1945 to Queen's University in partial fulfillment of the requirements for the degree of Master of Science. Our thanks are due to the Associate Committee on Explosives of the National Research Council for financial assistance.*

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Experimental

Materials

Anhydrous nitric acid was prepared as described in an earlier paper (10). Acetic acid (commercial grade, m.p. 16.47°C.) was two-thirds frozen and after removal of the liquid phase the remainder was distilled over anhydrous calcium sulphate using a 20 in. Vigreux column. The middle fraction (about 50%), which was used in the measurements, possessed a specific conductance of about 1×10^{-8} mhos; its melting point was 16.60°C.

Carbon tetrachloride, used in calibrating the thermometer, was purified by successive washings with concentrated sulphuric acid, water, aqueous potassium hydroxide, and water, followed by distillation after drying over calcium chloride.

Procedure

The freezing point measurements were made in a simple Beckmann apparatus using dry ice and alcohol as the freezing mixture. A pentane thermometer (range +35° to −135°C.) calibrated against the melting points of carbon tetrachloride [−22.85°C.(11)] and of anhydrous nitric acid (−41.5°C. (3)) was used. Melting points were determined by the thaw-melt method of Rheinboldt, Hennig, and Kircheisen (9), and are believed precise to ±0.2°C.

For the conductance runs acetic acid was added to the nitric acid in the cell by means of a Lunge weighing pipette. Cooling of the nitric acid was undertaken in order to minimize decomposition due to the heat evolved when the liquids are mixed. The details of the electrical measurements have been given in an earlier paper (10).

Results

A. Freezing Point Measurements

In Table I are presented the melting points of various nitric acid – acetic acid mixtures. The data are plotted in Fig. 1, on which the data of Briner,

TABLE I

THE MELTING POINTS OF NITRIC ACID – ACETIC ACID MIXTURES

Mole % HNO_3	Melting point, °C.
0.000	16.6
19.55	− 6.8
27.12	−24.9
32.57	−41.1
40.42	−30.0
49.43	−24.7
49.84	−23.9
61.72	−30.6
70.45	−45.9
86.74	−49.9
100.0	(−41.6)

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Susz, and Favarger, and those of Miskidzh'yan and Trifonov are included for comparison.

B. Conductance Measurements

In Tables II, III, and IV are presented the conductances of nitric acid – acetic acid mixtures at 0°, 25°, and 40°C. respectively, together with the concentrations of the solutions expressed in mole % acetic acid. The results of at least three independent runs are reported. The data are plotted in Figs. 2, 3 and 4, on which are also included data obtained by Miskidzh'yan and Trifonov and by Naumova for purposes of comparison.

TABLE II

THE SPECIFIC CONDUCTANCES OF NITRIC ACID – ACETIC ACID MIXTURES AT 0°C.

Mole % CH_3COOH	$10^2\kappa$	Mole % CH_3COOH	$10^2\kappa$
0.000	3.593	53.49	0.1279
6.088	2.043	57.73	0.08369
12.28	1.303	61.05	0.05624
16.62	1.005	63.19	0.04705
20.85	0.8629	66.47	0.03186
26.31	0.7285	67.76	0.02668
31.74	0.5895	70.83	0.01826
34.94	0.5069	72.39	0.01479
44.24	0.2797	75.74	0.00906
70.92	0.01815		
72.84	0.01360		
76.12	0.00822		
79.83	0.00448		
83.05	0.00247		

TABLE III

THE SPECIFIC CONDUCTANCES OF NITRIC ACID – ACETIC ACID MIXTURES AT 25°C.

Mole % CH_3COOH	$10^2\kappa$	Mole % CH_3COOH	$10^2\kappa$
0.000	3.734	26.86	0.9541
8.150	1.842	30.51	0.8535
14.53	1.289	33.79	0.7535
19.88	1.110	36.08	0.6805
26.37	0.9700	40.70	0.5364
30.98	0.8456	43.27	0.4588
		48.11	0.3316
		52.13	0.2432
49.20	0.3060	74.50	0.02256
53.24	0.2233	85.21	0.003948
57.57	0.1516	92.17	0.000792
62.29	0.09538	94.58	0.000320
66.01	0.06379	97.00	0.0000695
68.20	0.04967		
70.73	0.03621		
73.35	0.02680		
75.30	0.02006		

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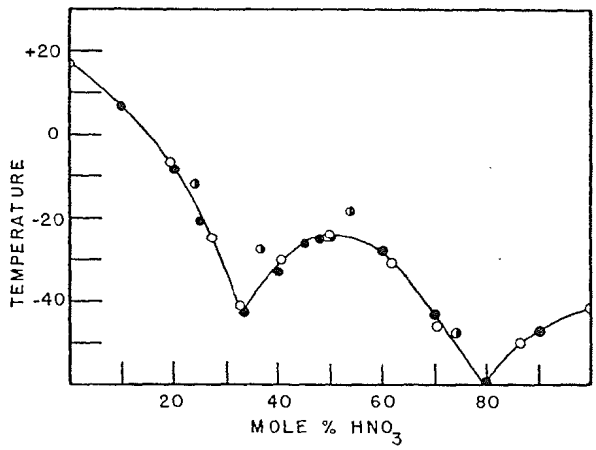

FIG. 1. *The melting points of nitric acid – acetic acid mixtures.* ○ *Present investigation;* ◑ *Briner, Susz, and Favarger;* ● *Miskidzh'yan and Trifonov.*

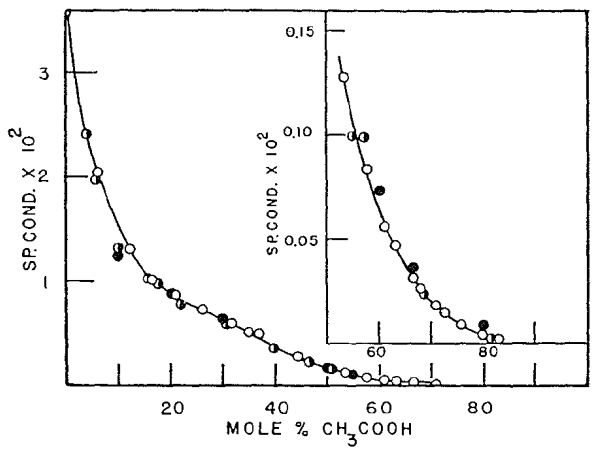

FIG. 2. *The conductance of nitric acid – acetic acid mixtures at 0°C.* ○ *Present investigation;* ● *Miskidzh'yan and Trifonov;* ◑ *Naumova.*

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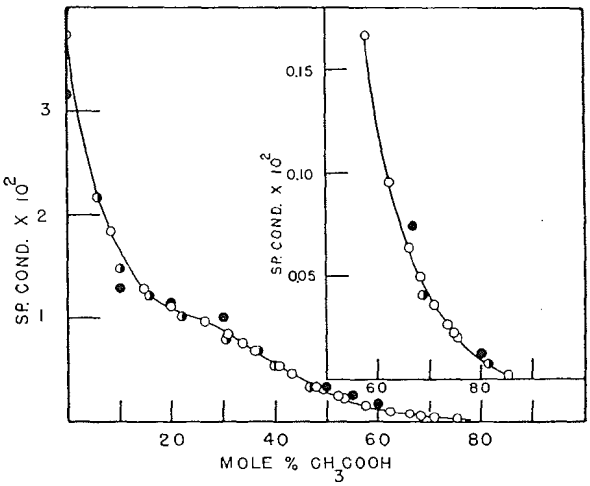

FIG. 3. *The conductance of nitric acid – acetic acid mixtures at 25°C.* ○ *Present investigation*; ● *Miskidzh'yan and Trifonov*; ◑ *Naumova.*

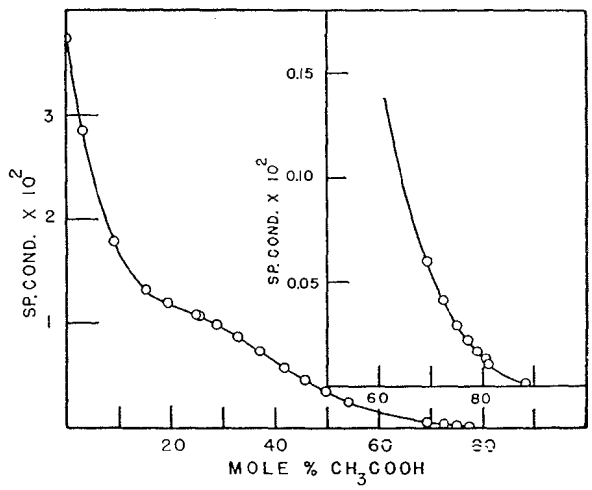

FIG. 4. *The conductance of nitric acid – acetic acid mixtures at 40°C.*

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TABLE IV

THE SPECIFIC CONDUCTANCES OF NITRIC ACID – ACETIC ACID MIXTURES AT 40°C.

Mole % CH_3COOH	$10^2\kappa$	Mole % CH_3COOH	$10^2\kappa$
0.000	3.739	25.49	1.064
3.045	2.852	28.81	0.9855
8.996	1.789	32.84	0.8695
15.18	1.322	37.02	0.7372
19.39	1.195	41.70	0.5851
24.94	1.080	45.80	0.4598
		49.81	0.3506
		54.07	0.2533
69.24	0.05987	80.94	0.01069
72.49	0.04118	88.15	0.002865
75.03	0.02963	93.16	0.000696
77.18	0.02222	95.97	0.000234
78.93	0.01681		
80.56	0.01360		

Discussion

A. Freezing Points

As indicated by the data of Briner, Susz, and Favarger, and confirmed by Miskidzh'yan and Trifonov, our results, shown in Fig. 1, point to the existence of a molecular compound—$HNO_3 \cdot CH_3COOH$. No indication is seen of the existence of diacetylorthonitric acid, of which such frequent mention is made throughout the literature following the early work of Pictet and Genequand (8) who reported the discovery of such a compound.

B. Conductances

Based on the ideas of Usanovich and Naumova (12) both Miskidzh'yan and Trifonov and Naumova have attempted to demonstrate the existence of compound formation in solution using plots of the temperature coefficients of conductance ($1/\kappa . \triangle\kappa/\triangle T$) against concentration. Marked changes in the slopes of such curves have been taken as indicative of compound formation. Miskidzh'yan and Trifonov state that for nitric acid – acetic acid mixtures there is a maximum in the plot of temperature coefficient of conductance at about 67 mole % acetic acid. This may be taken as evidence of the compound $HNO_3 \cdot 2CH_3COOH$ although their interpretation of the mechanism of the interaction between the two acids is then described in terms of the compound $HNO_3 \cdot CH_3COOH$ which is formulated as $(CH_3COOH_2)^+(NO_3)^-$. Naumova, on the other hand, notes the appearance of an inflection point at 67 moles % acetic acid which is taken as indicative of $HNO_3 \cdot 2CH_3COOH$.

We have calculated temperature coefficients of conductance from our results at 0°, 25°, and 40°C. It appears to us that the temperature coefficient rises steadily from about 1% at 20 mole % acetic acid to about 5% at 80 to 90 mole % acetic acid. To be sure, the curves are somewhat irregular, especially for the 0°–20°C. and 25°–40°C. ranges, but we attribute such discontinuities

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to the unavoidable errors in the interpolation from data which are not extremely precise. As justification for this view we find that the curve for the 0°–40°C. range is almost a straight line within the experimental error. In addition it must be remembered that since we are dealing with a difference in conductance, any errors in the actual conductance values are magnified and will cause larger errors percentagewise in the temperature coefficient of conductance. For the nitric acid – acetic acid system at least, it does not appear possible to us to deduce the existence of compound formation on the basis of conductance measurements.

C. Miscellaneous Observations

Viscosity isotherms reported by Miskidzh'yan and Trifonov (4) show maxima at about 60 mole % acetic acid. Those reported by Naumova (7) show maxima at about 62 mole % acetic acid although it is stated that the maxima occur at about 67 mole % acetic acid. Where comparison is possible (at 0°C.) there is but poor agreement between the viscosity–composition curves of these workers. Certainly the conclusion reached by Naumova indicating the existence of a compound $HNO_3 \cdot 2CH_3COOH$ does not appear valid. From surface tension and refractive index measurements Miskidzh'yan and Trifonov (5) found only evidence of a 1 : 1 molecular compound between acetic acid and nitric acid. Further evidence that the only interaction between the two acids is along these lines only has been adduced by Chedin and Feneant (2) on the basis of Raman spectra measurements.

The existence of Pictet's diacetylorthonitric acid thus appears unsupported by all available data. Since the discovery by Pictet and Genequand of what was taken as a definite compound—$(CH_3COO)_2N(OH)_3$—was based primarily on the results of a distillation procedure it was decided to investigate the liquid–vapor equilibria for the system nitric acid – acetic acid. The results are of a preliminary nature only but are strongly suggestive of the presence of a maximum boiling azeotrope at about 65 to 70 mole % acetic acid. In order to minimize decomposition the fractionations were carried out at reduced pressures. Two boiling point – composition curves were obtained—one at 100 mm. and the other at 200 mm.—the maximum boiling points being 77° and 95°C. respectively. The general shapes of the curves show an appreciable difference between the liquid and vapor compositions around the azeotropic composition. It is thus possible to explain the observations of Pictet and Genequand regarding the distillations of nitric acid – acetic acid mixtures. The large main fraction will obviously possess the azeotropic composition which corresponds roughly with the formula assigned by them to diacetylorthonitric acid. As confirmation for our view that this so-called "compound" is merely a mixture of the two acids we have determined the "molecular weights" of (1) a 2 : 1 mole mixture of acetic acid and nitric acid respectively and (2) the "diacetylorthonitric acid" prepared according to the distillation method described by Pictet and Genequand. Freezing point depressions in ethylene bromide yield values of approximately 170 for the "molecular weight" in both cases, in

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reasonable agreement with a value of 185 recorded for "diacetylorthonitric acid" by Pictet and Genequand. The simple mixture thus appears to be identical with the "compound" obtained on distillation. The high observed "molecular weight" can perhaps be attributed to departure from ideal behavior or to intermolecular association. In acetic acid as a solvent we have obtained cryoscopic molecular weights of from 215 to 240, while Pictet and Genequand report a value of 238 for the "compound". These values are, however, readily explained since if we really have a mixture of 1 mole of nitric acid and 2 moles of acetic acid the calculated molecular weight of *nitric* acid comes out about 70. Furthermore, a rough measurement of the "molecular weight" of the "compound" from the freezing point depression in dioxane gave a value of 66.

Pictet and Genequand report that the specific gravity of "diacetylorthonitric acid" is 1.189 at 23°C. and that its refractive index is 1.3843 (μ_D at 23°C.). Both these constants are suspiciously close to those obtained for a straight 1 : 2 mole mixture of nitric acid and acetic acid—density, 1.187 at 25°C. (7) and refractive index 1.3816 (μ_D at 35°C.) (5).

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DROPPING AMALGAM ELECTRODES[1]

By R. C. Turner and C. A. Winkler

Abstract

The anodic limiting current at a lead amalgam dropping electrode is shown to be proportional to the concentration of the lead in the amalgam, at constant flow rate. The original Ilkovic equation does not apply to the anodic limiting current from dropping amalgam electrodes.

The anodic limiting currents with lead and cadmium amalgams have been found to agree with the 2nd approximation of the Ilkovic equation, as derived by Strehlow and Stackelberg for this process, for flow rates in the region below approximately 1.2 mgm. per sec. With flow rates greater than this, the lead amalgams gave a linear relation between the anodic limiting current divided by concentration and the mass flow rate. With cadmium amalgams no such linear relation was evident and the magnitude of the limiting current depended on the size of the drops as well as on the mass flow rates. The half wave potentials of lead and cadmium were found to depend on the flow rate of the dropping electrode.

Introduction

Strehlow and Stackelberg (6) have shown, both theoretically and experimentally, that the original Ilkovic equation does not apply to the limiting current from the oxidation of metals in an amalgam dropping electrode. They derived, as second approximation of the Ilkovic equation, the following expression for this process:

$$I_{d-} = 607nCD^{1/2}\, m^{2/3}\, t^{1/6}\,(1 - KD^{1/2}\, m^{-1/3}\, t^{1/6}) \qquad (1)$$

or

$$I_{d-}/Cm^{2/3}\, t^{1/6} = 607nD^{1/2} - 607nKDm^{-1/3}\, t^{1/6}\,, \qquad (2)$$

where C is the concentration (millimoles per liter) of metal in the amalgam, I_{d-} is the anodic limiting current (microamperes), D is the diffusion coefficient of the metal in the amalgam (square centimeters per second), m and t are respectively the mass flow rate (milligrams per second) and drop time (seconds per drop) and K is a constant. In the same paper, it was shown that the half wave potential of a metal soluble in mercury is not independent of the mass flow rate and drop time of the dropping electrode.

In a thesis presented at this University by one of the authors (8) in September 1949, results were given which showed, among other things, that the anodic limiting current from the oxidation of the metals in lead, cadmium, and zinc amalgam dropping electrodes is not expressed by the original Ilkovic equation, as had been formerly assumed (2, 3). A calculation was also given to show that the half wave potential from a dropping amalgam could not be strictly constant with changing rates of flow for these metals. This was done by assuming I_{d-}/c equal to k_a in the equation

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$$E_{1/2} = E^1 + \frac{RT}{nF} \ln \frac{f_s\, k_a}{f_a\, k_s}, \qquad (3)$$

where $E_{1/2}$ is the half wave potential, E^1, R, n, T, and F are constants, f_s and f_a are respectively the activity coefficients of ions in solution and metals in the amalgams at the amalgam–cell solution interface, and k_s is equal to 605 $nD^{1/2}\, m^{2/3}\, t^{1/6}$ (of the Ilkovic equation $I_d = 605\, nD^{1/2}\, m^{2/3}\, t^{1/6}\, C$). At the time when the paper by Strehlow and Stackelberg appeared, work was in progress to determine (*a*) the true relation between the anodic limiting current, mass flow rate, and drop time of a dropping amalgam electrode, and (*b*) the effect, if any, of the flow rate on the half wave potential of lead and cadmium.

In the present paper are given the results of the investigations that have been made in this laboratory. The amalgams used were 6 to 15 times more dilute than the cadmium amalgam used by Strehlow and Stackelberg (6) and the range of flow rates was greater. In general, the results are in agreement with their conclusions.

Experimental

For part of the work, the polarographic equipment was essentially of the standard manually operated type (3). There was, however, a small glass cup, supported by a handle attached to the stopper of the cell, under the end of the dropping electrode. This served to prevent the amalgam from falling into the quiet pool of mercury and allowed the amalgam to be removed to determine

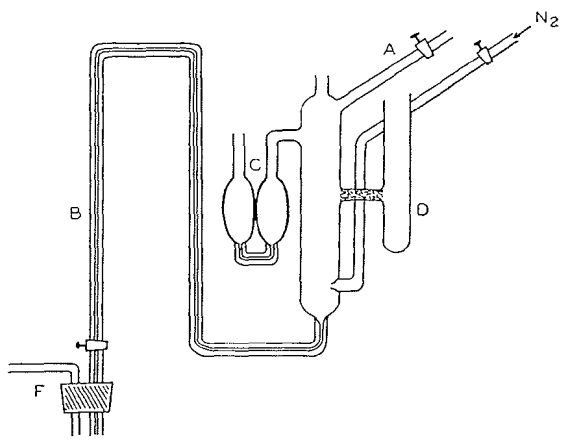

FIG. 1. *Polarographic cell.*

its weight. During the investigation, the cell shown in Fig. 1 was introduced for operational convenience. The capillary of the dropping electrode (0.05 mm. bore) passed through the hole in the top of the cell and was sealed in place with de Khotinsky cement. The cell could be supplied with electrolyte through *A* without dismantling the apparatus. Amalgam could be removed to determine its weight, or the cell completely emptied, through the capillary

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B by suction supplied to an Erlenmeyer flask attached to F. The quiet electrode D, which was a saturated calomel electrode, was attached to the cell through an asbestos packed tube. A trap, C, allowed escape of the purified nitrogen (9) which was bubbled through the solution to remove oxygen. The cell, except the straight part of capillary B to which F was attached was suspended in a constant temperature water bath which was maintained at 25 ± 0.02°C.

Amalgams were prepared in an Erlenmeyer flask; the flask had a short piece of glass tubing sealed to the bottom, and one end of the electrode capillary was sealed into the tubing with de Khotinsky cement. The flask was swept with nitrogen or carbon dioxide prior to dissolving the metal in the mercury. The mass flow rate of the amalgam was controlled with nitrogen or carbon dioxide pressure.

The indifferent electrolyte was 0.1 M potassium chloride and the maximum suppressor used was methyl violet in the early work which was later replaced with 0.01% gelatine. Dilute amalgams were generally used as the dropping electrodes but a few experiments were made using mercury. All currents were corrected for residual current.

During the investigation into the effect of mass flow rate on the half wave potential, the potential of the quiet electrode was checked, at the beginning and at intervals during each experiment, against a second saturated calomel electrode. The potential of the dropping electrode was calculated from the external potential applied, with reference to the saturated calomel electrode used for checking the working half cell. Correction was applied for the IR drop of the cell and the circuit resistance in series with the cell. Half wave potentials were determined from plots of $\log \frac{I - I_{d-}}{I_{d+} - I}$ versus E (7), where I is the current corresponding to a given potential E, and I_{d+} is the cathodic diffusion current, with the convention that I_{d-} is negative and I_{d+} is positive.

Results and Discussion

During the early work, a beaker was used as the electrolytic cell and the mass flow rate was determined immediately after an experiment was made. Fig. 2 shows the proportionality obtained between the anodic limiting current and lead concentration when this concentration was varied from 0 to 0.89 millimolar. The effect of variation in flow rate on the anodic limiting currents for lead, cadmium, and zinc amalgams are shown respectively in Tables I, II, and III. In all cases the quantity $I_{d-}/Cm^{2/3}t^{1/6}$ varied directly with flow rate while with lead and cadmium the ratio $I_{d+}/Cm^{2/3}t^{1/6}$ was relatively constant. When sufficient methyl violet was added to the cell solution to prevent a maximum in the anodic current from the zinc amalgam, it was found that the cathodic current was practically nonexistent regardless of the zinc concentration in solution. The results in Table III were therefore obtained without the addition of zinc ions to the solution.

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It was found that changing the concentration of lead acetate in solution from 0 to 2.5 millimolar had an insignificant effect on the anodic limiting current, with a lead amalgam of 0.82 millimolar concentration. It was concluded that the anodic limiting current was not affected by the rate at which metal ions diffused away from the drop.

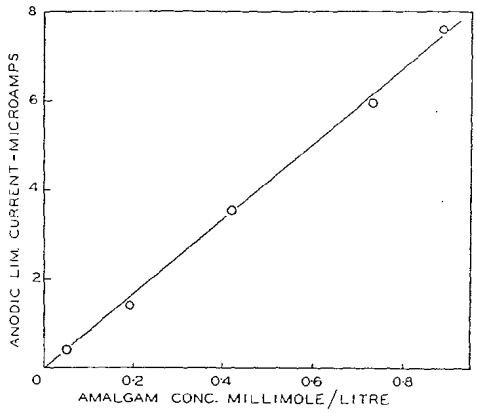

FIG. 2. *Effect of concentration of lead amalgam on the anodic limiting current.*

TABLE I

EFFECT OF FLOW RATE OF LEAD AMALGAM ON THE LIMITING CURRENTS

Amalgam concentration: 0.69 millimolar.
Electrolyte: 0.1 *M* potassium chloride, 0.002 *M* hydrochloric acid, 0.50 millimolar lead acetate, trace of methyl violet

Drop time, sec./drop	Flow rate, mgm./sec.	$m^{\frac{2}{3}} t^{\frac{1}{6}}$	$I_{d+}/m^{\frac{2}{3}} t^{\frac{1}{6}}$*	$I_{d-}/m^{\frac{2}{3}} t^{\frac{1}{6}}$
3	2.49	2.21	2.31	3.33
4	1.93	1.95	2.28	3.05
5	1.59	1.78	2.30	2.89
6	1.29	1.60	2.31	2.59

* *Subsequent analysis of the lead acetate salt used in this experiment showed that it contained more lead than was indicated by the formula on the reagent bottle.*

TABLE II

EFFECT OF FLOW RATE OF CADMIUM AMALGAM ON THE LIMITING CURRENTS

Amalgam concentration: 1.20 millimolar.
Electrolyte: as in Table I, except 1.00 millimolar cadmium chloride instead of lead acetate

Drop time, sec./drop	Flow rate, mgm./sec.	$m^{\frac{2}{3}} t^{\frac{1}{6}}$	$I_{d+}/m^{\frac{2}{3}} t^{\frac{1}{6}}$	$I_{d-}/m^{\frac{2}{3}} t^{\frac{1}{6}}$
3	2.62	2.28	3.71	7.57
4	2.14	2.09	3.57	6.00
5	1.67	1.84	3.66	5.82
6	1.40	1.69	3.73	5.75

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TABLE III

EFFECT OF FLOW RATE OF ZINC AMALGAM ON THE ANODIC LIMITING CURRENT

Amalgam concentration: 2.08 millimolar.
Electrolyte: 0.1 *M* potassium chloride, 0.002 *M* hydrochloric acid, methyl violet.

Drop time, sec./drop	Flow rate, mgm./sec.	$m^{\frac{2}{3}}t^{\frac{1}{6}}$	$I_{d-}/m^{\frac{2}{3}}t^{\frac{1}{6}}$
3	2.51	2.22	10.95
4	1.85	1.90	10.32
5	1.56	1.69	9.88
6	1.20	1.52	9.67
7	1.05	1.43	9.09

In the subsequent work the cell shown in Fig. 1 was used, carbon dioxide replaced nitrogen over the amalgams, and gelatine was used in place of methyl violet. The mass flow rates were determined while the limiting currents were flowing. The lead amalgams varied from 0.30 to 1.37 millimolar and the cadmium amalgams were 0.47 and 0.54 millimolar. Cadmium chloride, 0.54 millimolar, or lead nitrate, 0.50 millimolar, was added to the cell solution when the presence of cadmium or lead ions was desired. By using three different capillaries, mass flow rates varying from 0.07 to 6.66 mgm. per second were obtained.

(*a*) *Relation Between Flow Rate of Dropping Amalgam Electrodes and Anodic Limiting Currents*

The lower section of Fig. 3 shows that a plot of the anodic limiting current divided by the concentration of lead in the amalgams against mass flow rate gave a linear relation over a range of flow rates from about 0.5 to 4.4 mgm. per sec., regardless of the size of the drops. On the other hand, with the cadmium amalgam (upper section of Fig. 3) this linear relation does not exist, even for a given drop size. The magnitude of the limiting current apparently depends on both the size of the drops and the mass flow rate. With both metals, however, the curves in Fig. 3 are similar in the region below mass flow rates of 0.5 mgm. per sec., in that they both bend sharply toward zero current for zero flow rate. The curves calculated from Equation (1) (the values for D and K are explained later) agree reasonably well with the experimental results up to mass flow rates of roughly 1.2 mgm. per sec.

The results taken from Fig. 3 were plotted to conform to the treatment used by Strehlow and Stackelberg (6), that is, $I_{d-}/Cm^{2/3}t^{1/6}$ is plotted against $t^{1/6}/m^{1/3}$. According to Equation (2), this should yield a straight line with slope $-607\ nkD$ and intercept on the $I_d-/Cm^{2/3}t^{1/6}$ axis equal to $607\ nD^{1/2}$. Sufficient results were available for only 8.70 mgm. drops with cadmium amalgams and 9.35 mgm. drops with lead amalgams to indicate a definite trend. A few results for very slow flow rates with lead amalgams of drop weights between 6.00 and 7.00 mgm. are also shown. In the lower section of Fig. 4 the straight line is that found experimentally by Strehlow and Stackelberg for cadmium amalgam with K equal to 28.5. It apparently fits the

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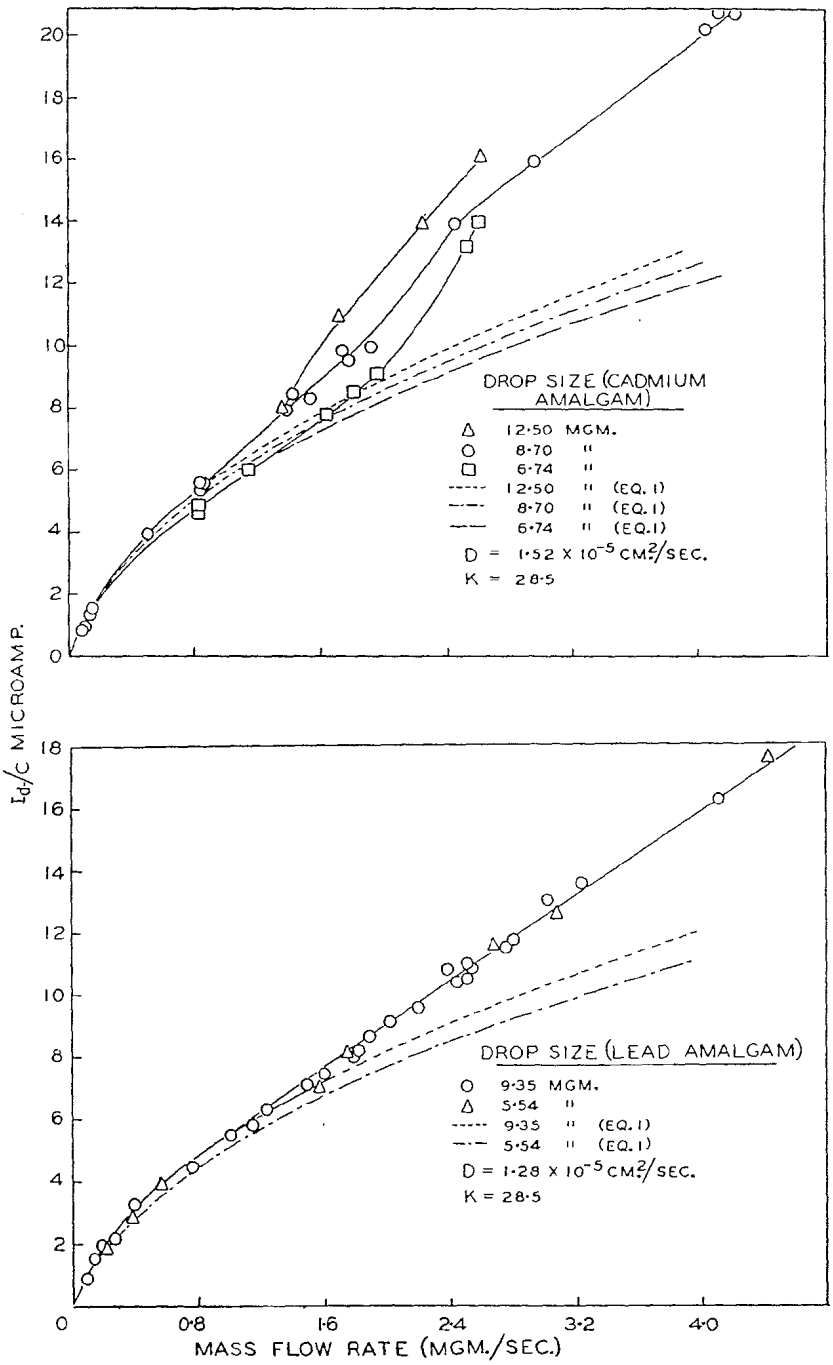

FIG. 3. *Effect of flow rate of amalgam on the anodic limiting current.*

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present results for values of $t^{1/6}/m^{1/3}$ from 1.4 to 5.2. For values of $t^{1/6}/m^{1/3}$ below 1.2 the experimental values deviate from the line rather abruptly, supposedly because of the rinse effect (6). In the upper section of Fig. 4, which shows the same plot for lead amalgams, the straight line was drawn through the experimental points with a slope and intercept given by Equation

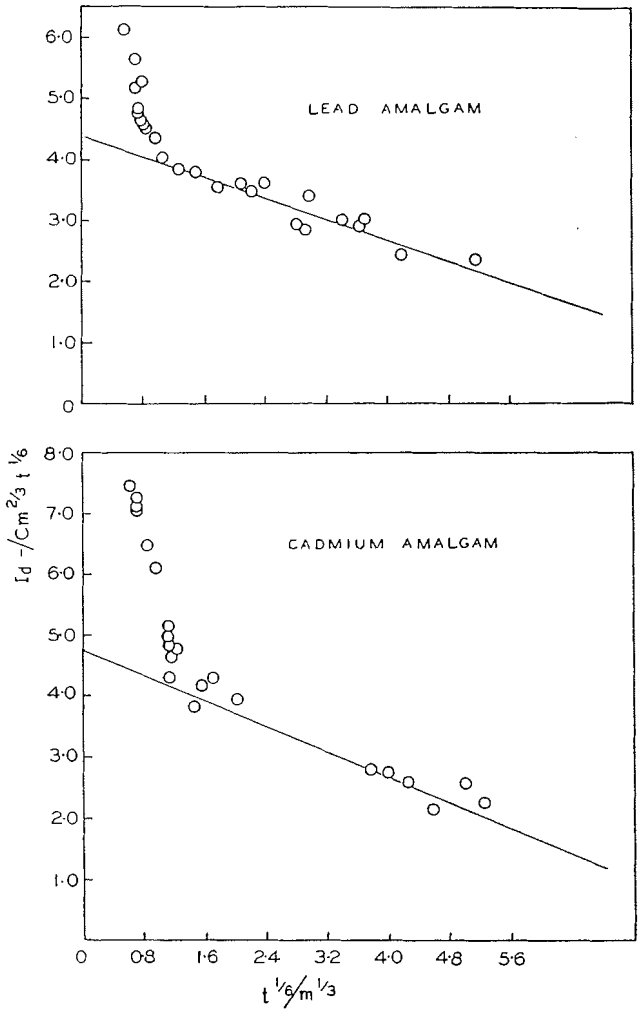

FIG. 4. *$I_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$ versus $t^{\frac{1}{6}}/m^{\frac{1}{3}}$ plot for amalgams.*

(2) (K equal to 28.5). The diffusion coefficient for cadmium in mercury, calculated from the straight line in the lower section of Fig. 4, is 1.52×10^{-5} cm^2. per sec. (6) and for lead the diffusion coefficient, calculated in the same way from the upper section of Fig. 4, is 1.28×10^{-5} cm^2. per sec. Admittedly, slightly different straight lines could be drawn in Fig. 4, which would fit the experimental results and Equation (2), and thus correspond to somewhat differ-

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ent diffusion coefficients. However, the fact that the calculated diffusion coefficients are of the right order of magnitude (1, 10) increases confidence in Equation (1).

Some of the average anodic limiting currents with flow rates less than 0.2 mgm. per sec. were calculated from the area under current–time curves for individual drops. This procedure gave essentially the same results as the usual method with a damped galvanometer.

(b) Effect of Flow Rate on the Half Wave Potential of Lead and Cadmium

The log $\dfrac{I - I_d -}{I_{d+} - I}$ versus E plots were straight lines for both lead and cadmium (Fig. 5) with reciprocal slopes of -0.032. This is in general agree-

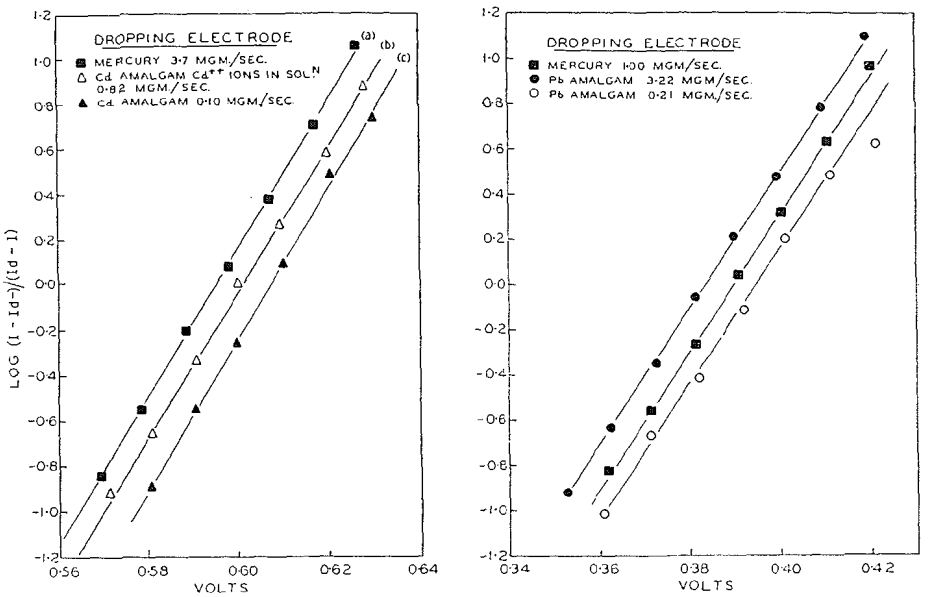

FIG. 5. *Current-potential relation.*

ment with the results reported for dropping amalgam electrodes (5) and also conforms to the theoretical reciprocal slope of -0.03 for 25°C. Apparently, from the left section of Fig. 5, the type of electrode reaction taking place had no effect on the shape or slope of the curves, since Curve (*a*) was entirely reduction of ions, Curve (*b*) was entirely oxidation of metal atoms, and Curve (*c*) was both oxidation and reduction.

The effect of mass flow rate of the dropping electrode on the half wave potential is summarized in Fig. 6. The results were similar for the two metals, that is, an increase of flow rate was accompanied by a less negative half wave potential. This agrees with the results of Strehlow and Stackelberg (6) for

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the reduction of cadmium and tellurium ions. At very slow flow rates the half wave potentials were much more negative than for flow rates generally used in polarography. Possibly convection currents in the cell solution became an important factor at the very fast flow rates (4).

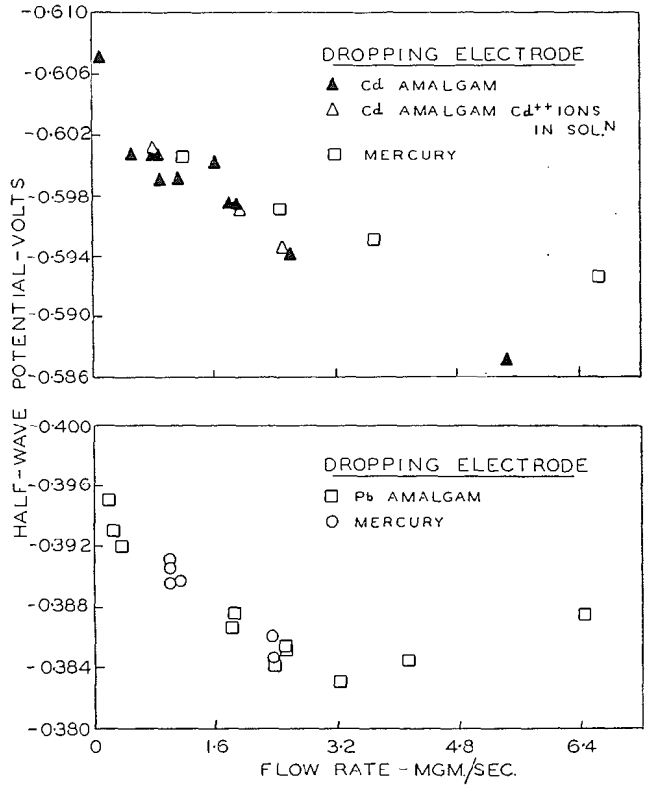

FIG. 6. *Effect of flow rate of the dropping electrode on half wave potentials.*

Acknowledgment

Grateful acknowledgment is made to the Committee on Research, McGill University, for financial assistance in the preparation of this manuscript.

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PREPARATION OF N-SUBSTITUTED UREAS FROM NITROSOMETHYLUREAS[1]

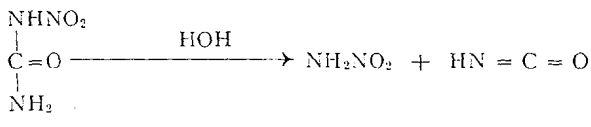
By Jean L. Boivin[2] and Paul A. Boivin[3]

Abstract

Good yields of N-substituted ureas were obtained by reacting amines with N-nitroso-N-methylurea in aqueous solution. It has been shown that N-nitroso-N-methylurea decomposed into methylnitrosamide and isocyanic acid. Similarly, N-nitroso-N, N'-dimethylurea and amines gave rise to good yields of N-substituted-N'-methylureas.

Introduction

Davis and Blanchard (4) have shown that nitrourea (I) decomposed in aqueous solution into isocyanic acid (III) and nitramide (II) which is transformed into nitrous oxide (IV) and water. The formation of isocyanic acid was inferred from the reaction of nitrourea in aqueous solution with amines to yield N-substituted ureas, quantitatively in several instances.



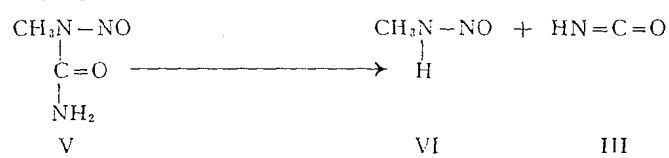
(1)

I II III

(2)

IV

The reaction of nitrosoureas with amines has not been studied. However, it may be postulated that N-methyl-N-nitrosourea (V) decomposes in aqueous solution into N-methyl-N-nitrosamide (VI) and isocyanic acid (III) according to the mechanism suggested by T. L. Davis (Equations (1) and (2)). In strongly alkaline solution compound V is known to yield diazomethane. When N-methyl-N-nitrosourea (V) was boiled in aqueous solution, the stoichiometric amount of nitrogen was evolved and the solution was found to contain isocyanic acid and methanol. With amines, as was expected, the isocyanic acid produced yielded N-substituted ureas (VII) according to the following equation:–



(3)

V VI III

[1] *Manuscript received January 8, 1951.*
Contribution from the Organic Section of the Canadian Armament Research and Development Establishment, Valcartier, Quebec, and the Chemical Laboratories of University of Ottawa, Ottawa, Ont.
[2] *Defence Research Board, Valcartier, Quebec.*
[3] *University of Ottawa, Ottawa, Ontario.*

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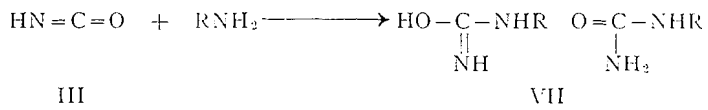


(4)

Table I shows some of the substituted ureas prepared, together with their physical properties and yields. Nearly quantitative yields were obtained and in several cases purification was unnecessary.

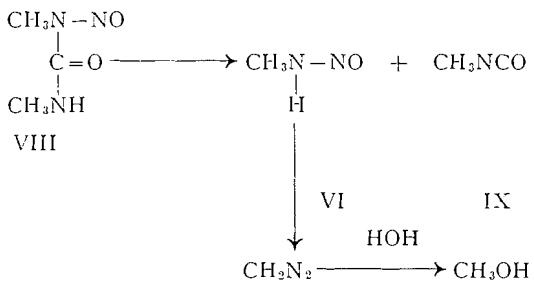
TABLE I

N-SUBSTITUTED UREAS[1], $RNHCONH_2$ (VII)

N-Substituent R	Reaction time, min.	Yield, %	M.p. °C. Observed	M.p. °C. Recorded	Solvents	Ref.
Methyl	5	96.1	101	102	Ethanol plus ether	4
Ethyl	5	92.1	92	92-92.4	Ethanol plus ether	4
n-Propyl	5	86.8	107	107	Ethanol plus ether	3
n-Butyl	5	85.8	96	96	Ethanol plus ether	4
n-Amyl	3	70.8	75[2]	75	Water	5
n-Hexyl	5	88.6	109.5	109.5	Water	7
Cyclohexyl	12	86.8	195-196	195-196	Water	11
Phenyl	20	91.0	146-147	147	Water	4
Benzyl	15	80.0	147-147.5	147-147.5	Water	13
Amino	1	100	227-234d	214-235d	Ethanol	10
Anilino	5	100	172	171-172	Ethanol	8
p-Tolyl	20	85.3	181-182	181-182	Ethanol	12
p-Chlorophenyl	30	90.4	212d	212d	Ethanol	15
Diethyl	1	91.9	75	75-75.3	Ether	4

[1] *All melting points are uncorrected.* [2] *Isolated as the nitrate.*
[3] *Semicarbazide isolated as its benzal derivative.*

In addition to this series of N-substituted ureas, other derivatives of ureas were made from N, N′-dimethyl-N-nitrosourea (VIII). This starting material has been found to decompose in aqueous solution according to the following scheme:–



(5)

When compound VIII was boiled with water, nitrogen was evolved quantitatively in accordance with Equation (5), and methyl isocyanate (IX) was formed as was shown by its hydrolysis to methylamine and carbon dioxide. Similarly to N-nitroso-N-methylurea, the reaction of amines with N-nitroso-N, N′-dimethylurea proceeded through the formation of methyl nitrosoamide

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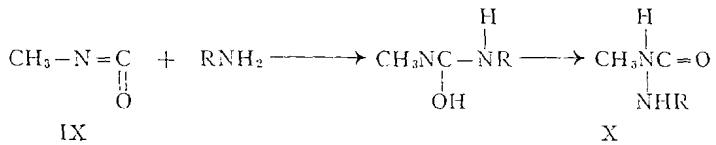
(VI) and methyl isocyanate (IX), the latter reacting with amines to yield N-methyl-N′-substituted ureas (X).



(6)

IX X

The yields were excellent and, in most cases, the N-substituted-N′-methylureas did not require further purification. The results are given in Table II.

TABLE II

N-SUBSTITUTED-N′-METHYLUREAS, $RNHCONHCH_3$ (X)

N-Substituent R	Reaction time, min.	Yield, %	M.p. °C.		Solvents	Ref.
			Observed	Recorded		
Methyl	12	73.8	100	100	Ether	6
Ethyl	3	88.0	52-53	52-53	Ether	14
n-Propyl[1]	5	84.3	67-68		Ether	
n-Amyl[2]	2	94.3	75-76		Diluted ethanol	
Cyclohexyl[3]	3	90.4	157-158		Diluted ethanol	
Phenyl	12	77.7	150.5-151.5	150.5-151.5	Diluted ethanol	6
Benzyl	4	84.2	98-99	98-99	Diluted ethanol	9
Anilino	20	76.0	154-155	154-155	Water	6
Amino	2	92.1	114-115	112-118	Ethanol plus ether	2
p-Tolyl	10	87.1	178	178	Ethanol	1
p-Chlorophenyl	10	88.7	200	200	Diluted ethanol	1

[1]*Calc. for* $C_5H_{12}ON_2$: *N, 24.1%. Found: N, 23.8%*
[2]*Calc. for* $C_7H_{16}ON_2$: *N, 19.4%. Found: N, 19.3%.*
[3]*Calc. for* $C_8H_{16}ON_2$: *N, 17.9%. Found: N, 17.2%.*

Experimental

Effect of Boiling Water on N-methyl-N-nitrosourea

In a flask equipped to measure the gas evolved was placed N-methyl-N-nitrosourea (3.8450 gm.; 0.0414 mole) and water (125 ml.). The mixture was boiled and the solid dissolved with evolution of gas. The volume of gas which was collected over a solution of sodium hydroxide (20%) was found to be 808 ml. (calc. 816 ml.). The presence of isocyanic acid was shown in the following way: A slight excess of silver nitrate was added to the solution and a white precipitate soluble in ammonia and nitric acid was formed. However, the amount of isocyanic acid produced was not quantitative.

The presence of methyl alcohol was shown by the oxidation of a portion of the solution with potassium dichromate in strong sulphuric acid. After distilling a portion of this solution, the distillate contained formaldehyde as was shown by the derivative obtained with 2, 4-dinitrophenylhydrazine, m.p. 166–167°C.

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Effect of Boiling Water on N-Nitroso-N, N'-dimethylurea

Using the procedure described above, N-nitroso-N, N'-dimethylurea (2.6920 gm.) was boiled with water. Nitrogen evolved: 542 ml. (calc. 552 ml.). No precipitation took place with a silver nitrate solution, indicating the absence of isocyanic acid. The formation and identification of methylamine and carbon dioxide indicated the transient formation of methyl isocyanate. The presence of methyl alcohol was demonstrated as described above.

Preparation of N-substituted ureas (VII)

N-Methyl-N-nitrosourea (0.1 mole) was reacted with an amine (0.1 mole) in aqueous solution (200 ml.). The solution was boiled until the evolution of gas ceased. Then it was evaporated under reduced pressure and the residue recrystallized from a suitable solvent. Results are listed in Table I. In several cases, recrystallization did not change the melting point of the product.

Preparation of N-Substituted-N, N'-dimethylurea (X) from N, N'-Dimethyl-N-nitrosourea (VIII)

The procedure used for the preparation of these substances was the same as the one described above for the preparation of N-substituted ureas (VII). The results are listed in Table II.

Acknowledgment

The authors express their thanks to the Defence Research Board of Canada for permission to publish this paper.

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6-IODOMETAMECONINE AND 3-IODOMETAHEMIPINIC ACID[1]

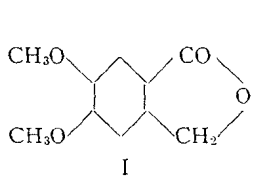
By J. A. McRae, R. B. VanOrder, F. H. Griffiths, and Thelma Eskin Habgood

Abstract

6-Iodo-*m*-meconine has been prepared from *m*-meconine by several steps and oxidized to 3-iodo-*m*-hemipinic acid. The orientation of the iodo-*m*-meconine is based on its conversion to 4, 5, 6-trimethoxyphthalide. The identity reported by Rây and Robinson of the bromo-*m*-meconine made directly by similar steps from *m*-meconine with that from 2-bromoveratric acid and formaldehyde could not be confirmed. The former substance has the orientation ascribed to it by Rây and Robinson but the identity and orientation of the latter substance is left in doubt. Attempts to form a substituted diphenyl ether from dimethyl 3-iodo-*m*-hemipinate and the potassium salt of methyl vanillate failed.

Some years ago we became interested in the halogenated metameconines as possible intermediates in the synthesis of 2, 3, 2′-trimethoxydiphenyl ether-5, 6, 4′-tricarboxylic acid which it was thought might be a degradation product of the alkaloid cularine (12). Our efforts to make this substance have so far failed but the substituted metameconines themselves proved to be of considerable interest and we now report on our work on some of these.

Owing to the work of Edwards, Perkin, and Stoyle (3) and that of Rây and Robinson (16) *m*-meconine (I) is now a relatively easily accessible substance.



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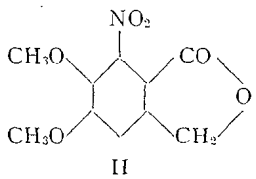

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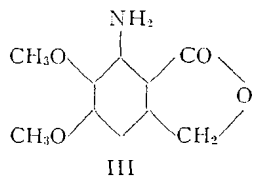

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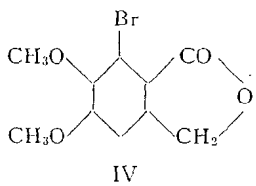

IV

Rây and Robinson stated also that *m*-meconine could be easily nitrated in the 6-position to give II and that this nitro compound could be reduced to the amine (III) which in turn could be transformed through a diazo reaction into 6-bromo-*m*-meconine (IV), melting point 223°C. This same bromo-*m*-meconine, according to these authors, could be produced also by the action of formaldehyde on 2-bromoveratric acid (V), a method of synthesis which seemed to leave no doubt as to the structure of the 6-bromo-*m*-meconine made from

[1] *Manuscript received November 6, 1950.*
Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.

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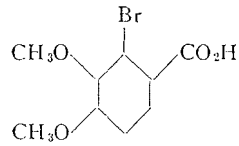
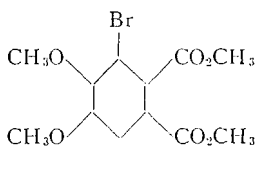


V

m-meconine, and thus establishing as well the orientation of compounds (II) and (III). When their work was repeated nitro-*m*-meconine and amino-*m*-meconine were found to have the melting points ascribed to them by Rây and Robinson but the 6-bromo-*m*-meconine produced from amino-*m*-meconine melted at 207°C. More significantly this bromo-*m*-meconine was found not to be identical with the substance made from 2-bromoveratric acid which had indeed a melting point of 223°C. A mixed melting point determination made on these two substances showed a large depression; these observations have been repeatedly verified by ourselves and other workers in these laboratories. The proof of the orientation of the substance IV offered by Rây and Robinson was clearly inadequate.

The orientation advanced by Rây and Robinson for 6-nitro-*m*-meconine (IV) and for the corresponding amino and bromo compounds is nevertheless correct. When the bromo-*m*-meconine, melting point 207°C. made from amino-*m*-meconine was oxidized, and the acid produced esterified by means of diazomethane, dimethyl 3-bromo-*m*-hemipinate (VI) was obtained identical in properties with the authentic ester described by Faltis and Frauendorfer



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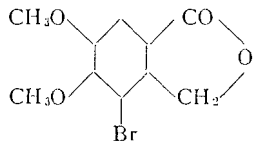

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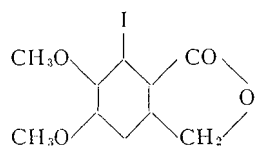
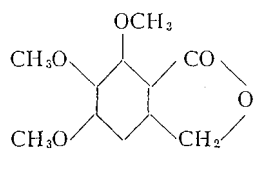
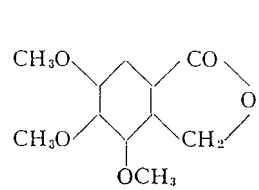


VIII

(4). The bromo-*m*-meconine was therefore either 6-bromo-*m*-meconine (IV) or 3-bromo-*m*-meconine (VII). When diazotized amino-*m*-meconine was treated with potassium iodide an iodo-*m*-meconine (VIII) was obtained. This on treatment with potassium methylate gave the new substance 4, 5, 6-trimethoxyphthalide (IX). The structure of this phthalide was obvious since it proved to be not identical with the known 3, 4, 5-trimethoxyphthalide (X)



IX



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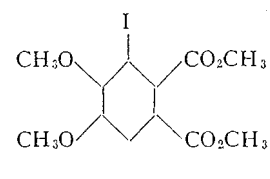

XI

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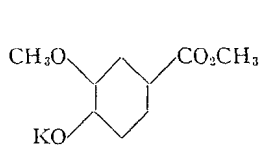
made from gallic acid by Alimchandani and Meldrum (1) and by King and King (11) and therefore structure (IX) was the only other possibility for the substance made from this iodo-*m*-meconine. In this way the orientation of substances (II), (III), and (IV) was verified.

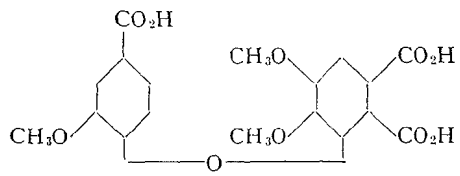
The reactions just mentioned provide a convenient route to certain substituted *m*-meconines and the corresponding *m*-hemipinic acids, otherwise difficult to obtain. Faltis and Frauendorfer (4) prepared 3-bromo-*m*-hemipinic acid by a lengthy synthesis from papaverine; Manske, Ledingham, and Holmes were unable to obtain 4, 5, 6-trimethoxyphthalide (IX) from 2, 3, 4-trimethoxybenzoic acid with either formaldehyde or chloral. We have been unable to synthesize phthalides bearing an iodo or nitro group by the action of formaldehyde on iodo-or nitro-veratric acids respectively. In contrast 3-iodo-*m*-hemipinic acid was readily prepared by the oxidation of 6-iodo-*m*-meconine (VIII) and characterized as its dimethyl ester (XI).

The structure of the substance of melting point 223°C. derived in very small yield from 2-bromoveratric acid and formaldehyde is still under investigation.

Dimethyl 3-bromo-*m*-hemipinate and 3-iodo-*m*-hemipinate were applied in an attempted synthesis of 2, 3, 2′-trimethoxydiphenyl ether-5,6,4′-tricarboxylic acid (see formula XIII). Faltis, Holzinger, Ita, and Schwarz (5) pointed out that the formation of diphenyl ether – carboxylic esters from metallic phenolates and halogenated methoxybenzoic esters becomes rapidly more difficult as the number of groups ortho to the proposed ether linkage increases. This difficulty has been verified by Manske (12) and ourselves. No reaction occurred when dimethyl 3-bromo-*m*-hemipinate (VI) was heated under a variety of conditions with the potassium salt of methyl vanillate (XII) in the presence of copper powder. When the more reactive dimethyl 3-iodo-*m*-hemipinate was used in place of the bromo ester the expected ether (XIII) was not produced. Instead veratric acid was the only substance isolated, the dimethyl 6-iodo-*m*-hemipinate acting as a methylating agent. This interesting example of methylation was observed by us in 1939 prior to the description of similar instances by King (9) and King and Wright (10). The latter authors have discussed the subject fully. Following the example of Faltis, Holzinger, Ita, and Schwarz (5) we sought to avoid this undesired reaction by reacting 6-iodo-*m*-meconine with potassium methyl vanillate, hoping thereby to form a substance which could be oxidized to the desired tricarboxylic acid. Although a reaction occurred a pure product was not isolated. Experiments with these reactants are being continued.



XII



XIII

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Experimental

meta-Meconine

Some changes were made in the method of Rây and Robinson (16). Veratric acid was made from vanillin by methylation (2) and oxidation (3). Then veratric acid (50 gm.), glacial acetic acid (250 ml.), concentrated hydrochloric acid (200 gm.), and a solution of formaldehyde (40%, 60 ml.) were heated together with stirring under reflux at 90 – 95°C. for 10 hr. and then at 100°C. for a further three hours. The crude material was sometimes isolated by the method of Rây and Robinson in yields of 55–65%; recrystallization from glacial acetic acid gave a pure product of melting point 155°C. At other times the reaction mixture was diluted with water (500 ml.), cooled with stirring, and filtered from some deposited tars. The filtrate was then evaporated almost to dryness, the residue taken up in boiling water (1500 ml.), again filtered from a fragrant tar, and the filtrate cooled. Fawn-colored needles, melting point 154–156°C*., were recovered in a yield of 33%.

6-Nitro-m-meconine

The method here described was found to give greater yields than the method of Rây and Robinson (16). A cold mixture of concentrated sulphuric acid (10 ml.) and concentrated nitric acid (40 ml.) was mechanically stirred and cooled in an ice bath while *m*-meconine (28 gm.) was added over a period of one hour. After the addition was complete, more concentrated nitric acid (100 ml.) was added, the mixture stirred for four hours, and treated with ice (300 gm.). The yellow precipitate was recovered, washed repeatedly with water, and then with boiling alcohol (100 ml.). When crude *m*-meconine isolated by the method of Rây and Robinson was used for nitration, the yield of the crude 6-nitro-*m*-meconine was only 48–56%, but when the purer *m*-meconine obtained by the alternative method described above was nitrated, the yield of crude 6-nitro-*m*-meconine was 71%, and its melting point was 178.5–179.5°C. Repeated recrystallization of the product from ethanol and from glacial acetic acid raised its melting point to 182.0–182.5°C.; Rây and Robinson reported 183–184°C.

6-Amino-m-meconine

The nitro compound was converted to the hydrochloride of 6-amino-*m*-meconine by the method of Rây and Robinson (16) in yields of 75%. Conversion of the salt to the free amine followed by recrystallization of the amine from dilute alcohol gave 6-amino-*m*-meconine of melting point 159.5–160.5°C.; Rây and Robinson reported 158°C.

6-Bromo-m-meconine

Recrystallized 6-amino-*m*-meconine (8 gm.) was treated with water (120 ml.) and hydrobromic acid (16 ml. of density 1.585) and the mixture mechanically stirred and cooled to −5°C. while a solution of sodium nitrite (3.4 gm.) in

* *All melting points are corrected.*

water (20 ml.) was slowly added. Diazotization occurred very slowly; stirring and cooling were continued for 160 min. after the addition was complete, and then the excess nitrous acid was destroyed with urea. The solution was then added to a cold solution of cuprous bromide (made from 10 gm. of copper sulphate pentahydrate) in hydrobromic acid (15 ml. of density 1.585), the mixture was heated for a few minutes on the steam bath, cooled, and the product recovered in 74% yield. Repeated recrystallizations from butanol with charcoal and from mixtures of ethanol and acetic acid gave colorless needles in a yield of 3.7 gm. or 35%, melting point 207–207.5°C. Calc. for $C_{10}H_9O_4Br$: Br, 29.26%. Found: Br, 29.48%. The same substance was also made by following the directions of Rây and Robinson who used hydrochloric acid instead of hydrobromic acid in the diazotization.

Oxidation of 6-Bromo-m-meconine

6-Bromo-*m*-meconine (3 gm.) was oxidized with alkaline permanganate in the usual way, and the resulting 3-bromo-*m*-hemipinic acid after being recrystallized from water melted at 174.5°C. Faltis and Frauendorfer (4) reported a melting point of 175–176°C. Calc. for $C_{10}H_9O_6Br$: equivalent weight, 153: Found: equivalent weight, 155.

The acid was converted into its dimethyl ester in yields of 95% by means of diazomethane; after recrystallization from methanol, the dimethyl ester of 3-bromo-*m*-hemipinic acid so obtained had a melting point of 88°C., while Faltis and Frauendorfer reported 87–88.5°C.

Reaction of 2-Bromoveratric Acid and Formaldehyde

2-Bromoveratric acid was made either from 2-aminoveratric acid (14) by the method of Rây and Robinson (16) or by the method of Raiford and Perry (15); the same product of melting point 205°C. was obtained by both routes. In each of numerous trials, 2-bromoveratric acid (4 gm.) was heated with formaldehyde, hydrochloric acid, and acetic acid, as described by Rây and Robinson. After being repeatedly recrystallized, the product had a melting point of 223°C. as reported by these authors, but when the product was mixed with the 6-bromo-*m*-meconine of melting point 207°C. obtained from 6-amino-*m*-meconine, the melting point fell to 180–193°C.

6-Iodo-m-meconine

6-Amino-*m*-meconine hydrochloride (5.9 gm.) was diazotized with sodium nitrite and hydrochloric acid. After the excess nitrous acid had been destroyed, a solution of potassium iodide (6 gm.) in water (15 ml.) was added and after the reaction the free iodine was removed with sodium bisulphite. The orange precipitate that separated in 72% yield was collected and recrystallized repeatedly from glacial acetic acid with charcoal to give pale yellow needles of 6-iodo-*m*-meconine, melting point 169–170°C. Calc. for $C_{10}H_9O_4I$: I, 39.69%. Found: I, 39.40%.

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3-Iodo-m-hemipinic Acid

When 6-iodo-*m*-meconine (11 gm.) was oxidized at 50–60°C. with alkaline permanganate, and the acid product repeatedly recrystallized from water, 3-iodo-*m*-hemipinic acid was obtained in a yield of 70%, melting point 177.5°C. Calc. for $C_{10}H_9O_6I$: equivalent weight, 176; I: 36.08%. Found: equivalent weight, 179; I, 35.82%.

Dimethyl Ester of 3-Iodo-m-meconine

The foregoing acid was converted with almost quantitative yield into the dimethyl ester by means of diazomethane. Recrystallized from methanol the ester had a melting point of 81.5°C. Calc. for $C_{12}H_{13}O_6I$: I, 33.42%. Found: I, 33.30%.

4, 5, 6-Trimethoxyphthalide

Potassium (0.8 gm.) was dissolved in thoroughly dried methanol (50 ml.), mixed with 6-iodo-*m*-meconine (3.2 gm.) and copper bronze (Kahlbaum's No. 02219, 0.1 gm.), and heated under reflux for 12 hr. The copper bronze was then removed and the filtrate diluted and acidified. The product that separated (1.7 gm.) was repeatedly recrystallized from water with charcoal to give colorless needles of melting point 136.5–137°C. Calc. for $C_{11}H_{12}O_5$: C, 59.0; H, 5.35; OCH_3, 41.5%. Found: C, 58.7, 58.8; H, 5.29, 5.25; OCH_3, 39.36%.

Samples of 3,4,5-trimethoxyphthalide were made by Dr. Manske and by one of us (J.A.M.) respectively, according to the directions of King and King (11) and found to melt at 135°C. as described. Mixed melting point determinations made with each of these samples and 4,5,6-trimethoxyphthalide melted indefinitely at 111–114°C. Both the 4,5,6-trimethoxyphthalide and 3,4,5-trimethoxyphthalide on oxidation produced phthalic acids which melted at 173–173.5°C. with frothing, and a mixed melting point of the two acids showed no depression. The proof of identity was inconclusive because of the dependence of the so-called melting points upon the rate of heating. According to Alimchandani and Meldrum (1), 3,4,5-trimethoxyphthalic acid has a melting point of 176–177°C.

Attempts to produce 4,5,6-trimethoxyphthalide from 6-bromo-*m*-meconine did not succeed.

Attempts to Synthesize 2,3,2'-Trimethoxydiphenyl Ether-5,6,4'-Tricarboxylic Acid

Vanillic acid (Schuchardt) was converted into methyl vanillate in the usual way. Efforts to bring about ether formation between this phenolic ester and methyl 3-iodo-*m*-hemipinate were made in three ways.

Following the procedure for diphenyl ether formation used by Faltis and Frauendorfer (4), potassium (0.4 gm.) was dissolved in absolute methanol (15 ml.) and added to methyl vanillate (4.5 gm.), the last-named chemical

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being in considerable excess. A solution of dimethyl 3-iodo-*m*-hemipinate (3.8 gm.) in methanol (10 ml.) was added and the mixture evaporated to dryness under reduced pressure. The dry material was mixed with copper bronze (British Drug Houses, 0.07 gm.) and copper acetate (0.04 gm.) and heated in an oil bath for one hour at 154°C. and then for two hours at 165°C. On cooling, the mixture was extracted thoroughly with ether and the ethereal solution shaken with 2*N* sodium hydroxide solution and dried over sodium sulphate. Evaporation of the ether left an oil which solidified. This was recrystallized from methanol when 1 gm. of material was obtained. It was hydrolyzed by methanolic potassium hydroxide and on acidification veratric acid was obtained, since its melting point of 178°C. was not depressed by admixture with authentic veratric acid, and since its methyl ester had the same melting point (58°C.) as that reported for methyl veratrate. No other pure compounds could be isolated. When methyl vanillate was used in amounts equivalent to the potassium methylate, similar results were obtained.

The second variation was according to the modification used by Faltis and Zwerina (6). Potassium methylate was prepared by adding potassium (0.7 gm.) to absolute methanol (10 ml.). To this was added methyl vanillate (3.5 gm.) and the whole evaporated to dryness under reduced pressure with slight warming. The dry potassium salt of the ester was mixed as rapidly as possible with a mixture of dimethyl 3-iodo-*m*-hemipinate (6 gm.), Kahlbaum's copper bronze (Natur kupfer C) (0.1 gm.), and cupric acetate (0.1 gm.); the whole was heated in an oil bath at 150–170°C. for three hours. Only veratric acid could be isolated from the reaction mixture.

The third essay was based upon the procedure used by Harington and Barger (7) in the synthesis of thyroxine. Dimethyl iodo-*m*-hemipinate (1.5 gm.) was heated under reflux for 24 hr. with methyl vanillate (1 gm.), anhydrous potassium carbonate (2 gm.), copper bronze (0.05 gm.), and copper acetate (0.03 gm.) in anhydrous dioxane (30 ml.) No iodide ions were produced, showing that the conditions used were too mild. Even when potassium methylate and methanol were used in place of potassium carbonate and dioxane respectively no action occurred, and the use of triethylene glycol at 170°C. as the solvent in place of methanol did not bring about the reaction in six hours.

6-Iodo-m-meconine and Methyl Vanillate

A mixture of potassium (0.6 gm.) dissolved in absolute methanol (15 ml.), methyl vanillate (4.5 gm.), and 6-iodo-*m*-meconine (3.2 gm.) was evaporated to dryness under reduced pressure. Copper bronze (0.07 gm.) was mixed with the dry residue and the mixture heated for one hour at 155°C. and for two hours at 165°C. There was ample evidence that reaction had occurred, but prolonged attempts did not lead to the isolation of any pure products. Further trials will be made with this general method.

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Acknowledgments

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HYDROGEN PEROXIDE AND ITS ANALOGUES

III. ABSORPTION SPECTRUM OF HYDROGEN AND DEUTERIUM PEROXIDES IN THE NEAR ULTRAVIOLET[1]

By M. K. Phibbs and Paul A. Giguère

Abstract

The absorption of ultraviolet light between 3000 and 4000 Å by solutions of hydrogen peroxide in water and of deuterium peroxide in heavy water has been measured at various concentrations. Both peroxides show slight but real deviations from Beer's law at high concentrations. Substitution of hydrogen by deuterium shifts the absorption continuum by about 390 cm.$^{-1}$ towards shorter wave lengths. This shift is of the same order as that calculated from the difference in zero-point energy of the two isotopic molecules.

A number of investigators (1, 3, 5, 9, 10, 11, 12, 15) have shown that hydrogen peroxide absorbs very strongly in the ultraviolet, beginning in the neighborhood of 4000 Å and increasing rapidly without any sign of reaching a maximum, at least as far as 2000 Å. Most of the measurements were made on dilute solutions, however. Recently Taylor and Cross (14) measured the absorption of concentrated solutions, 50% and 90%. As part of a research program on the properties of deuterium peroxide a small amount of this compound was prepared by passing an electric discharge through the vapor of heavy water. It was felt of interest to study its absorption in the near ultraviolet in order to compare it with that of ordinary hydrogen peroxide.

Experimental

The measurements were made with a Beckman DU spectrometer using a pair of matched quartz cells 10 mm. thick. In all cases the absorption of the solutions was compared with that of the pure solvent. Even under ultraviolet illumination the peroxide solutions were quite stable so that interference from gas bubbles was negligible. The hydrogen peroxide solutions were prepared by diluting a 99.3% solution obtained by vacuum distillation of Becco's 90% commercial product. It was observed that the solutions were much more stable when a dilute peroxide solution rather than redistilled water was used as diluent. The method of production of deuterium peroxide will be fully described in a subsequent paper. A 6.5% and a 30.7% solution of the isotopic compound in heavy water essentially free of ordinary hydrogen were available for this investigation.

Discussion of Results

In Table I are listed the values of a, the absorption coefficient in Beer's law, $\log I/I_0 = -a\,c\,d$, where the concentration c is in moles of peroxide per

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TABLE I

ABSORPTION COEFFICIENTS OF HYDROGEN AND DEUTERIUM PEROXIDES IN THE NEAR ULTRAVIOLET

Wave length in Å	Wt % H_2O_2 in H_2O			Wt % D_2O_2 in D_2O	
	6.5	54.9	99.3	6.5	30.7
3050	1.55			1.12	
3100	1.12			0.794	
3200	0.550			0.398	0.331
3300	0.251	0.178		0.186	0.170
3400	0.117	0.0977	0.0776	0.0852	0.0795
3500	0.0537	0.0457	0.0389	0.0427	0.0372
3600	0.0256	0.0209	0.0182	0.0195	0.0170
3700	0.0112	0.0102	0.00871		0.0085
3800	0.00661	0.00540	0.00437		0.00428
3900	0.00399	0.00302	0.00224		0.0019
4000		0.00208	0.00120		
4100			0.000562		
4200			0.000257		
4300			0.000141		

liter of solution and d, the thickness of the absorbing layer in cm. The plot of log a at various wave lengths (Fig. 1) fits closely a straight line for each concentration; this is not surprising as the range covered is limited and seemingly far from any absorption maximum. A slight parabolic curvature becomes apparent when the plot is extended to 2000 Å using the data of previous workers. The results of Taylor and Cross agree quite well with the present

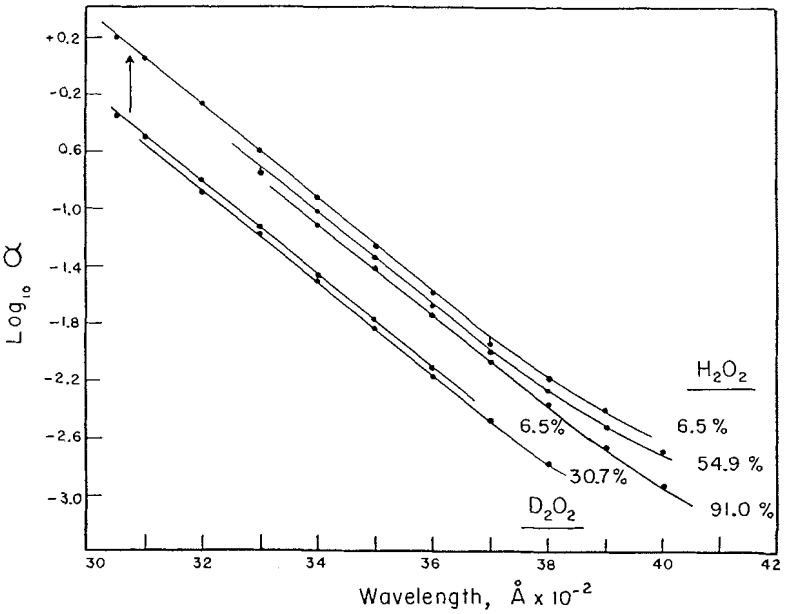

FIG. 1. *Absorption coefficient of hydrogen and deuterium peroxides at various concentrations. The curves for deuterium peroxide have been shifted down by 0.4 unit of the ordinate scale to avoid confusion.*

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ones except at longer wave lengths, where they show a certain dip away from straight lines. The fact that these authors used the photographic method may account for the small difference. At any rate they were the first to report the deviation from Beer's law which the present results substantiate. They suggested the repression of ionization in concentrated solutions

$$HOOH = H^+ + OOH^-$$

as responsible for part of the decrease in absorption. Indeed, Bredig and his coworkers (3) have shown that addition of sodium hydroxide to hydrogen peroxide enhances markedly the ultraviolet absorption of the latter. Their data and interpretation would indicate that the absorption coefficient of the OOH^- ion is about ten times greater than that of the neutral molecule. However, this cannot account for more than a fraction of the noted deviation since pure hydrogen peroxide is very slightly ionized, in fact hardly more so than water. Rather it is likely that the deviation is due to molecular association in the liquid state; both water and hydrogen peroxide form strong hydrogen bonds and there is little doubt that the potential energy curves of molecules are modified by their environments. As far as can be judged from the data in Table I, solutions of deuterium peroxide deviate from Beer's law to the same extent as those of hydrogen peroxide.

The other noticeable result of this investigation is the shift towards shorter wave lengths of the absorption continuum of deuterium peroxide with respect to that of hydrogen peroxide. Such isotope shifts, at least on the long wave length side of the absorption curve, are exhibited by other molecules involving excitation to an upper repulsive energy level. In the case of water this effect amounts to 900–1200 cm.$^{-1}$ (6); the present results for 6.5% solutions indicate an average shift of 390 cm.$^{-1}$ for the peroxides. As it is unlikely that isotopic substitution can alter significantly the potential energy surfaces the main effect must be due to difference in zero-point vibrational energy between the two molecules.

Now the various fundamental frequencies of both peroxides are known with fair accuracy so that an approximate calculation of the isotope shift is possible. The data in Table II are based on recently measured infrared and Raman spectra of the two compounds in the liquid state (4, 7, 13). The zero-point energy difference in the ground state, given by the difference in the half sum

TABLE II

FUNDAMENTAL VIBRATIONS OF HYDROGEN AND DEUTERIUM PEROXIDES*

Mode	H_2O_2	D_2O_2
ν_1	3410 cm.$^{-1}$	2530 cm.$^{-1}$
ν_2	1400	1030
ν_3	880	880
ν_4	660	540
ν_5	3430	2500
ν_6	1350	1010

* *Rounded-off figures.*

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of these frequencies, is therefore 1320 cm.$^{-1}$ From this quantity must be substracted the zero-point energy difference between the two OH and the two OD radicals formed by dissociation. For the present purpose this difference was taken as 940 cm.$^{-1}$, the average between the values for the ground state and the first electronically excitated state (8). Indeed, energy considerations (15) indicate that absorption of ultraviolet light by a peroxide molecule must produce one normal and one excited radical,

$$H_2O_2 + h\nu = OH(^2\Pi) + OH(^2\Sigma).$$

The calculated shift is therefore 1320–940 = 380 cm.$^{-1}$, as compared with the observed one, 390 cm.$^{-1}$

The agreement is certainly better than could be expected in view of the oversimplifications made. One needs only mention here the case of such simple molecules as the hydrogen halides (2) where the observed shift in the ultraviolet spectrum of the deuterated molecules is about three times that calculated from the zero-point vibrational energies. Differences in the ground-state eigenfunctions and in the form of energy curves have been assumed to account for these facts. The absence of any structure in the spectrum of hydrogen and deuterium peroxides precludes further interpretation of the above results at present.

Acknowledgment

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Résumé

L'absorption de la lumière ultra-violette par des solutions de peroxyde d'hydrogène dans l'eau et de peroxyde de deutérium dans l'eau lourde a été mesurée à différentes concentrations dans la région s'étendant de 3000 à 4000 Å. Pour les deux composés l'absorption ne suit pas rigoureusement la loi de Beer surtout aux concentrations élevées. La substitution de l'hydrogène par le deutérium déplace le seuil d'absorption du peroxyde d'environ 390 cm.$^{-1}$ vers l'ultraviolet. Cet effet est dû surtout à la différence d'énergie au point zéro des deux molécules isotopiques.

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THE DIELECTRIC CONSTANT OF DISULPHUR DECAFLUORIDE[1]

By N. R. S. Hollies[2] and R. L. McIntosh[3]

Abstract

A method is described for obtaining the dielectric constant and conductivity of disulphur decafluoride in both liquid and gaseous forms. The freezing point of the liquid and the molecular weight of the vapor are established as criteria of purity. All the measurements lead to the conclusion that disulphur decafluoride is nonpolar. Its molar polarizations in the two forms are compared with those of other members of the sulphur fluoride and carbon fluoride homologous series as well as with hexane, benzene, and toluene.

Introduction

From the reported properties of disulphur decafluoride (S_2F_{10}) it is difficult to classify the liquid as nonpolar or polar. The reported values of Trouton's constant, 23.3 (18) and 23.0 (6), would seem to indicate that disulphur decafluoride is normal in behavior. The temperature independent parachor, 246.5 (18), is also typical of a nonassociated compound. In the absence of any data on the sulphur fluoride homologous series of which disulphur decafluoride is the second member, the high density, 2.09 at 0°C. (18), and high boiling point, 29°C. (6), could be interpreted as indicating that this fluoride is associated. In addition, all the reported vapor pressure equations for disulphur decafluoride (6, 18) yield an entropy of vaporization of 28.2 or greater. This value is calculated at a vapor concentration of 0.005 moles per liter and when compared with the tabulated values of Hildebrand (17) places disulphur decafluoride in a class between polar and nonpolar compounds.

In this investigation of the dielectric properties of carefully purified samples of disulphur decafluoride it was found that neither liquid nor gaseous phases exhibited any dipole moment, tending to confirm the nonassociated physical structure of the compound (4, 29, 31, 34). The magnitude and the slight temperature dependence of the specific conductivity, 1.94×10^{-10} mho per cm., supports this interpretation (11). The molar polarization of 33.4 cc. places disulphur decafluoride among that group of nonpolar compounds which exhibit a normal "field" volume (8). Hence the electric properties indicate that disulphur decafluoride is a nonpolar, nonassociated, sulphur fluoride.

Dielectric Theory

The determination of dipole moments involves the measurement of dielectric constants. Both the theory of such measurement (4, 10, 36) and the devices used (3, 30, 36) are treated thoroughly elsewhere.

[1] *Manuscript received December 6, 1950.*
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The polarization of a gas and of some liquids (15, 9) may be calculated by means of the Clausius–Mosotti equation

$$\frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho} = 4/3\pi N\left(\alpha_0 + \frac{\mu^2}{3kT}\right) = P_T = (P_E + P_A) + P_0, \qquad (I)$$

where ϵ = dielectric constant, M = molecular weight, ρ = density, N = Avogadros' number, α_0 = polarizability, μ = dipole moment, k = Boltzmann's constant, T = absolute temperature, P_T = molar polarization, P_E = electronic polarization, P_A = atomic polarization, P_0 = orientation polarization.

The Clausius–Mosotti expression introduces considerable error when applied to polar liquids. Onsager (28) developed a corresponding equation which allows for interdipole action. Kirkwood (20) has generalized Onsager's theory and arrived at the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}\frac{M}{\rho} = 4/3\pi N\left(\alpha_0 + \frac{\mu'^2 g}{3kT}\right) = P_T = (P_E + P_A) + P_0, \qquad (II)$$

where μ' for the liquid is slightly larger than the moment in the gaseous state and g is a parameter whose value differing from unity is a measure of the hindering of a molecule by its neighbor. Often the gaseous moment can be evaluated quite accurately from further relations developed by Onsager and Kirkwood (28, 20).

*Physical and Chemical Properties of Disulphur Decafluoride**

Disulphur decafluoride was first identified by Denbigh and Whytlaw-Gray (6). They found it to be a colorless volatile liquid of b.p. 29±1°C., m.p. −92±1°C., density 2.08 ±0.03 gm. per cc. at 0°C., surface tension 13.7±3% dynes per cm., Trouton's constant 23.0, parachor 236, and with the equation for its vapor pressure as a function of temperature, $\log p = -1530/T + 7.95$. More recently a freezing point of −55°C. and a vapor pressure equation $\log p = 2190/T + 24.015 - 6.0 \log T$ have been reported. Experience in handling disulphur decafluoride has shown that the vapor pressure and particularly the freezing point are quite sensitive to impurities, and these facts aid considerably in the recognition of the purity of the compound.

Impurities expected in the disulphur decafluoride samples used in this work were sulphur hexafluoride (SF_6) (24), sulphur monofluoride (S_2F_2) (2), and sulphur tetrafluoride (SF_4) (7) as well as oxyfluorides like thionyl fluoride (SOF_2) (27), and sulphuryl fluoride (SO_2F_2) (37). Silicon tetrafluoride (SiF_4) and carbon tetrafluoride (CF_4) are also formed in the presence of glass and rubber in the reaction system.

A practical separation of disulphur decafluoride from these products depends for the most part on the fact that it is inert to alkali (5), a property shared only by sulphur hexafluoride (24), carbon tetrafluoride (39), and

**Extreme care should be exercised in handling disulphur decafluoride because of its toxicity.*

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sulphuryl fluoride (26). Hence an alkaline wash serves to remove all but these three impurities from disulphur decafluoride samples (7, 14, 25, 26, 32). In addition, according to the vapor pressure equation of Yost and Claussen (42), silicon hexafluoride has a vapor pressure of 2665 cm. at 0°C. compared with 23.5 cm. of disulphur decafluoride. In contrast sulphuryl fluoride has a vapor pressure of 24.1 cm. at −80°C. (26) and the vapor pressure of carbon tetrafluoride at −128°C. is 76 cm. (14). Hence simple fractionation should be sufficient to remove these remaining impurities in disulphur decafluoride samples. In actual experience the purification process had to be refined further. To remove adhering traces of still another sulphur fluoride the samples were very carefully fractionated. This new product has not been identified but appears to have a higher molecular weight than disulphur decafluoride.

Experimental

(*a*) *Purification*

Crude disulphur decafluoride was passed through a scrubbing train of 10% sodium hydroxide into a conventional vacuum manifold where it was stored in 100 cc. bulbs surrounded by liquid air. Sulphur hexafluoride was removed from these by slow fractionation from one bulb at 0°C. to another at −78°C. and the excess volatile component pumped off through a charcoal trap. For final treatment all dielectric samples were fractionated in a 60 cm. column constructed on the design of Bowen and Cooke (1). In order to obtain reliable freezing points of the various disulphur decafluoride fractions and to establish these freezing points as criteria of purity the cell depicted in Fig. 1 was used.

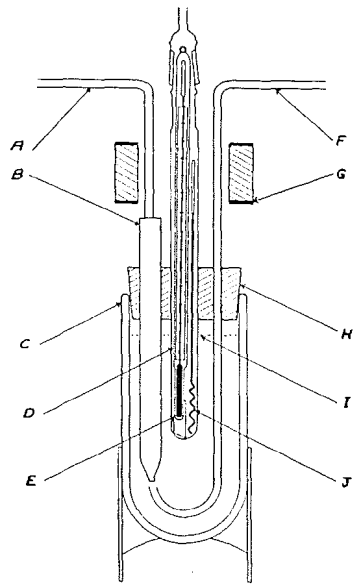

FIG. 1. *Freezing point cell.*
A — Liquid air inlet; B—copper reservoir; C—Dewar flask;
D — sample level; E—pentane thermometer; F—compressed air inlet;
G — stirrer solenoid; H—insulating cork; I—acetone level;
J — magnetic stirrer.

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When attached directly to the vacuum manifold a sample could be condensed in the inner bulb and its freezing point determined. The pentane thermometer in the inner bulb, a German standard, which could be read to 0.1°C., was checked at the Dry Ice – acetone and mercury points where the error in its reading was less than 0.1°C. so its values were used directly in all experimental results. The cooling rates were easily controlled and plots of time vs. temperature revealed long flat regions when the cooling was very slow. The temperatures of these regions corresponded to the first appearance of crystals in the bulb and were taken as the true freezing points of the samples under investigation.

The other main criterion of purity was sought in molecular weight determinations of the various fractions used. These were determined by the well known vapor density method. The molecular weights were plotted against pressure and the value obtained by extrapolation to zero pressure was taken as the true experimental molecular weight.

(*b*) *Dielectric Measurements*

Capacity measurements for dielectric work are made in various ways. Perhaps the most versatile of these come under the classification of "Bridge Methods" (13, 16, 33). These possess some advantage over other methods in that condenser leakage can be measured directly and determinations can be carried to quite low frequencies. The Schering circuit used in this investigation is shown in Fig. 2. Both the detector and oscillator employ some special techniques which bear consideration.

In order to obtain sufficiently accurate measurements on gaseous disulphur decafluoride, the filter network also shown in Fig. 2 was added (a parallel resonant filter tuned to 3440 c.p.s.). Detection was carried out using two Sylvania oscilloscopes in series in a manner similar to that adopted by Lamson (21).

The R-C oscillator of Fig. 3 in conjunction with a voltage regulated power supply acted as the power source. The design of the driver circuit was that suggested by Dr. Watson (38) based on those described by Ginzton and Hollingsworth (12). The highly stable output (120 v., 8 w.), negligible frequency drift (over the range of 400 to 6000 c.p.s.), and low harmonic content of the output (less that 1%) make the oscillator particularly useful in such bridge applications where the power source ratings and characteristics are quite exacting. With these generator and detector circuits it was possible to maintain the consistency of the Schering bridge at one part in seventy thousand.

(*c*) *Dielectric Cells*

The cell used for dielectric measurements on liquid disulphur decafluoride is shown in Fig. 4. The brass condenser cylinders were insulated from one another by small Lucite rings at each end, and four holes drilled in the outer shell gave the liquid sample access to the interior. A supply of ethylene glycol was circulated through the copper cooling coil surrounding the cell.

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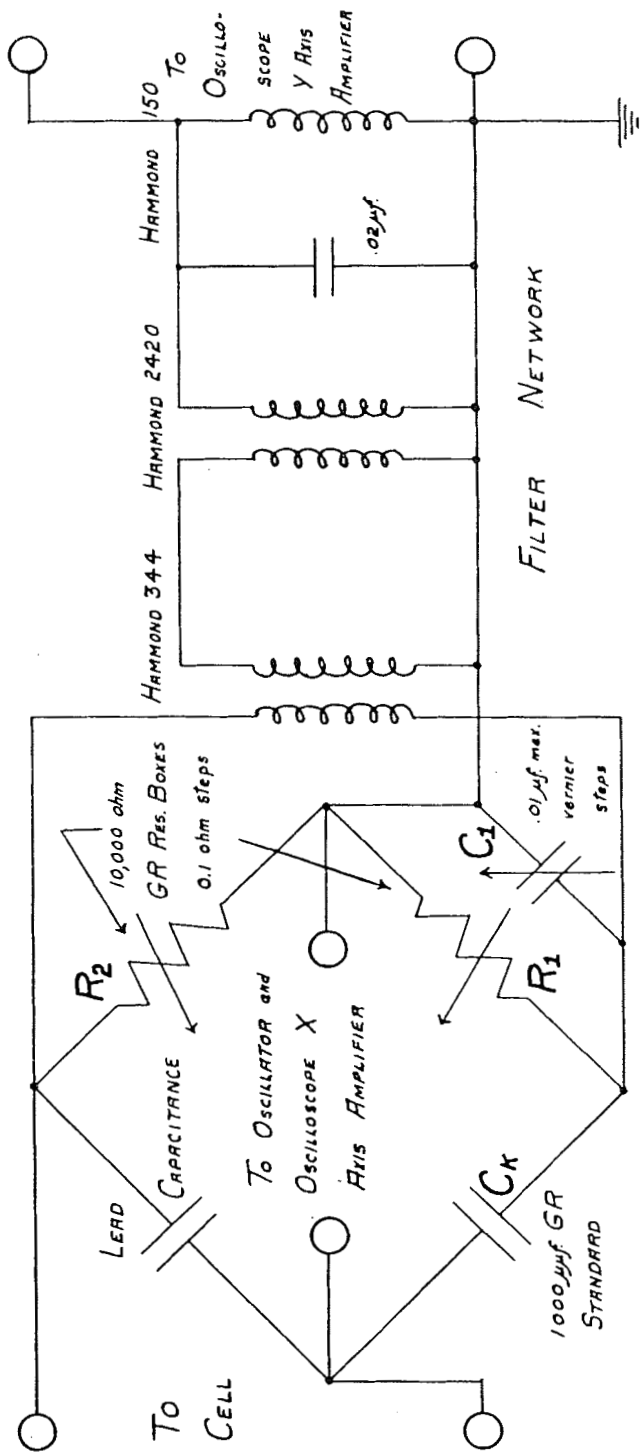

FIG. 2. *Schering bridge.*

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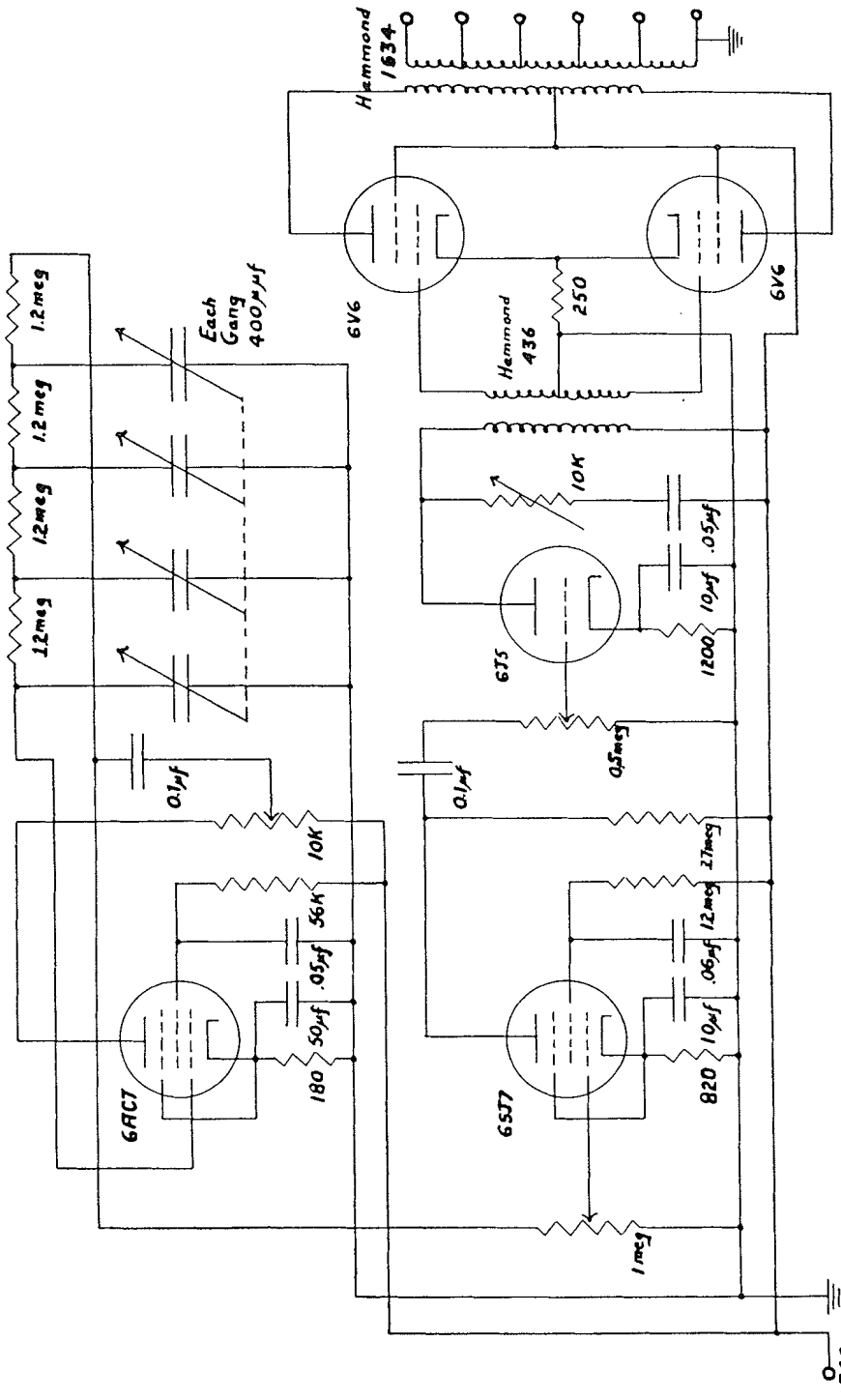

FIG. 3. *Phase shift oscillator.*

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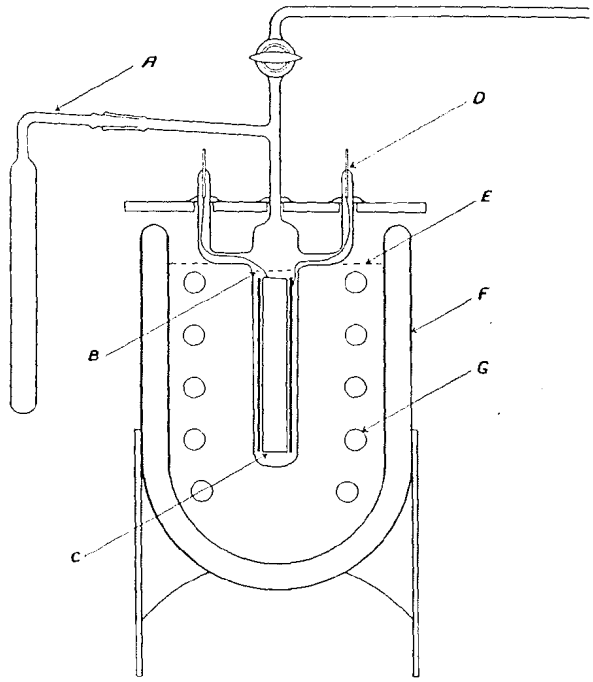

FIG. 4. *Dielectric cell for liquids.*
A — Filling bulb; B—sample level; C—cell condenser;
D — metal-to-glass seal for lead; E—glycol level;
F — Dewar flask; G—cooling coil.

This supply originated in a four gallon storage tank which could be cooled by a commercial refrigerator or warmed with electric heaters. With such a temperature controlling scheme it was possible to maintain the cell within 0.002°C. of any temperature from −30 to +60°C. for periods up to several hours. The temperature was followed in all runs by a pentane thermometer immersed in the Dewar next to the cell. Filling was accomplished by means of the side arm and bulb attached to the top of the cell. Samples were condensed by liquid air into the bulb and on warming were poured into the cell proper by simple rotation about the ground glass joint. The cell was shielded by grounding the metal holder, copper cooling coil, and metal framework which held it in place. The 200 $\mu\mu$f. capacity of the cell showed complete stability with time which was interpreted as revealing that both the brass and Lucite were not attacked by disulphur decafluoride.

The cell used with gaseous disulphur decafluoride was constructed along very similar lines but with a higher evacuated capacity of 1360 $\mu\mu$f. designed to match the optimum sensitivity range of the Schering circuit used. It consisted of two concentric brass cylinders 25 cm. long, 4 cm. in diameter with 0.003 in. clearance, again separated by Lucite rings and the cell drilled to give the vapor easy access to the interspace. The cylinders were mounted hori-

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zontally in a Pyrex bulb and connected to the bridge leads through widely spaced side arms and Pyrex-tungsten seals. In this case ample electric shielding was provided by grounding the metal frame of the 25°C. water bath surrounding the cell. Any desired vapor pressure of disulphur decafluoride could be maintained in the cell by connecting it directly with the freezing point cell in which the temperature of the liquid phase could be controlled. The equilibrium pressure was easily read from the U-tube manometer which was left connected to the manifold during any gaseous dielectric run. Again, capacity stability of this cell at 25°C. even over long periods of evacuation not only indicated inertness of the cell materials to disulphur decafluoride but also revealed that there was negligible sorption of disulphur decafluoride by the insulating rings.

Results

(*a*) *Importance of Purity*

Preliminary runs on the various liquid disulphur decafluoride fractions revealed evidence of the type depicted in Table I. The molecular weights given were determined at 235 mm. pressure and the dielectric constants at 10°C.

TABLE I

ANALYSIS OF FRACTIONATION 13

Fraction		1st	2nd	3rd
Molecular weights	Before dielectric runs	255	259	257
	After dielectric runs	255	259	256
		255	258	257
Freezing points	Before dielectric runs	−54.2	−55.5	−55.3
	After dielectric runs	−55.0	−55.8	−55.4
Dielectric constant		2.029	2.031	2.032

These results indicated clearly that in the relatively pure state, molecular weights of disulphur decafluoride varied little from fraction to fraction, whereas the freezing points were highly sensitive not only to fractionation but to a large extent to handling and storage of the various samples. Hence the freezing points of best fractions could be used as a delicate test of the purity of the sample. Allied with this, such figures also showed that the measured dielectric constant was affected very slightly by the impurities, increasing the significance of any dielectric figures obtained on fairly pure samples. This is borne out in the comparison of the more detailed dielectric studies on fractions 13-3 and 15-2.

(*b*) *Variation of the Dielectric Constant with Temperature*

Table II shows the observed dielectric data of two purified samples of disulphur decafluoride as a function of temperature. Lead capacity cor-

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TABLE II

LIQUID DIELECTRIC CELL CAPACITIES AS A FUNCTION OF TEMPERATURE

Sample no.	F.p., °C.	T, °C.	C, $\mu\mu f.$	$C_{evac.}$, 0°C. $\mu\mu f.$	dC_{evac}/dT $\mu\mu f./°C. \times 10^3$
13-3	−55.4	21.9	402.3	239.8	11
		20.0	403.1		
		17.6	404.1		
		14.7	405.3		
		12.0	406.5		
		8.8	407.6		
		5.7	409.0		
		2.4	410.2		
		−1.2	411.6		
		−4.7	413.0		
15-2	−54.2	20.50	405.79	243.05	9.3
		12.90	409.00		
		6.65	411.64		
		1.40	414.76		
		−3.05	415.58		
		−8.05	417.58		
		−11.30	418.88		

rections have already been made. The figures given for fraction 15-2 were obtained using all the bridge refinements developed for measurements on gases.

Plots of these values gave smooth curves which were interpolated at the temperatures of Table III. Dielectric constants were evaluated using the evacuated cell constants of Table II. Molar polarizations were calculated from Equations (I) and (II) in order to compare the Clausius–Mosotti approach with that of Kirkwood and Onsager. These along with liquid densities of disulphur decafluoride, determined by Hugill (18), are recorded in Table III.

As a check on the purity of fraction 15-2 a portion of the sample was analyzed by the vapor density procedure, and the molecular weight curve of Fig. 5, obtained. The intercept at zero pressure, 253.5, lies within experimental error of the theoretical value, 254.1, and is used in all the polarization calculations on this sample.

TABLE III

MOLAR POLARIZATIONS OF LIQUID DISULPHUR DECAFLUORIDE

Sample No.	Temp., °C.	Dielectric constant	Density, gm./cc.	Polarization, cc.	
				C–M	K–O
13-3	−4.0	2.071	2.107	31.74	35.65
	4.0	2.054	2.081	31.75	35.58
	12.0	2.037	2.054	31.77	35.50
	20.0	2.020	2.028	31.78	35.42
15-2	−10.0	2.0847	2.1270	31.69	35.62
	0.0	2.0638	2.0936	31.70	35.55
	10.0	2.0423	2.0607	31.72	35.46
	20.0	2.0202	2.0274	31.74	35.58

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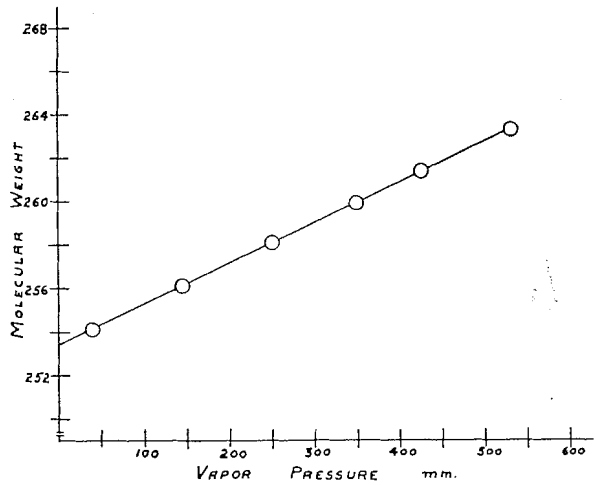

FIG. 5. *Molecular weight as a function of pressure for disulphur decafluoride fraction 15-2.*

The a-c. conductivity of these samples can be calculated from the resistive loss figures obtained at every bridge balance point. From the geometry of the cell and these values the specific conductivity at 3440 c.p.s. and 0°C. is 1.94×10^{-10} mho per cm. It exhibits a very small temperature coefficient.

(c) Dielectric Constant of Gaseous Disulphur Decafluoride

As a check on the results obtained with liquid disulphur decafluoride, measurements were made on the purified gas at 25.0°C. as a function of pressure. Data for a typical run can be seen in Table IV.

These values are plotted in Fig. 6. Again it was deemed legitimate to interpolate capacity values at intervening pressures and in particular for those pressures for which the vapor densities were known (Fig. 5.). These values, along with the empty cell capacity (1402.88 $\mu\mu$f.), were corrected for lead error (42.52 $\mu\mu$f.) and the dielectric constant as a function of pressure evaluated as in Table V. In conjunction with the determined molecular weight of

TABLE IV

GASEOUS DIELECTRIC CELL CAPACITY AS A FUNCTION OF PRESSURE USING FRACTION No. 15-2, f.p. −54.2°C.

Pressure, mm.	Capacity, $\mu\mu$f.
9.6	1403.02
48.8	1403.26
115.6	1403.74
171.3	1404.14
219.0	1404.50
292.2	1405.04
351.8	1405.50
406.2	1405.92
475.0	1406.46
518.7	1406.78

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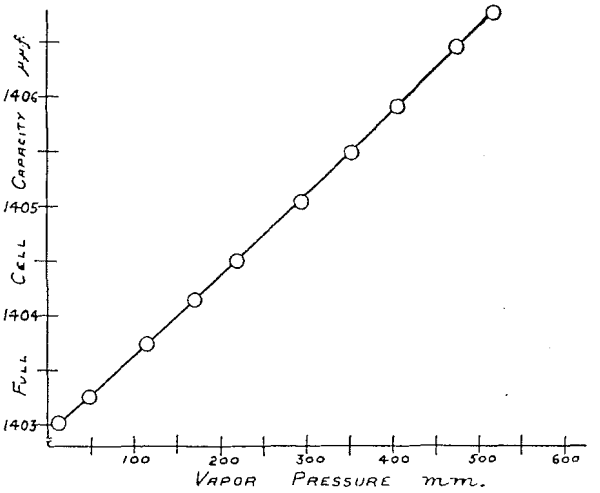

FIG. 6. *Gaseous dielectric cell capacity as a function of pressure using fraction 15-2.*

TABLE V

DIELECTRIC CONSTANT OF SAMPLE NO. 15-2 (GASEOUS)

Pressure, mm.	Density, gm./cc.	Dielectric constant	Molar polarization, cc.
39.4	0.0005352	1.00023	36
144.2	0.0019698	1.00078	33.5
249.0	0.0034334	1.00136	33.5
349.0	0.0048387	1.00191	33.3
426.0	0.0059406	1.00234	33.3
532.2	0.0074765	1.00295	33.3

sample No. 15-2 and the Clausius–Mosotti equation, the ϵ values were used to compute the molar polarizations of the table.

We have an alternative way of obtaining the true gaseous molar polarization value if we assume that the vapor is ideal and use ideal densities (8). Taking the equation

$$P_T = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho}$$

then using $\rho = \dfrac{pM}{RT}$

and letting $\epsilon + 2 = 3.0$ (true for gases at low pressures)

$$P_T = \frac{RT}{3}\lim_{p\to 0}\frac{\epsilon - 1}{p_{mm}} = 2.097 \times 10^4\, T \lim_{p\to 0}\frac{\epsilon - 1}{p_{mm}}.$$

Applied to the values obtained for Fig. 6 we extrapolate at zero pressure to a $\dfrac{\epsilon - 1}{p}$ ratio of 5.37×10^{-6} mm.$^{-1}$ The corresponding P_T value is 33.6 cc., agreeing within experimental error with previous average value of 33.4 cc.

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Discussion of Results

(*a*) *Polarization Values*

Within the range of experimental error, molar polarizations calculated from the two basic equations reveal no temperature dependence. Then in the light of the given theory disulphur decafluoride must have a dipole moment indistinguishable from zero. Weight is added to this conclusion when an attempt is made to correlate the polarization values obtained by the different methods. These are seen in Table VI.

TABLE VI

SUMMARY OF MOLAR POLARIZATIONS

Compound	Liquid polarizations		Vapor polarizations
	C-M	K-O	C-M and K-O
Disulphur decafluoride	31.74	35.55	33.4
n-Hexane	29.77	32.30	30.04
Benzene	26.67	30.96	26.88
Toluene	33.65	39.68	34.13

It is to be noticed that the "vapor" value is slightly larger in magnitude than those resulting from liquid dielectric runs calculated from the Clausius–Mosotti expression. This is to be expected from the theoretical assumptions of Debye's theory which assumes no intermolecular action only in the case of gases and predicts anomalous discrepancies in applications to the much more highly condensed liquid molecules. Hence use of the Clausius–Mosotti equation would be expected to give slightly lower P_T values with liquids, even in the absence of any dipole moment as is observed.

In contrast, however, the molar polarization values calculated by means of the Kirkwood–Onsager equation are, in general, higher than the vapor value. It would seem that this approach tended to weight the interaction contributions a little too heavily. To indicate, however, just how normal disulphur decafluoride is in this respect, data for other nonpolar liquids are also included in the table. Polarizations have been calculated from existing dielectric constant tables (35, 36, 40) and in many cases from the original literature.

If we give the most prominent significance to those P_T values obtained with gaseous disulphur decafluoride (omitting the "out of range" 36 cc. value) and obtain their average as a representative quantitative figure, then we can make a correlation with sulphur hexafluoride and the corresponding hydrocarbons utilizing the figures of Fuoss (8) (Table VII).

It is to be noted that the dielectric molar volume is practically doubled in progression in each series, an observation tending to confirm the normal rather than the abnormal behavior of disulphur decafluoride. Secondly this conclusion is reinforced by the fact that the other three compounds also have no dipole moment.

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TABLE VII

DISULPHUR DECAFLUORIDE AS A MEMBER OF THE SULPHUR FLUORIDE HOMOLOGOUS SERIES

Compound	Polarizations, cc.		Dipole moment
	P_T	P_A	
CF_4	9.7	3.3	0
CF_3CF_3	17.2	6.4	0
SF_6	16.8	5.1	0
SF_5SF_5	33.4	12.1	0

As is often done (36), we can carry the analysis of polarizations further and evaluate the electronic and atomic contributions for the atoms and bonds involved. In Equations (I) and (II) it has been shown that $P_0 = 0$ so $P_T = P_E + P_A$*. If we take the S–S bond P_E value obtained on organic compounds (22) as 1.73 cc. and at the same time use the S–F bond P_E value obtained on sulphur hexafluoride (36), 1.95, then

$$P_A(S_2F_{10}) = 33.37 - 1.73 - 10(1.95) = 12.14 \text{ cc.}$$

Carbon tetrafluoride, dicarbon hexafluoride, and sulphur hexafluoride can be treated in the same manner and these results are also shown in Table VII.

(b) Conduction

The low conductivity of disulphur decafluoride and its small negative temperature dependence are also significant for they indicate covalent rather than electrovalent bonding in this sulphur fluoride (19, 23) and very small dissociation of the compound (11). From these figures we can estimate the direct current specific conductance value as lying between 10^{-12} and 10^{-14} mho per cm. (41), placing disulphur decafluoride well into the "insulator" range.

(c) General

Finally, from a purely empirical point of view dielectric liquids with small dielectric constants always exhibit low conductivities. As Gemant (11) clearly points out, all compounds such as nitrobenzene, ethanol, etc., which have high dielectric constants, also possess large dipole moments. The dipoles of the solvent orient themselves radially around the individual ions, being directed by the electrical forces of these ions. In this manner they bind their true charges and diminish their free charges. The attractive forces between the ions are weakened in this way, and dissociation is made easier. The remarkable relationship between dielectric constant and conductivity thus becomes intelligible. As disulphur decafluoride has large values of neither dielectric constant nor conductivity its position is again clear.

* *Owing to the toxicity and volatility of the compound determinations of its refractive index were not made.*

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We may say in conclusion that its electric properties establish that disulphur decafluoride is a highly stable nonpolar dielectric. The remaining evidence existing for association in the liquid state may be more apparent than real if one takes into account the high molecular weight and scanty thermal data available for disulphur decafluoride. For the present, in any case, we are left to postulate only the one electronic configuration for disulphur decafluoride—that involving two sulphur atoms linked together and in turn each surrounded by five fluorine atoms, all covalently linked.

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THE KINETICS OF THE THERMAL DECOMPOSITION OF DISULPHUR DECAFLUORIDE[1]

By W. R. Trost[2] and R. L. McIntosh[3]

Abstract

The thermal decomposition of the gas disulphur decafluoride has been studied in a metal reactor. Analytical evidence showed that the reaction proceeds according to the equation $S_2F_{10} = SF_6 + SF_4$. The reaction was found to be largely homogeneous, as the heterogeneous reaction accounted for less than 5% of the total process. The homogeneous reaction was shown to be first order, and in the temperature range investigated the rate is given by $\ln k = 47.09 - 49{,}200/RT$. A chain reaction is postulated to explain the observed rate of the reaction. The effect of nitric oxide and acetylene dichloride on the rate and products of the reaction was investigated.

Introduction

Sulphur hexafluoride, SF_6, and disulphur decafluoride, S_2F_{10}, are the first two and only known members of the family of saturated sulphur fluorides. Sulphur hexafluoride has been familiar since the early work of Moissan and Lebeau (9). Disulphur decafluoride, a colorless liquid boiling at 29°C., was originally prepared by Denbigh and Whytlaw-Gray (3). On the basis of an experimental parachor, they assigned a structure to this molecule in which hexavalent sulphurs are linked to each other and to five fluorine atoms by covalent bonds. Evidence in favor of this model has been obtained by Hollies and McIntosh (6), who established that disulphur decafluoride has no permanent moment.

The strength of the S–F bond in sulphur hexafluoride as calculated from thermal data given by Bichowsky and Rossini (2) is 89.9 kcal. From the dissociation of S_8, the covalent S–S link has been evaluated as 63.8 kcal. (14), which may be taken as an upper limit to the strength of the S–S bond in disulphur decafluoride.

It is apparent that these sulphofluorides have a structure comparable to that of the hydrocarbons and the fluorocarbons. They are similar as well in that the peripheral bonds (S–F, C–H, C–F) are considerably stronger than the central bond (S–S, C–C) in each type. Significant differences between the series are the possibilities of unsaturation in the carbon compounds, and the facility with which sulphur forms stable compounds in different valence states. This combination of similarity and dissimilarity suggested that a study of the thermal decomposition of disulphur decafluoride might be a worthwhile extension of experimental kinetics.

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Experimental

Materials

The crude gas was purified by passage through concentrated caustic and was then fractionated until a product with a vapor pressure of 235 mm. at 0°C. and a molecular weight of 256-257 at 180 mm. pressure was obtained. Compared with reported data (3), these values indicate that the final product was 99–100% pure.

Apparatus

Since disulphur decafluoride reacts vigorously with glass or mercury at higher temperatures an inert metal reactor and metal pressure measuring instrument were required (Fig. 1). The assembly consisted of a copper cylinder R closed at the bottom end by a pressure sensitive corrugated brass diaphragm D. A liquid filler and manometer system translated the pressure of the membrane into a pressure reading. The 0.003 in. membrane D, 4 in. in diameter, covered the oil-filled diaphragm chamber C. In A, the mercury used in the U-tube F came into contact with the dibutyl phthalate used in C. The level of the mercury in F, as read from the scale N, was utilized as the null indicator. The pressures required to reproduce the null level were measured on the absolute manometer H. A slightly elevated ring E, and lead gaskets, provided an effective vacuum seal when the reactor was assembled. In practice, pressure measurements using the null method were accurate to within a millimeter.

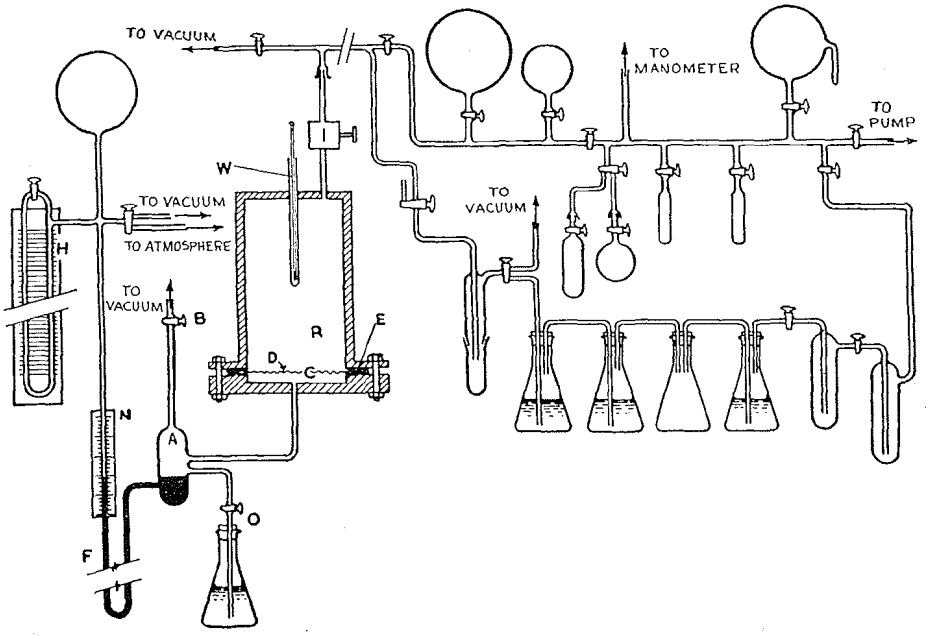

FIG. 1. *Apparatus*

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Temperature Control

The furnace consisted of two concentric thick walled magnesia cylinders heated electrically to temperatures within a few degrees of each other. By suitable manipulation of the current in the coils of the two furnaces, the temperature of the reactor, read on the thermometer W, could be kept constant within 0.1°C.

Decomposition of Disulphur Decafluoride

1. Products of the Decomposition

For purposes of analysis the products of a decomposition were passed through $2N$ sodium hydroxide solution where sulphofluorides other than sulphur hexafluoride and disulphur decafluoride were removed. The latter gases were condensed out in liquid air and subsequently identified and measured by standard gas analysis methods, (fractionation, vapor pressures, molecular weights). No gases other than these passed through the caustic bubblers. Analysis of the gases that dissolved in the caustic was performed on the basis of the following information obtained from the literature for sulphur halides (12). Upon hydrolysis the sulphur halides react in a manner that would be expected for the acid halides of sulphoxy acids.

Thus
$$S_2X_2 + 2H_2O = S_2(OH)_2 + 2HX$$
$$SX_2 + 2H_2O = S(OH)_2 + 2HX$$

and by analogy
$$SX_4 + 4H_2O = S(OH)_4 + 4HX$$

The initial products of hydrolysis are not always stable. There is eventually obtained, according to Stamm and Goehring, in the first case a mixture of free sulphur, sulphite, sulphate, and polythionates, and in the second case largely thiosulphate and a very small amount of free sulphur and sulphate. It may therefore be expected that, in the third case, largely sulphite would be obtained when solution occurs in alkali. Accordingly iodimetric titrations were carried out on aliquots taken from the sodium hydroxide solution after passage of the product gases to determine the valence state of the sulphur compounds dissolved in it. Total sulphur was determined by hydrogen peroxide oxidation and a gravimetric analysis for sulphate (9). Fluorine was measured by precipitation and separation of triphenyl tin fluoride (1). The amount of gas that was taken into solution by the caustic was calculated from PV data. For these gases the analytical results from 10 decompositions can be summarized in the statement

1 gas molecule = 1 atom sulphur = 4 atoms fluorine = 0.96 ion sulphite.

Experimentally this statement was never in error by more than 3%. On the above basis the gas that dissolved in caustic was presumed to be sulphur tetrafluoride.

The amounts of the gases introduced into, produced by, and recovered from the decompositions are shown in Table I.

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TABLE I

RECOVERY OF SULPHUR HEXAFLUORIDE, SULPHUR TETRAFLUORIDE, AND DISULPHUR DECAFLUORIDE FROM PRODUCT GASES

Run	Moles × 10^3							
	S_2F_{10} *at* t_0	Gas *at* t_f	S_2F_{10} *recov.*	S_2F_{10} *decom.*	SF_6 *recov.*	SF_4 *recov.*	Gas *recov.*	*SA/V*
4	10.9	17.3	4.3	6.6	6.5	6.3	17.1	1
5	11.0	17.5	4.2	6.8	6.6	6.5	17.3	1
6	16.2	25.6	6.8	9.4	9.2	9.6	25.6	1
7	18.3	34.2	2.6	15.7	15.6	15.7	33.9	3
8	15.5	—	5.3	10.2	9.5	10.4	25.2	3
9	15.0	25.0	4.9	10.1	9.7	10.0	24.6	3

The data in columns 2 and 3 are calculated from measured pressures in the reactor at the beginning and the end of a run. Analytical data are given in the other columns. Sulphate is reported as SF_4. SF_6 and S_2F_{10} were determined from mixed molecular weights in most instances. The reliability of this method was satisfactorily checked by fractionation of the mixture into its component parts. SA/V = surface area to volume ratio of the reaction vessel.

A comparison of columns 5, 6, and 7 shows that the decomposition may be represented by the equation

$$S_2F_{10} = SF_6 + SF_4$$

within an experimental error of about 3%. To confirm the analytical methods suitable blanks were done, such as sulphate and fluorine determinations in the presence of sodium sulphite and each other; the disulphur decafluoride loss when passed through the cold reactor and bubbler system, etc. The error as assessed from the blanks was of the order of 2%.

2. Kinetics

Experimentally the first order rate constants were to some extent dependent on the surface area to volume ratio, and on the initial pressure of disulphur decafluoride in the reactor. Rate constants were determined, therefore, for a series of runs over a wide range of initial pressures for each of three values of the surface area to volume ratio at each of three temperatures. The rate constants were calculated from the times required for half the disulphur decafluoride to decompose as shown by the pressure readings corresponding to the equation $S_2F_{10} = SF_6 + SF_4$, by means of the expression

$$k = (\ln 2)/t^{0.5}.$$

For this purpose the initial pressure had to be known accurately. With the aid of measurable values for the pressures before and after expansion into the reactor, the rate of decomposition, and the length of time required for the reactor to fill, the extrapolation was confined to a 1 mm. range, which was considered satisfactory.

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The surface area was altered by the addition of fine copper wire and was geometrically estimated. For comparative purposes, the surface area to volume ratio of the unpacked reactor was assigned a value of unity. The complete pressure versus time data for a sample run are given in Table II and Fig. 2.

TABLE II*

DATA FOR A SAMPLE RUN—NO. 27

P_H mm. Hg	Time, min.	Null	P_t mm. Hg	T, °Abs.
208.0	1.50	0	208.0	443.0
215.5	4.00	0	215.5	443.0
224.0	7.66	2	226.0	443.0
235.0	11.50	0	235.0	443.0
243.0	15.00	0	243.0	443.0
253.5	19.50	1	254.5	443.0
262.0	23.33	0	262.0	443.0
276.0	31.00	0	276.0	443.0
290.0	39.00	0	290.0	443.1
298.5	45.00	0	298.5	443.0
306.0	50.00	0	306.0	443.0
316.0	57.00	0	316.0	443.0
324.5	67.15	0	324.5	443.1
337.0	82.00	0	337.0	443.1
348.0	96.50	0	348.0	443.0

*P_H *is the pressure read from the absolute manometer (H, Fig. 1);* P_t *is equal to* P_H *corrected for null deviations read from a millimeter scale.* P_t *is the pressure in the reactor at any time t.*

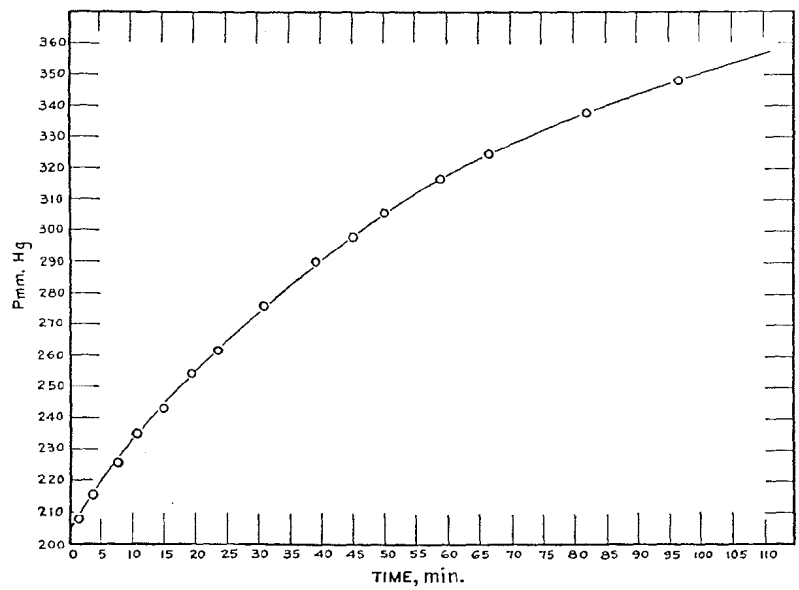

FIG. 2. *Pressure vs. time curve. Temperature = 444 0° K. SA/V = 3 Run No. 27.*

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Altogether about sixty runs were completed under the various conditions listed above. The rate constants for these runs are given in Tables III, IV, and V, and are plotted as functions of the initial pressure and the surface area to volume ratio in Figs. 3, 4, and 5.

TABLE III

THE OVER-ALL RATE CONSTANT AS FUNCTIONS OF P_0 AND SA/V
TEMPERATURE = 434.0°A.

Run	P_0	SA/V	k (min.$^{-1}$)$\times 10^3$
51	299	1	3.78
52	199	1	3.80
53	109	1	3.62
31	290	3	4.20
35	273	3	4.22
30	209	3	4.20
32	187	3	4.09
33	166	3	3.83
34	140.5	3	3.78
29	105	3	3.73
70	304	5	4.86
67	202	5	4.95
68	101	5	4.53
69	53	5	4.13
71	27.5	5	3.92

TABLE IV

THE OVER-ALL RATE CONSTANT AS FUNCTIONS OF P_0 AND SA/V
TEMPERATURE = 444.0°A.

Run	P_0	SA/V	k(min.$^{-1}$)$\times 10^3$
41	317	1	11.85
42	205	1	11.75
40	180	1	11.75
43	164	1	11.80
44	150	1	11.35
45	97.0	1	11.0
46	56.0	1	11.1
47	29.8	1	10.9
19	395	3	13.90
20	300	3	13.85
28	266	3	14.00
27	204	3	13.85
17	198	3	13.80
15	186	3	14.00
14	164	3	12.80
26	154	3	12.45
25	103	3	11.35
58	300	5	15.5
59	206	5	15.2
60	172	5	14.1
61	151	5	12.8
62	126.5	5	12.1
63	103.5	5	11.6
65	69.5	5	10.9
66	32.0	5	11.0

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TABLE V

THE OVER-ALL RATE CONSTANT AS FUNCTIONS OF P_0 AND SA/V
TEMPERATURE = 454.5°A.

Run	P_0	SA/V	$k(\text{min.}^{-1}) \times 10^3$
48	277	1	43.0
49	204	1	42.0
50	103.5	1	39.2
37	298	3	47.2
38	216	3	44.7
39	204	3	44.5
56	294	5	50.6
55	209	5	46.0
57	118	5	39.9
54*	217	5	46.0

* *The rate constants shown in Tables III, IV, and V are no longer valid beyond 70–75% conversion. When more than this amount of disulphur decafluoride has reacted, the rate begins to fall off rapidly until, at about 85–95% conversion, reaction has practically ceased. In run 41, for example, no pressure increase was observed after 18 hr., and after 36 hr. at 444.0°K, 5% of the original amount of disulphur decafluoride had not reacted.*

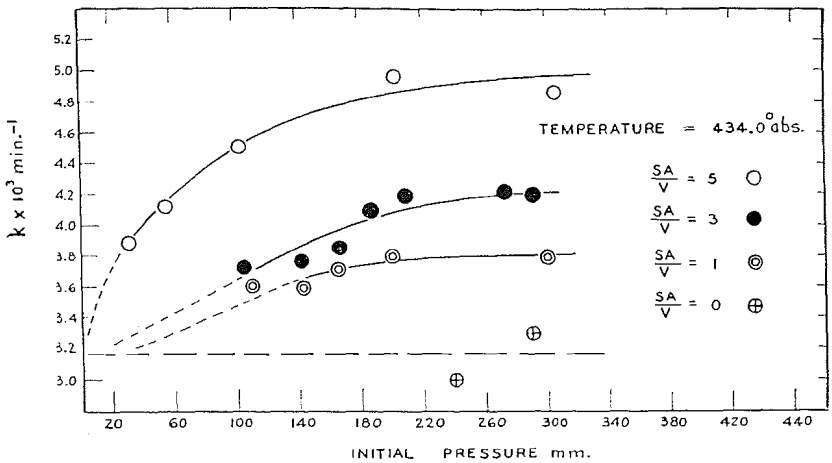

FIG. 3. *Rate constants vs. initial pressure.*

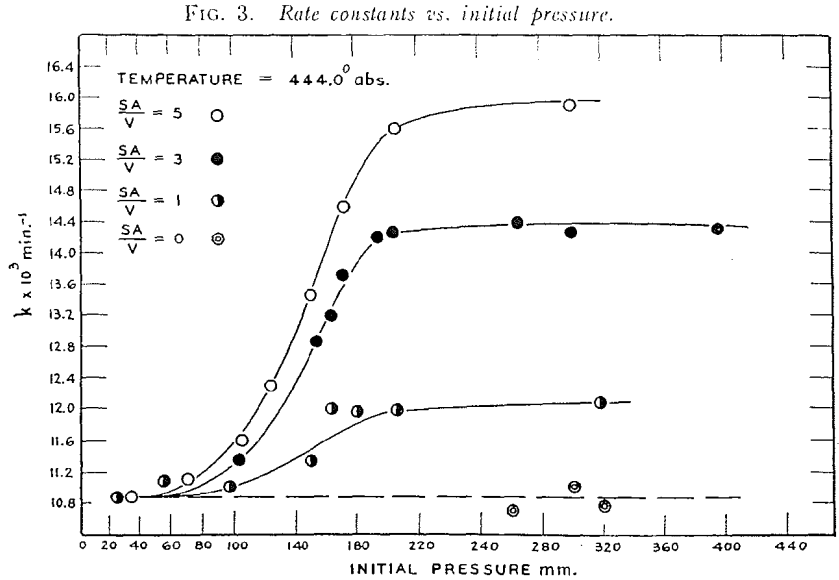

FIG. 4. *Rate constants vs. initial pressure.*

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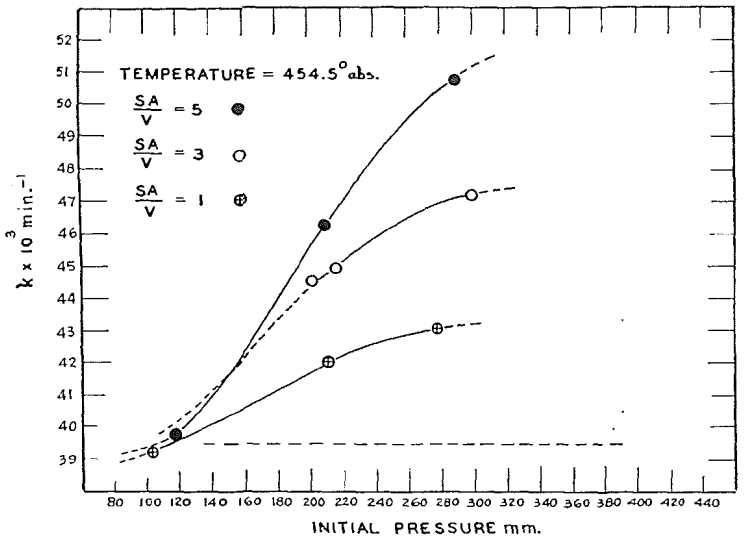

FIG. 5. *Rate constants vs. initial pressure.*

Separation of the Decomposition into Two Parts

Under the several conditions the over-all rate constants approach limiting values at high pressures. Assuming a roughly linear relationship between the surface area to volume ratio and the extent of the surface dependent reaction, a rate constant for the homogeneous decomposition may be obtained from an extrapolation of the limiting rates to $SA/V = 0$. These data are shown in Table VI.

TABLE VI

TEMPERATURE DEPENDENCE OF RATE CONSTANTS
MAXIMUM RATE CONSTANTS FOR THE DIFFERENT VALUES OF SA/V

Temp., °abs.	$SA/V=5$ k_5	$SA/V=3$ k_3	$SA/V=1$ k_1	$SA/V=0$ k_0
434.0	0.00491	0.00420	0.00380	0.00318
444.0	0.0153	0.0139	0.0118	0.0109
454.5	0.0506	0.0472	0.0430	0.0400

The values of the rate constants for the homogeneous reaction may be checked independently. At low pressures the over-all rate constants again become independent of pressure, but in this region they are unaffected by changes in the surface area, see Figs. 4 and 5. Within experimental error, the low pressure homogeneous rate constants are identical with those calculated by the extrapolation method above.

Temperature Dependence of Decomposition

(*a*) *Homogeneous Reaction*

The logarithms of the rate constants for the four surface area to volume ratios are plotted against the reciprocals of the absolute temperatures in Fig. 6, and the corresponding Arrhenius activation energies are given in Table VII.

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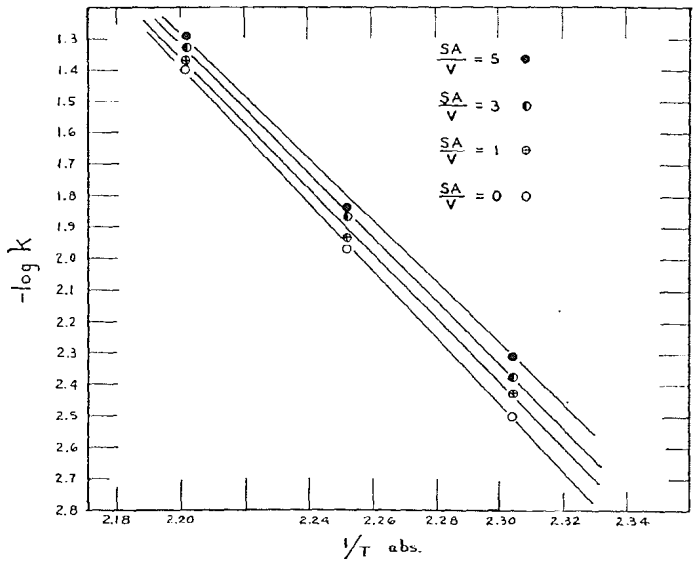

FIG. 6. *Temperature dependence of rate constants.*

TABLE VII

TEMPERATURE DEPENDENCE OF RATE CONSTANTS
ACTIVATION ENERGIES COMPARED WITH SA/V

SA/V	E (cal./mole)
5	44,800
3	46,500
1	47,800
0	49,200

With an activation energy of 49,200 cal. per mole, the absolute rate of the homogeneous decomposition in the range 160–180°C. may be expressed as

$$\ln k = 47.09 - 49{,}200/RT. \qquad (1)$$

(*b*) *Heterogeneous Reaction*

Assuming that a homogeneous first order decomposition occurs to the extent expressed in Equation (1), the temperature dependence of the remaining part of the reaction may be estimated. The slopes of the Arrhenius plots derived from the times and temperatures at which 5% of the total reaction has taken place on the surface, as obtained from the excess of the over-all as compared with the homogeneous rate, give values of 39 to 40 kcal. per mole for the activation energy of the heterogeneous reaction.

3. Effect of Foreign Gases

(*a*) *Nitric Oxide*

The effect of nitric oxide, in amounts from 0.1 to 4%, on the decomposition of disulphur decafluoride at 444°A., was studied in six runs at two different values of SA/V, 1 and 5. The initial pressures were about 200 mm. These kinetic data are assembled in Table VIII and Fig. 7.

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TABLE VIII

KINETIC DATA FOR THE DECOMPOSITION OF DISULPHUR DECAFLUORIDE IN THE PRESENCE OF NITRIC OXIDE

P_0 = 200 mm. Temperature = 444.0°A.

Run	%NO	SA/V	$k_{obs.}$	K_{NO} $(SA/V=1)$
	0	1	0.0118	0.0118
78	0.1	1	0.0120	0.0120
77	0.5	1	0.0141	0.0141
76	1.0	1	0.0172	0.0172
73	1.0	5	0.0216	0.0168
74	2.0	5	0.0265	0.0208
72	4.0	5	0.0314	0.0256

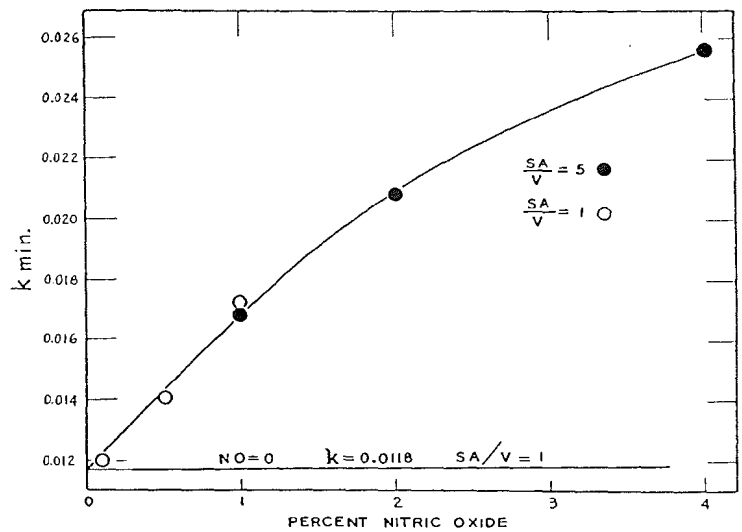

FIG. 7. *Rate constants vs. per cent nitric oxide. Temperature = 444.0°K.*

The values of the first order constants, as measured from the pressure–time curves developed for the runs, are given in column 4. In column 5, a rate constant, k_{NO}, is listed. These constants were obtained by correcting for the extra surface in the reactor, when it was packed.

(*b*) *Acetylene Dichloride*

The per cent concentrations of acetylene dichloride are given with the kinetic data for these runs in Tables IX and X, Figs. 8 and 9.

(*c*) *Order of the Catalyzed Reactions*

The first order rate constants, calculated at various times in the course of reactions catalyzed by nitric oxide and acetylene dichloride are given in Table XI.

(*d*) *Analytical Data for Catalyzed Reactions*

The products of the catalyzed decompositions were determined analytically in the same way as previously reported for the uncatalyzed reactions. Within

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TABLE IX

KINETIC DATA FOR THE DECOMPOSITION OF DISULPHUR DECAFLUORIDE IN THE PRESENCE OF ACETYLENE DICHLORIDE

$P_0 = 200$ mm. $SA/V = 1$

Run	Temp., °A.	% $C_2H_2Cl_2$	k
79	444.0	4	0.0179
80	444.0	3	0.0160
—	444.0	0	0.0118
81	454.5	4	0.0633
82	454.5	3	0.0543
—	454.5	0	0.0410

TABLE X

ACTIVATION ENERGIES FOR THE ACETYLENE DICHLORIDE CATALYZED DECOMPOSITION OF DISULPHUR DECAFLUORIDE

%$C_2H_2Cl_2$	Activation energy, cal./mole
4	49,000
3	48,000
0	47,800

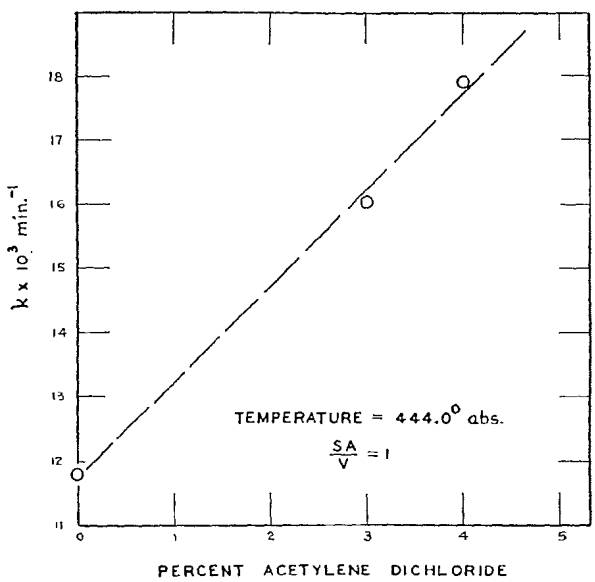

FIG. 8. *Rate constants vs. per cent acetylene dichloride.*

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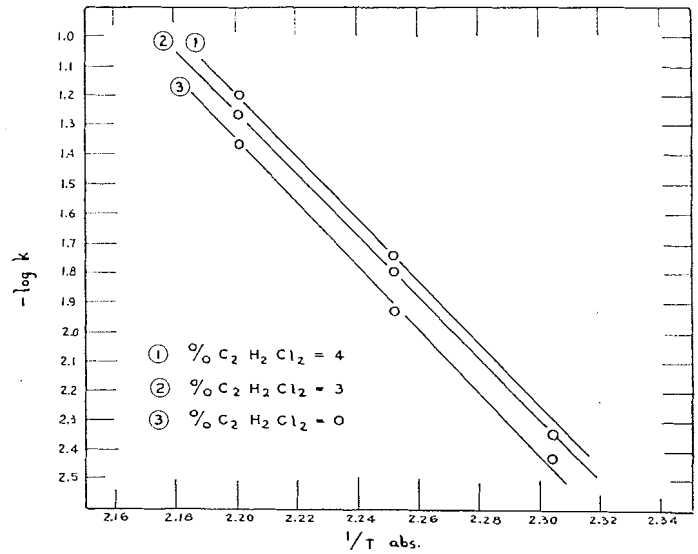

FIG. 9. *Temperature dependence of the catalyzed decomposition of disulphur decafluoride.*

TABLE XI

RATE CONSTANTS VS. TIME FOR CATALYZED REACTIONS

Run No. 79 4% $C_2H_2Cl_2$		Run No. 76 1% NO	
Time, min.	k min.$^{-1}$	Time, min.	k min.$^{-1}$
3	0.0173	2	0.0186
6	0.0181	4	0.0190
9	0.0175	6	0.0185
12	0.0179	8	0.0185
24	0.0185	10	0.0188
33	0.0179	20	0.0185
42	0.0179	30	0.0176
		40	0.0172

the experimental error, the end products were unaltered by the presence of catalyst. The data are assembled in Tables XII and XIII, in terms of sulphur hexafluoride and sulphur tetrafluoride recovered, and disulphur decafluoride reacted. The recovery of the catalyst itself was confirmed only qualitatively.

TABLE XII

ANALYTICAL DATA ON CATALYZED RUNS. NITRIC OXIDE
TEMPERATURE = 444.0°A.

Run	% Nitric oxide	S_2F_{10} dec.	SF_6 recov.	SF_4 recov.
77	0.5	5.9	5.9	6.1
78	0.1	9.6	9.4	9.4

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TABLE XIII

ANALYTICAL DATA ON CATALYZED RUNS. ACETYLENE DICHLORIDE

Run	% $C_2H_2Cl_2$	S_2F_{10} dec.	SF_6 recov.	SF_4 recov.	Temp. °K.
79	4	6.5	6.6	6.1	444.0
80	3	6.5	6.3	6.2	444.0
81	4	5.9	6.0	6.0	454.5
82	3	7.2	6.9	7.1	454.5

Discussion

The kinetic data, Figs. 3, 4, and 5, suggest that a homogeneous reaction with a first order rate independent of the pressure over the range 25–400 mm., and a heterogeneous reaction, the extent of which varies with temperature, pressure, and perhaps degree of conversion, together make up the over-all reaction. As the surface dependent reaction forms not more than 5–10% of the total decomposition in the unpacked reactor, the rate constants calculated for the homogeneous decomposition cannot be far in error.

The Homogeneous Decomposition

The absolute rate of the homogeneous decomposition may be expressed in the form

$$k = 2.99 \times 10^{20} e^{-49,200/RT} \text{ min.}^{-1}$$

over the temperature range 433 to 455°K. The value of the frequency factor, 2.99×10^{20}, is quite large compared with the values obtained for this constant in other unimolecular decompositions (4, 11). For first order reactions which may be explained as unimolecular rearrangements on the basis of the Lindemann mechanism (8) and an activation energy term expressed in n degrees of freedom as developed by Kassel (7), Hinshelwood (5) and others, frequency factors of the order of magnitude of 10^{16} are obtained. This value is deficient for the present case by a factor of 10,000. It is evident then, that a description of the decomposition of disulphur decafluoride as a unimolecular rearrangement is inadequate.

Chain Reactions in the Decomposition of Disulphur Decafluoride

It is possible to formulate a series of reactions involving a free radical chain to explain the decomposition of disulphur decafluoride. There is, however, outside of the exceptionally large value of the velocity constant, and the marked fall-off in rate at high conversions, nothing to indicate the presence of chains.

If the initial cleavage in the thermal degradation of an disulphur decafluoride molecule is assumed to be the symmetrical breaking of the S–S bond, two SF_5 free radicals would be released that may be considered capable of inducing the decomposition of further disulphur decafluoride molecules in a manner similar to the rather arbitrary selection of reactions below.

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$$S_2F_{10}^* = SF_5 + SF_5 \quad (1)$$
$$SF_5 + S_2F_{10} = S_2F_9 + SF_6 \quad (2)$$
$$S_2F_9 = SF_4 + SF_5 \quad (3)$$
$$SF_5 + SF_5 = SF_6 + SF_4 \quad (4)$$
$$SF_5 + S_2F_9 = SF_6 + 2SF_4 \quad (5)$$
$$SF_5 + \text{Wall} = SF_4 + CuF \quad (6)$$
$$S_2F_{10}^* = SF_6 + SF_4 \quad (7)$$

In 1 to 7 the chains are initiated by 1, propagated by a rapid repetition of 2 and 3, and terminated by 4, 5, and 6. In association with these a unimolecular decomposition 7 may be present. Disulphur decafluoride* represents an activated molecule.

As the surface increased the over-all rate it will be assumed that 6 may be ignored as a chain breaking reaction.

No reactions involving free fluorine atoms have been considered as, in the first place, the bonds involved have large energies and, secondly, no fluorine is formed in the decomposition.

Other possibilities than 1 to 7 could be suggested, but as these are adequate to explain a chain reaction and already include two compounds, SF_5 and S_2F_9, evidence for which is quite lacking, the list will not be extended.

From the usual steady state treatment for the above scheme,

$$(S_2F_9) = \frac{k_2(SF_5)\ (S_2F_{10})}{k_3 + k_5(SF_5)}. \quad (8)$$

Using 8 to substitute into the expression for $d(SF_5)/dt$ and equating this to zero there is obtained

$$\frac{2k_4k_5(SF_5)^3}{(S_2F_{10})} + \frac{2k_3k_4(SF_5)^2}{(S_2F_{10})} + 2k_2k_5(SF_5)^2 - 2k_1k_5(SF_5) - 2k_1k_3 = 0. \quad (9)$$

The first two terms in 9 include the concentration of S_2F_{10}. (SF_5) is certainly very small compared with (S_2F_{10}). These two terms may then drop out, leaving a quadratic and therefore a simple solution.

This consideration is not valid at high conversions, and experimentally the rate fell off rapidly at low per cent concentration of disulphur decafluoride. With these eliminations (SF_5) may be solved for

$$(SF_5) = \frac{k_1}{2k_2} + \left[\frac{(k_1)^2}{(2k_2)} + \frac{(k_1k_3)}{(k_2k_5)}\right]^{\frac{1}{2}}. \quad (10)$$

The rate of disappearance of disulphur decafluoride in this scheme is given by

$$\frac{d(S_2F_{10})}{dt} = -k_1(S_2F_{10}) - k_2(S_2F_{10})\ (SF_5) - k_7(S_2F_{10}). \quad (11)$$

Making the appropriate substitutions in (11), a first order rate constant is obtained for the over-all reaction.

$$\frac{d(S_2F_{10})}{dt} = -(S_2F_{10})\left(k_7 + \frac{3k_1}{2} + \frac{(k_1}{(2} + \frac{k_1k_2k_3)^{\frac{1}{2}}}{k_5\ )}\right) \quad (12)$$

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and where $k = \left(k_7 + \frac{3k_1}{2} + \frac{(k_1}{(2} + \frac{k_1k_2k_3)^{\frac{1}{2}}}{k_5)}\right)$ (13)

then $$\frac{d(S_2F_{10})}{dt} = -k(S_2F_{10}), \tag{14}$$

as required. Unless further extreme assumptions are made, 12 cannot be reduced to a simpler form. In this sense three possibilities exist. The whole reaction may proceed according to reaction 7, a case which has been discussed and does not seem satisfactory. Again, a chain decomposition may constitute the entire reaction, as Rice and Herzfeld suggested for the decomposition of ethane (11). In this circumstance $k_7 = 0$, and if k_1, the chain initiating rate, is small compared with the chain propagating rates k_2 and k_3, then

$$\frac{d(S_2F_{10})}{dt} = \left(\frac{k_1k_2k_3}{k_5}\right)^{\frac{1}{2}} (S_2F_{10}). \tag{15}$$

In this instance some meaning could be given to activation energies for

$$\frac{E_1 + E_2 + E_3 - E_5}{2} = E = 49{,}200 \text{ cal. per mole.} \tag{16}$$

16 is not a severe restriction. Reaction 5 represents a radical recombination and E_5 may then be quite small. If this is true, Equation (16) will probably be satisfied if $E_1 + E_2 + E_3$ is approximately equal to 100 kcal. Speculative values to satisfy this condition seem reasonable.

The magnitude of the frequency factor, 2.99×10^{20}, eliminates the possibility that the entire decomposition occurs by means of a unimolecular rearrangement. But reaction (7) could still contribute to the decomposition. In this case, the rate equations (12) and (13) could not be simplified. But the important characteristics of the decomposition, the large frequency factor, the first order rate, the rate fall-off at high conversions, the reaction products, and the size of the activation energy, would still be satisfied if reaction (7) accompanied the chain reaction.

Homogeneous Catalysis in the Decomposition of Disulphur Decafluoride

The addition of particular catalytic agents to a decomposition that consists of chain and/or nonchain parts may increase or decrease the rate of reaction (14). Presumably the catalyst can, among other things, either initiate chains or terminate them.

The information obtained from the decomposition of disulphur decafluoride when catalyzed by nitric oxide, and by acetylene dichloride, can be summarised as follows:

i. In both cases, the increase in rate was proportional to the amount of catalyst added, in the concentration range 0 to 4% catalyst.
ii. Good first order rates were obtained, indicating that the catalyst was not consumed during the course of the reaction.
iii. The experimental activation energy for the acetylene dichloride reaction

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was indistinguishable from that for the uncatalyzed decomposition. Nitric oxide was used only at one temperature.

iv. 2% nitric oxide doubled the rate. It was the more efficient catalyst by a factor of about 4.

v. The catalysis occurred in the gas phase as it was independent of the surface area to volume ratio.

vi. The nature and products of the decomposition were apparently unaffected by the presence of catalyst.

It is generally believed that a catalyst acts in a manner which permits a reaction with a simpler mechanism and a lower activation energy, and therefore a larger rate, to augment or displace the uncatalyzed reaction (13). However, if the data summarized in (i) to (vi) are reliable, the catalyzed decompositions could not have differed greatly from the uncatalyzed reactions in either mechanism or activation energy. If the reaction occurs solely by means of the rupture of the S–S bond in activated S_2F_{10} to give two SF_5 particles and the subsequent chain reactions of these particles, such a catalysis as was observed can occur only if the chains are lengthened or an additional reaction occurs between the catalyst and activated S_2F_{10} to produce more SF_5 free radicals. It is not likely that chains could be lengthened to the extent required.

A Possible Mechanism for the Decomposition of Disulphur Decafluoride

It will be assumed as is suggested by the data, that the disulphur decafluoride molecules decomposing to give SF_5 particles are activated to the same extent whether or not catalyst is present. Then, following a collision between an activated S_2F_{10} molecule and a catalyst molecule, unless a deactivating collision intervenes when no chemical reaction occurs, one or two SF_5 free radicals are produced and the catalyst is finally regenerated. This is analogous to the mechanism suggested for unimolecular rearrangements in the gas phase, and may therefore be compared with

$$S_2F_{10}^* = SF_5 + SF_5 \qquad (1)$$

$$S_2F_{10}^* = SF_6 + SF_4 \qquad (7)$$

If reactions 1 and 7 both contribute to the decomposition, an accelerated rate would result from any increase in the ratio of 1 to 7. In this circumstance a particular effect of a catalyst molecule upon a disulphur decafluoride molecule could be interference with the fluorine transfer as involved in 7, limiting the reaction to a rupture of the S–S bond, as in 1. If the catalyst were not consumed during the reaction, the products of the decomposition would be independent of the presence of catalyst. In addition, if the chain propagating reactions of SF_5 were rapid compared with the rate at which activated S_2F_{10} were consumed by 1 and 7, such a catalytic increase of the experimental rate would have little effect on the Arrhenius activation energy. The contribution of reaction 7 to the measured values of the absolute rate, as it does not involve a chain, will likely be very small, particularly as rather long chains are required to rationalize the speed of the reaction.

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Such a mechanism may explain the results obtained in this work. As a further check the several minimum chain lengths involved may be estimated.

The uncatalyzed homogeneous decomposition may be considered. It will be assumed that the expression developed by Hinshelwood (5)

$$\frac{Z \cdot e^{\frac{-E_0}{RT}} \left(\frac{E_0}{RT}\right)^{\frac{n}{2}-1}}{\left(\frac{n}{2}-1\right)!} \qquad (17)$$

gives a rough measure of the rate at which activated S_2F_{10} molecules may decompose by means of an S–S bond split. Here Z is the collision frequency, with the molecular diameter taken as 10^{-7} Å.; $E = 49.2$ kcal., $E_0 = 63.8$ kcal (reference 10); and $n/2 = 16$, evaluated from $E + \left(\frac{n}{2}-1\right)RT = E_0$. (17) will be more nearly true the lower the pressure, and at 30 mm. pressure is equal to $10^{11.9}$ molecules per cc. per sec. The total number of molecules that decompose per cubic centimeter per second when calculated from the observed reaction rate at 30 mm. is $10^{14.1}$. Then for every molecule of disulphur decafluoride that decomposes because of a rupture of the S–S bond, $10^{14.1-11.9} = 10^{2.2}$ decompose by some other mechanism. If this is the result of a chain reaction the minimum chain length is equal to 80 at 30 mm. as two SF_5 free radicals may arise from each molecule of S_2F_{10}.

With regard to the catalyzed decompositions, the minimum chain length is given by the number of molecules that do react as the result of catalysis, divided by the largest number of collisions between the catalyst and the reactant that could result in decomposition. Only collisions between activated S_2F_{10} and catalyst molecules count. Therefore a minimum chain length may be estimated by dividing $\triangle kN$ by an expression identical with (17) except that z now refers to the collision frequency between catalyst and disulphur decafluoride. $\triangle k$ is the catalytic increase in first order rate and N = molecules of disulphur decafluoride per cubic centimeter. The number that comes out of these manipulations is 1500. With the suggested mechanism, however, this number corresponds to a product value for two chains. Thus if one catalyst molecule participates in x collisions fruitful with respect to SF_5 production, and each of these SF_5 free radicals is subsequently involved in the decomposition of y molecules of S_2F_{10} as in reactions 2 and 3, then

$$2.x.y. = 1500. \qquad (18)$$

The minimum value for y as estimated from (17) for pure disulphur decafluoride at 30 mm. is certainly in as good agreement with (18) as could be expected, where x is unknown but likely much larger than 1, at 200 mm. disulphur decafluoride. At this pressure the required reaction rate is obtained if about half of the activated S–S bond ruptures give SF_5 particles. It is true that this agreement is in no way conclusive, as the assumptions involve the applicability of the Maxwell distribution in n square terms, as well as uncertifiable values of activation energies and molecular diameters.

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It is more difficult to suggest a simple mechanism for catalysis in the decomposition if reaction 7 is absent. If it is possible for a collision with a catalyst molecule to decrease the length of time required for an activated S_2F_{10} molecule to give 2 SF_5 particles, catalysis would occur. Although the picture is vague, the experimental results obtained in this work could perhaps be explained as well in some such manner.

Acknowledgments

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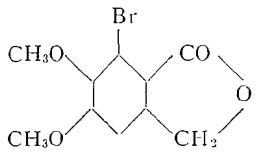
3-BROMOMETAMECONINE[1]

By R. H. Manske,[2] J. A. McRae,[3] and R. Y. Moir[3]

Abstract

3-Bromo-*m*-meconine was prepared in three ways: (*a*) by direct bromination of metameconine, (*b*) from 5-bromoveratric acid and formaldehyde, and (*c*) from 6-amino-*m*-meconine by a method which amounted to an independent derivation of the structures of 6-amino-*m*-meconine and its products of transformation. The structures obtained agreed with those previously reported by us. Carefully purified 6-bromo-*m*-meconine was found to melt at 207°C. in agreement with our previous work, rather than at 223°C. as reported by Rây and Robinson. During the investigation, a convenient synthesis of metaopianic acid was discovered, and the following new compounds were characterized: 6-acetamino-*m*-meconine, 6-diacetylamino-*m*-meconine, 6-acetamino-3-bromo-*m*-meconine, 6-amino-3-bromo-*m*-meconine, 2-iodoveratric acid, and 5-iodoveratric acid.

In a recent paper (10), it was shown that there had been some uncertainty about the nature of the compound regarded as 6-bromo-*m*-meconine (I).



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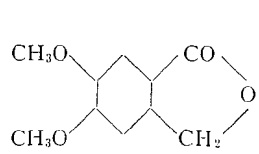

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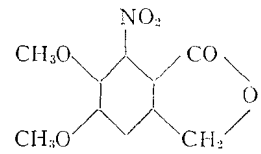

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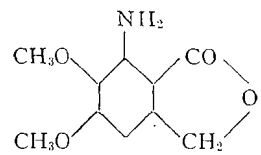

IV

This compound had been prepared by Rây and Robinson (17) from *m*-meconine (II) through the stages of nitration, reduction, and Sandmeyer replacement of the amino group by bromine, and was reported to melt at 223°C. Repeated attempts to confirm their work invariably yielded a bromo-*m*-meconine melting at 207°C. (10), and the same lower melting point was obtained when the synthesis was once more repeated with special precautions to ensure the purity of all the compounds, although the intermediate 6-nitro-*m*-meconine (III) and 6-amino-*m*-meconine (IV) had almost the same melting points as those reported by Rây and Robinson (17). Furthermore, these authors stated (17) that the condensation of 2-bromoveratric acid (V) with formaldehyde gave the same 6-bromo-*m*-meconine melting at 223°C. This was essentially their proof of

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Contribution from the Research Laboratories, Dominion Rubber Company, and from the Department of Chemistry, Queen's University.
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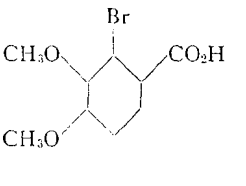
orientation. Our attempts to prepare 6-bromo-*m*-meconine by this method did not give it although a small yield of a product of melting point 223°C. was usually obtained. The structure of this compound is under investigation.



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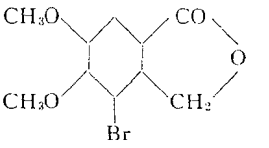

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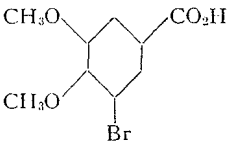

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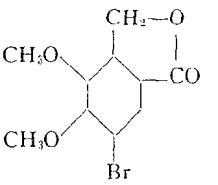
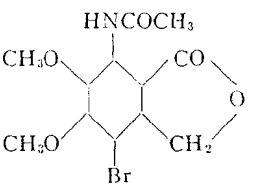
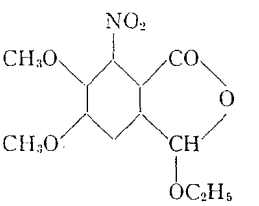


VIII

Since only two ring-brominated bromo-*m*-meconines are possible, preparation of the alternative 3-bromo-*m*-meconine (VI) was of some importance. The compound has now been prepared by three different routes. First of all, 5-bromoveratric acid (VII) when condensed with formaldehyde gave a small yield of a compound melting at 183°C. which might have been either 3-bromo-*m*-meconine (VI) or its isomer (VIII). However, reductive elimination of the bromine yielded *m*-meconine and therefore only structure VI was possible. Secondly, direct bromination of *m*-meconine yielded the same compound, and since I cannot be obtained from 5-bromoveratric acid by condensation with formaldehyde, nor VIII by bromination of *m*-meconine, structure VI was confirmed. Thus bromination and nitration occur at different positions on the ring. Finally, the 6-amino-*m*-meconine (IV) of Rây and Robinson (17) was acetylated and then brominated, and the resulting 6-acetylamino-3-bromo-*m*-meconine (IX) deacetylated and the amino group eliminated *via* the diazo



IX



X

compound with the aid of hypophosphorous acid. The resulting bromo-*m*-meconine was identical with the product (VI) obtained by the above two independent routes. This series of reactions confirmed the orientation of 6-amino-*m*-meconine which previously (10) had been obtained by bringing it into relation with 3-methoxy-*m*-meconine (1, 9). Both the 6-bromo-*m*-meconine of

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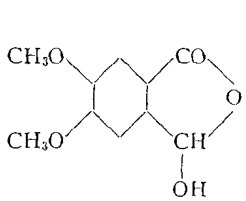
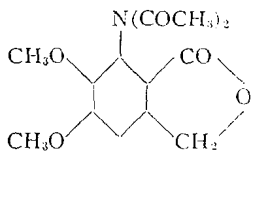
melting point 207°C. and the 3-bromo-*m*-meconine of melting point 183°C. have been oxidized to the same 3-bromo-*m*-hemipinic acid (5), a further confirmation of the structures assigned to them.

A number of other points had to be considered before the structures of the bromo-*m*-meconines could be finally assigned. For example, it may be noted that our structures are not independent of the proper orientation of *m*-meconine and of the bromoveratric acids. The structure of *m*-meconine has been firmly established (4, 12), while the correct orientation of the bromoveratric acids has been thoroughly verified by the work of a number of chemists (2, 3, 7, 8, 11, 14, 15, 18, 19). At various times it seemed possible that some of the compounds regarded as *m*-meconines might actually be pseudo-esters of *m*-opianic acid. For example, Rây and Robinson (17) prepared 6-nitro-*m*-meconine (III) by the action of nitric acid upon *m*-meconine and purified the crude, acid-contaminated product by extraction with boiling alcohol. These conditions seemed favorable (4, 6) for the formation of the pseudo-ester (X) whose carbon content is not very different from that of III. The point was easily settled since 6-nitro-*m*-meconine prepared out of all contact with ethanol was identical with the material made by the method of Rây and Robinson. By various means, the other compounds were also shown not to be derivatives of *m*-opianic acid.

There is recorded in the experimental section a convenient synthesis of *m*-opianic acid (XI) (4, 6, 13) from *m*-meconine, as well as the characterization of the new compounds 6-diacetylamino-*m*-meconine (XII), 2-iodoveratric acid (XIII), and 5-iodoveratric acid (XIV) which were incidental to the main portion of our work. Investigation of other substituted *m*-meconines is in progress.



XI



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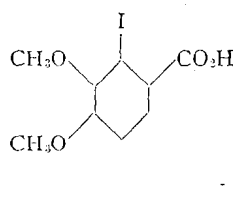

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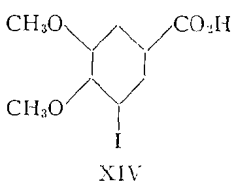

XIV

Experimental

All melting points were corrected.

3-Bromo-m-meconine (VI)

The procedure was similar to that used by Rây and Robinson (17) for the production of *m*-meconine. Acetic acid (40 cc.), formaldehyde (7 cc. of a 35% solution), concentrated hydrochloric acid (20 cc.), and 5-bromoveratric acid

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(7 gm.) were heated on the steam bath intermittently for a total of 54 hr.; at the end of the first 30 hr. of heating another portion of formaldehyde solution (5 cc.) and a portion of acetyl chloride (5 cc.) were added. At the end of the heating period, the mixture was diluted with much ether and the ethereal solution thoroughly washed with water. Washing with sodium bicarbonate solution served to remove the unchanged bromoveratric acid (2.8 gm.) from the ethereal solution, which was then evaporated to dryness. Three crystallizations of the residue from methanol gave an almost pure product of melting point 178°C. which had a carbon and hydrogen content in fairly close agreement with the theoretical for 3-bromo-*m*-meconine. Reduction of a portion of this material with zinc and aqueous potassium hydroxide yielded a substance of melting point 154–155°C. which proved to be identical with *m*-meconine. Oxidation of the bromo-*m*-meconine with permanganate and treatment of the product with diazomethane gave the dimethyl ester of 3-bromo-*m*-hemipinic acid (5, 10).

In another preparation on a larger scale, 5-bromoveratric acid (71.8 gm.) was heated for 28 hr. on the steam bath with glacial acetic acid (250 cc.), concentrated hydrochloric acid (174 cc.), and formaldehyde (60 cc. of a 40% solution). Water (100 cc.) was then added and the yellow-brown precipitate immediately recovered. Fractional crystallization of this precipitate from dilute ethanol gave 3-bromo-*m*-meconine, m.p. 182.4–182.8°C., and 5-bromoveratric acid, m.p. 189.5–190°C. The filtrate of the reaction mixture was concentrated and yielded considerable amounts of a new substance which after five recrystallizations formed white needles of m.p. 240.5–242°C. The constitution of this material is still under investigation.

A crude sample of the 3-bromo-*m*-meconine (m.p 178–178.5°C., 6.80 gm.) made in the above reaction was later purified by successive recrystallizations from methanol and glacial acetic acid. Large, colorless needles of m.p. 181.9–183.6°C. were obtained in a yield of 4.64 gm. Calc. for $C_{10}H_9O_4Br$.: C, 43.96%; H, 3.30%. Found: C, 43.61%; H, 3.33%.

meta-Meconine (II)

Veratric acid (402.6 gm.) was converted to *m*-meconine essentially by the method of Rây and Robinson (17). The crude *m*-meconine was very thoroughly extracted with aqueous sodium bicarbonate solution, in which it was insoluble, and then with water. After being dried, the extracted crystals were twice recrystallized from *n*-butanol, distilled at 175–185°C. (0.1 to 0.2 mm.), once again recrystallized from *n*-butanol, and finally dried *in vacuo* over sulphuric acid. The pure white crystals of 'purified *m*-meconine' weighed 149.1 gm. (35% yield); m.p. 157.1–157.5°C. Two other crops of less pure *m*-meconine were also obtained: one from the mother liquors by distillation *in vacuo* and two crystallizations from *n*-butanol, yield 30.5 gm. or 7%, m.p. 151–156°C.; the other from various tars obtained in the experiment by extraction with much hot water, recovery of the soluble crystals, extraction of the crystals with sodium

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bicarbonate solution, distillation, and recrystallization. The yield of impure *m*-meconine obtained from the tars in this way was 14.1 gm., or 3%, m.p. 151–155°C. The tars themselves were quite lachrymatory, pointing to the presence of chloromethyl groups. Veratric acid was recovered in very small amounts in a very impure condition.

Bromination of m-Meconine

m-Meconine (purified as above, 50.0 gm.), glacial acetic acid (508 cc.), bromine (13 cc.), iron powder (0.1 gm.), and aluminum metal (0.1 gm.) were mechanically stirred together and heated intermittently over the course of several days at about 40–83°C. for 27 hr. altogether; the temperature during the heating periods was usually 50–60°C. Then more bromine (1.8 cc.) dissolved in glacial acetic acid (5 cc.) was added. Next morning the reaction mixture was rinsed onto much ice and brought to neutrality with sodium hydroxide, sodium bisulphite, and water. The precipitated solid was recovered, thoroughly extracted with dilute hydrochloric acid, with aqueous sodium bicarbonate, and with water, and dried in the air. The crude crystals (57 gm.) were fractionally recrystallized from methanol. Several fractions of low melting point were obtained, as well as four fractions which melted above 179°C. and so were already almost pure. The four fractions of high melting point were combined (yield 7.9 gm. or 11%), and recrystallized several times, once from methanol and three times from glacial acetic acid, charcoal being used once. The glistening white crystals (3.0 gm.) so obtained had a melting point of 182.3–183.2°C. Calc. for $C_{10}H_9O_4Br$: C, 43.96; H, 3.30%; molecular weight 273. Found: C, 43.76, 44.15; H, 3.49, 3.54%; molecular weight by Rast camphor method: 279. Since the mother liquors from the four final crystallizations yielded 3.3 gm. of product of m.p 180.9–182.4°C., it seemed that the analyzed product must have been pure. A mixed melting point showed that the analytical material was identical with the 3-bromo-*m*-meconine obtained from the reaction of 5-bromoveratric acid and formaldehyde.

Prolonged attempts were made to separate pure compounds from the crystalline fractions of low melting point, but after fractional distillation, fractional crystallization from *n*-butanol, and sublimation of the crystals, a number of impure fractions were obtained which all melted approximately in the range 130–150°C.

6-Nitro-m-meconine (III)

The method was that of McRae *et al.* (10), except that the use of ethanol was avoided to prevent confusion of the product with the ethyl psuedo-ester of 6-nitro-*m*-opianic acid. *m*-Meconine (purified, as above, 30.1 gm.) was added with mechanical stirring to a cooled mixture of concentrated nitric acid (170 cc.) and concentrated sulphuric acid (38 cc.), the temperature being kept below 8°C. Stirring was continued for one hour, then the mixture was kept below 5°C. for three hours, and finally poured onto ice (1200 gm.) with stirring. Next morning, the cream-colored crystals were recovered and very thoroughly ex-

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tracted with water to remove the inorganic acids as completely as possible. The wet crystals were then twice recrystallized from glacial acetic acid. After the first recrystallization, the very large, very slightly yellow needles were washed only with acetic acid, but, after the second, they were washed with acetic acid and then repeatedly with methanol before being thoroughly dried. The yield of pale yellow needles of m.p 182.3–183.1°C. was 26.6 gm. or 72%. Calc. for $C_{10}H_9O_6N$: C, 50.21; H, 3.77%. Found: C, 50.69, 50.43; H, 3.91, 3.81%.

6-Amino-m-meconine (IV)

Pure 6-nitro-*m*-meconine (25.8 gm.), made from pure chemicals, was converted to crude 6-amino-*m*-meconine by the method of Rây and Robinson (17). The crude amine was twice recrystallized from methanol with the help of 'Filter-Cel', giving beautiful white needles of m.p. 160.0–160.6°C., yield 14.4 gm. or 64%. Calc. for $C_{10}H_{11}O_4N$: C, 57.41; H, 5.26%. Found: C, 57.48, H, 5.10%.

6-Acetamino-m-meconine

(1) Pure 6-amino-*m*-meconine (10.0 gm.), made from pure chemicals, was dissolved in warm glacial acetic acid (55 cc.) and treated with acetic anhydride (7.0 cc.). The solution was kept at 72–84°C. for 40 min., cooled with shaking, diluted with water (65 cc.) and chilled. White crystals separated and were recovered and thoroughly washed with water. After one recrystallization from water, the pure crystals had a melting point of 228.3–230.0°C., yield 5.0 gm. or 42%.

(2) Crude 6-amino-*m*-meconine (13.6 gm.) made during the previous investigation (10) was converted to the crude acetyl derivative in the same way as just described. The crude product was recrystallized twice from glacial acetic acid, charcoal being used once; the crystals so obtained weighed 3.1 gm., m.p. 229.3–230.3°C. One more recrystallization from water gave the analytical sample in large colorless plates, m.p. 229.8–230.4°C. Calc. for $C_{12}H_{13}O_5N$: C, 57.37; H, 5.18; OCH_3, 24.70%. Found: C, 57.73, 57.99; H, 5.10, 5.16; OCH_3, 24.72, 24.64%. A mixed melting point with the material made from the pure chemicals showed no depression, so that the identity of the 6-amino-*m*-meconine used previously (10) was firmly established. Additional amounts of the acetyl derivative were recovered from the mother liquors.

6-Diacetylamino-m-meconine (XII)

Crude 6-acetamino-*m*-meconine (0.91 gm.) was heated under reflux for five hours with acetic anhydride (11.2 cc.). The solution was chilled in a bath of ice and salt and the crystals which separated were recovered and washed with water. After one recrystallization from dilute acetic acid, the glistening white crystals had a melting point of 202.6–203.8°C. Calc. for $C_{14}H_{15}O_6N$: C, 57.34; H, 5.12; OCH_3, 21.16%. Found: C, 57.28, 57.59; H, 5.01, 5.22; OCH_3, 21.34, 21.25%.

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6-Acetamino-3-bromo-m-meconine (IX)

A solution of bromine (1.6 cc.) in glacial acetic acid (7 cc.) was added to glacial acetic acid (6 cc.), and 6-acetamino-*m*-meconine (3.4 gm. of m.p. 229.4–230.8°C.); the mixture was shaken thoroughly and allowed to stand for five hours. The resulting solution was diluted with water, treated with enough sodium bisulphite to remove excess bromine and with enough sodium bicarbonate to remove the mineral acid, and then chilled. The crystals which deposited were recovered, thoroughly extracted with water, and twice recrystallized from dilute methanol. Glistening white needles were obtained in a yield of 3.25 gm. or 73%, m.p. 188.2–189.2°C. Calc. for $C_{12}H_{12}O_5NBr$: C, 43.64; H, 3.64%. Found: C, 43.16, 43.31; H, 3.82, 3.59%.

6-Amino-3-bromo-m-meconine

Pure 6-acetamino-3-bromo-*m*-meconine (2.77 gm.) was heated under reflux for one and one-half hours with dioxane (10 cc.) and concentrated hydrochloric acid (12 cc.). The mixture was then cooled, brought to neutrality, and chilled. Brown, somewhat tarry crystals deposited, and were recovered, washed with water, and recrystallized from dilute methanol with the help of charcoal. The light brown needles so obtained, m.p. 122.2–124.7°C. were then sublimed under a pressure of 0.1 mm. and again recrystallized from dilute methanol. Pure white needles of m.p. 125.2–126.0°C. were obtained in a yield of 0.98 gm. or 41%. Calc. for $C_{10}H_{10}O_4NBr$: C, 41.67; H, 3.47%. Found: C, 41.69, 41.58; H, 3.42, 3.51%.

Deamination of 6-Amino-3-bromo-m-meconine

Pure 6-amino-3-bromo-*m*-meconine (0.408 gm.) was heated with water (50 cc.) and concentrated hydrochloric acid (8.4 cc.), but it did not all dissolve. The suspension was cooled to 0°C., treated with a solution of sodium nitrite (0.124 gm.) in water (15 cc.) and mechanically stirred at a temperature of less than 0°C. for two and one-quarter hours. The clear yellow solution was filtered onto ice; the filtrate was treated with hypophosphorous acid (5.2 cc. of a 30–32% solution) and kept in an ice bath for two hours and then in the refrigerator for 39 hr. Bright yellow crystals separated from the solution and were recovered, washed with water, and recrystallized four times from methanol, charcoal being used in the last three crystallizations. Pure white needles were obtained whose melting point was 182.9–183.6°C. Calc. for $C_{10}H_9O_4Br$: C, 43.96; H: 3.30%. Found: C, 44.13; H, 3.44%. A mixed melting point of these crystals with the pure 3-bromo-*m*-meconine obtained by direct bromination of *m*-meconine showed no depression.

Oxidation of m-Meconine

m-Meconine (m.p. 151–156°C., 15.6 gm.), acetic anhydride (66 cc.), and glacial acetic acid (49 cc.) were warmed together on the steam bath, the mixture being protected from atmospheric moisture. Red lead oxide (Merck's reagent Pb_3O_4, 70.5 gm.) was added in portions during the course of 25 min.,

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and then the reaction mixture was heated on the steam bath for four hours. A portion of the solvent was removed by distillation *in vacuo* and the undistilled residue was diluted with water (304 cc.) and chilled. Crystals were deposited and recovered, thoroughly washed with water, and dried in the air; yield 14.2 gm. These crystals were boiled for a few minutes with a dilute solution of potassium carbonate in order to decompose the acetyl derivative of *m*-opianic acid (13), and then filtered hot, the negligible precipitate being discarded. Acidification of the filtrate gave crystals which after being recovered and washed were very thoroughly extracted with cold dilute sodium bicarbonate solution for 45 min. The insoluble crystals were *m*-meconine since after recrystallization from water they melted at 154.6–155.0°C. not depressed by admixture with pure *m*-meconine. The recovery of *m*-meconine was 8.1 gm., or 52%. When the sodium bicarbonate extracts of the recovered *m*-meconine were acidified, crystals were recovered in a yield of 1.8 gm., m.p. 170–176°C., and a further 1.0 gm. of crystals soluble in sodium bicarbonate solution was recovered from various aqueous extracts from the experiment. The crude *m*-opianic acid (2.8 gm. or 17%) was twice recrystallized from methanol, charcoal being used in the first recrystallization, and the well shaped white needles which resulted weighed 1.65 gm. Their melting point of 140.7–141.6°C. showed them to be the almost pure methyl pseudo-ester of *m*-opianic acid (6). Calc. for $C_{11}H_{12}O_5$: C, 58.93; H, 5.36%. Found: C, 58.68, 58.41; H, 5.21, 5.28%. The conversion of the acid to its pseudo-ester was surprisingly easy, but the fact should be noted that the analysis for carbon and hydrogen was not a good criterion of the extent of the conversion.

Reaction of Some Substituted m-Meconines with Alkali

m-Meconines and the pseudo-esters of *m*-opianic acids dissolve slowly in alkali while *m*-opianic acids themselves dissolve instantly even in the cold. On acidification of their alkaline solutions, the *m*-meconines are recovered unchanged, the pseudo-esters are converted to the free acid, and the *m*-opianic acids are either unchanged or undergo the Cannizzaro reaction. When these characteristic tests are used to distinguish between these three classes of compounds, alcohols cannot be used to purify the recovered materials, on account of the easy formation of pseudo-esters.

6-Methoxy-m-meconine (m.p. 134.5–136.5°C. 0.32 gm.) made in the previous investigation (10) was heated on the steam bath with a dilute aqueous solution of potassium hydroxide. The solid dissolved completely after about two minutes. Heating was continued for about four hours; the warm solution was then cautiously acidified and chilled. The recovered crystals after one recrystallization from water were slender, glistening needles of m.p. 136.5–137.5°C., yield 0.22 gm. A mixed melting point showed them to be identical with the original material.

Pure *3-bromo-m-meconine* (0.80 gm.) from the direct bromination of *m*-meconine was treated in the same way. Solution required 20 min., and, after

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one recrystallization of the product from dilute acetic acid, pure starting material was recovered in a yield of 0.73 gm. and identified by its melting point and mixed melting point.

6-Bromo-m-meconine (m.p. 206.2–207.2°C., 0.41 gm.) (10) after being heated with caustic, acidified, and recrystallized from dilute acetic acid, gave needles of m.p. 206.7–207.0°C. in a yield of 0.35 gm., which a mixed melting point showed to be the original material. Nearly 25 min. was required to bring about the solution of the crystals in hot caustic.

5-Iodoveratric Acid (XIV)

5-Iodoveratric aldehyde (37 gm.) (15) was stirred with water and sodium bicarbonate at 80–90°C. A warm solution of potassium permanganate (30 gm.) in water was slowly added. When the oxidation was complete, the manganese dioxide was removed and well washed with water. On acidification of the filtrate, a white flocculent precipitate of 5-iodoveratric acid was obtained in a yield of 94%. After it had been recrystallized from benzene or from glacial acetic acid, the 5-iodoveratric acid melted at 182–183°C. Calc. for $C_9H_9O_4I$: I, 41.23%. Found, by the method of Stepanow: I, 41.58%.

2-Iodoveratric Acid (XIII)

Crude 2-iodoveratric aldehyde (22.0 gm.) (16) was mixed with stabilized acetone (150 cc.), water (25 cc.), and sodium bicarbonate (4 gm.). Finely powdered potassium permanganate (18 gm.) was slowly added to the warm mixture, and the oxidation was soon complete. The reaction mixture was diluted with water, heated, and filtered, and the precipitate was thoroughly washed with hot water. Excess permanganate was destroyed with sodium bisulphite, the solution was filtered again, and the filtrate acidified to yield 2-iodoveratric acid. After one recrystallization from dilute alcohol with charcoal, the crystals were obtained in a yield of 16.2 gm. or 70%, m.p. 202–203.5°C. One more recrystallization gave the pure acid of m.p. 205–206°C. which was depressed by about 5° by admixture with either 2-chloroveratric acid or 2-bromoveratric acid. Calc. for $C_9H_9O_4I$: I, 41.23%; equivalent weight, 308.1. Found: I, 41.91, 42.07%; equivalent weight, 306.6.

6-Bromo-m-meconine (I)

6-Bromo-*m*-meconine (m.p. 206.2–207.2°C., 0.341 gm.) from the previous investigation (10) was once recrystallized from methanol, and the colorless crystals so obtained were as usual rigorously dried. The melting point of the purified crystals was 206.2–206.8°C. Calc. for $C_{10}H_9O_4Br$: C, 43.96; H, 3.30%; molecular weight: 273. Found: C, 43.53, 43.67; H, 3.40, 3.77%; molecular weight (on another analytical sample by the Rast camphor method): 296.

Acknowledgments

Microanalyses reported in the experimental section were performed by Mr. A. E. Ledingham and Mr. Ralph Mills of the Dominion Rubber Company.

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THE MEASUREMENT OF THE ABSOLUTE RATES OF REMOVAL OF LEAD AND TELLURIUM MIRRORS BY A FREE RADICAL STREAM[1]

BY D. M. MILLER[2] AND C. A. WINKLER

Abstract

Two new methods for measuring the rates of removal of mirrors in a Paneth apparatus have been developed. By measuring the rates of removal of lead and tellurium mirrors it was shown that the same number of radicals react with each atom of both metals. It is suggested that lead dimethyl and tellurium dimethyl are the compounds formed.

Introduction

Since it was first shown by Paneth and Hofeditz (5) that metallic mirrors could be removed by free radicals a number of methods have been devised to measure the rate at which the mirrors disappear. Prileshajeva and Terenin (6) made use of a lamp and photoelectric cell and measured the change in optical density of the mirror as it was being removed. Leighton and Mortensen (4) used mixtures of Radium D, E, and F as mirrors and measured their rate of disappearance by the effect of the radiation on a β-ray electroscope placed near the mirror. The products were caught in a trap, treated with excess bromine, evaporated under vacuum, and the residue tested by the electroscope. This method was used only in a qualitative way, to show the existence of radicals of which the concentration was too small to detect in any other way. Burton, Ricci, and Davis (1) also used this method but modified it by passing the products through a cracking furnace which decomposed the metal alkyl and formed a new mirror. The portion of the tube with the new mirror was cut off and treated with dilute nitric acid to dissolve the active lead. The acid was evaporated and the activity of the residue measured by a Lind electroscope. Feldman, Ricci, and Burton (3) used long heavy lead mirrors to remove the radicals. The products in the trap were analyzed by a micromethod to determine the amount of lead removed. Whittingham (7) followed the disappearance of lead mirrors by measuring the change in their electrical conductivity as a function of the mirror thickness. Most of these methods are, however, only comparative rather than absolute; that is, the actual number of moles of metal removed cannot be found directly.

[1] *Manuscript received January 29, 1951.*
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The present work is concerned with the development of two methods for measuring the absolute rate of removal of lead and tellurium mirrors; the first, a direct weight method, the second a radioactive method.

I. Direct Weight Method

In this method the amount of metal removed was measured by the change in weight of a mirror deposited on a metallic form suspended from a quartz spiral balance (Fig. 1).

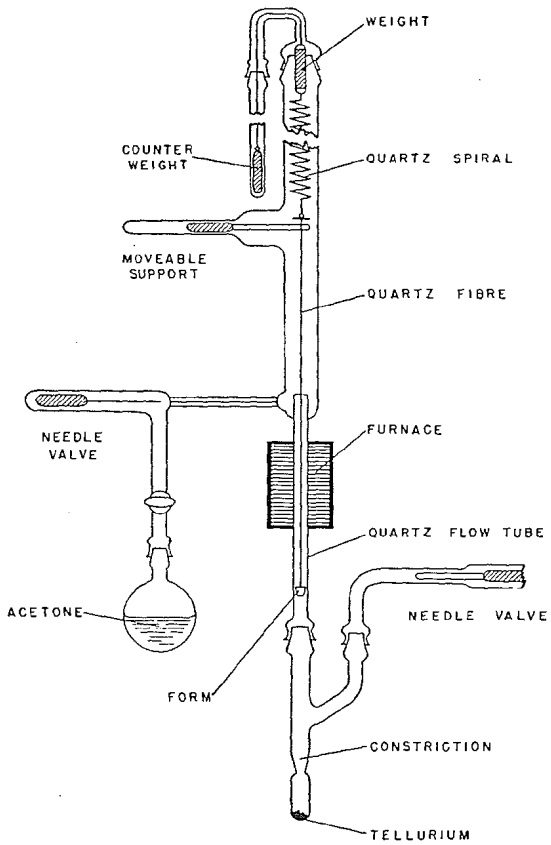

FIG. 1

Acetone vapor, as a source of free radicals, was pumped through a vertical quartz tube heated at its upper end by an electric furnace. The form on which the mirror was deposited was connected by a long quartz fiber to a calibrated quartz spiral, so as to be freely suspended in the tube a short distance below the bottom of the furnace. The top of the quartz fiber was bent to form a circle at right angles to the fiber. During periods of flow this ring rested on a forked support moved into place by a magnet. The position of the form was thus fixed during an experiment.

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The top of the spiral was attached to a weight counterbalanced by an iron weight enclosed in glass, to which it was connected by a silk thread. The form could thus be raised and lowered by moving the counter weight with a magnet.

Deposition of the mirror presented the greatest difficulty. The first method attempted was to lower the form into a well at the bottom of the tube containing a chip of tellurium, and to sublime the tellurium on to the form. However, the form, which was of low heat capacity, was itself warmed up, thus preventing the tellurium from condensing on it. By making the form a tapered cylinder open at both ends and lowering it into a constricted well of the same taper, the form was cooled by contact with the glass and the tellurium could then be deposited on the inside surface.

The procedure used in making an experiment was very simple. The forked support holding the spiral in position was withdrawn and the form lowered into the well where a mirror was deposited. The form was again raised, the position of the bottom of the spiral noted with a cathetometer, and the support moved into place. Acetone vapor was then passed through the system for a measured length of time, after which the system was evacuated and the position of the bottom of the spiral again determined with the cathetometer. From the change in extension of the calibrated spiral the change in weight of the mirror could be readily deduced.

To test the reproducibility of the results obtained with this apparatus, several mirrors were deposited and subjected to the free radical stream. The results are given in Tables I and II.

For the results in Table I a platinum form was used, while those in Table II were obtained using a lighter aluminum form and a more sensitive spiral. The aluminum form was probably rendered inert by the cohesive layer of oxide on its surface; in any case, it appeared to be entirely satisfactory.

In Table I, Expt. 6*b* may be rejected since the mirror was probably depleted during Expt. 6*a*. No explanation can be offered for the high value of 1.35 mm. extension. The average value, if Expts. 3 and 6*b* are discarded, is 0.83 mm., the average deviation being 0.06 mm., or 7%.

TABLE I

PLATINUM FORM, 5 CM. FROM FURNACE. TEMPERATURE OF FURNACE, 815°C. PRESSURE 2.5 MM. (AT INLET TO TUBE). TIME OF FLOW, 5 MIN.

Experiment number*	Change in extension of spiral, mm.
1	0.85
2	0.85
3	1.35
4	0.70
5	0.80
6*a*	0.95
6*b*	0.50

* *The numbers indicate mirror deposited, while the letters indicate number of experiments on the same mirror.*

TABLE II

ALUMINUM FORM, 7 CM. FROM FURNACE. TEMPERATURE OF FURNACE, 870°C. PRESSURE, 2.5 MM. (AT INLET TO TUBE). TIME OF FLOW, 6 MIN.

Experiment number*	Change in extension of spiral, mm.
1	0.80
2*a*	1.60
2*b*	1.80
2*c*	0.90
3	1.75
4	1.80
5*a*	1.85
5*b*	1.50
6	1.55

* *The numbers indicate mirror deposited, while the letters indicate number of experiments on the same mirror.*

In Table II, Expt. 2*c* gave a low result owing to depletion of the mirror. If Expts. 2*c* and 1 (which was unaccountably low) are discarded, the average value is 1.69 mm. with an average deviation of 7%.

The number of radicals reacting with the mirror can be obtained directly from the weight of metal removed. Thus it can be seen that this method is absolute rather than comparative and that it provides a rapid and fairly reproducible means of measuring the rate of mirror removal.

II. Radioactive Method

This was a refinement of the method of Leighton and Mortensen (4). Radioactive lead and tellurium mirrors were employed in the usual Paneth apparatus, and the products of the reaction caught in a liquid air trap. The metal alkyls were converted to nonvolatile salts, the excess organic material evaporated, and the radioactivity of the residue compared with that of a weighed standard sample, to determine the weight of the metal removed.

Experimental

Dimethyl ether and acetone were used as radical sources. The organic vapor was carried through a quartz tube of 25 mm. diameter heated electrically and then through an 8 mm. quartz flow tube in which the mirrors were deposited. In all experiments the velocity of the vapor in the flow tube was 3500 cm. per sec., the pressure at the mirrors being 0.87 mm. The mirrors were all deposited in a stream of hydrogen with the leading edge of the first mirror 11 cm. from the furnace and the length adjusted to 2.0 cm. In experiments in which two mirrors were used, the second mirror was 2.0 cm. from the first and was itself 2.0 cm. in length.

The procedure used in making an experiment was as follows. The mirror metals were contained in side arms from which a portion of them could be distilled into the flow tube in a stream of hydrogen to form the mirrors. The

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organic vapor was then passed through the system with the furnace at about 800°C. When the required time (usually an hour) had elapsed, the flow was stopped and the trap containing the products removed. Ten cubic centimeters of 20% nitric acid was added to the trap and its temperature slowly raised to the boiling point. This solution was then transferred by small portions to a 35 mm. watch glass and evaporated under a heat lamp. The activity of the sample thus prepared was compared with that of a standard sample of the same metal by means of the usual counting equipment. Since the activity of the sample was proportional to the amount of metal present, the number of moles of metal removed from the mirror could be calculated.

Standard samples of both metals were prepared by weighing out about 50 mgm. of each metal, dissolving in acid, and diluting to 25 ml. with water. A 1 ml. sample of each solution was evaporated on a 35 mm. watch glass to form the standard.

To test the accuracy of the method, weighed chips of the radioactive metals were distilled onto the walls of the flow tube and totally removed by passing acetone vapor through the system. The weight of metal found in the trap, as determined by the counting technique, agreed within 3% with the known weight of the mirror. In actual experiments, heavy mirrors were used which were only partly removed, and very little change in the appearance of the mirror could be noticed during an experiment. The mirrors were redeposited before each experiment.

Results and Discussion

A number of determinations of the rates of removal of lead and tellurium mirrors were made using both acetone and dimethyl ether as a radical source. The average deviations for about ten determinations range from 9% for tellurium to 20% with lead. The average rates of removal found with acetone as a radical source were:

$$7.3 \times 10^{-8} \text{ mole tellurium per min.} \quad (1)$$
$$7.7 \times 10^{-8} \text{ mole lead per min.,} \quad (2)$$

and with dimethyl ether as a radical source:

$$7.0 \times 10^{-8} \text{ mole tellurium per min.}$$
$$6.7 \times 10^{-8} \text{ mole lead per min.}$$

That the same rate of removal should be found for both lead and tellurium is quite unexpected since the compounds formed by the reaction of the radicals with the mirrors are $Pb(CH_3)_4$ and $Te(CH_3)_2$, and twice as much tellurium as lead would be expected to react with the same number of radicals. It was thought possible, however, that the tellurium mirrors were only half as efficient at removing methyl radicals as lead. To test this possibility, inactive mirrors placed in the usual position were followed at 2 cm. by radioactive mirrors of the same dimensions. With acetone as a radical source the rates at which the second mirrors were found to be removed were:

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First mirror Te, second mirror Te, 2.3×10^{-8} mole Te per min. (3)
First mirror Te, second mirror Pb, 1.9×10^{-8} mole Pb per min. (4)
First mirror Pb, second mirror Pb, 1.8×10^{-8} mole Pb per min. (5)
First mirror Pb, second mirror Te, 4.4×10^{-8} mole Te per min. (6)

From the relative rates of removal of the first and second mirrors the efficiency, e, of the mirrors themselves can be found thus:

$$\text{For tellurium: } \frac{1}{1-e} = \frac{7.3}{2.3}, \quad e = 0.69$$

$$\text{For lead: } \frac{1}{1-e} = \frac{7.7}{1.8}, \quad e = 0.77$$

The number of moles of radicals arriving at the first mirror per minute may be obtained as

$$n = \frac{r \text{ (moles metal consumed)}}{e},$$

where r = number of radicals consumed per atom of metal. If it is assumed that lead tetramethyl and tellurium dimethyl are formed, the values of n determined from (1) and (2) are 2.1×10^{-7} mole per min. and 4.0×10^{-7} mole per min. respectively. On the same basis, the rates of removal of radicals by *both* mirrors are: 1.9×10^{-7} mole per min. from (1) and (3)
2.2×10^{-7} mole per min. from (1) and (4)
3.8×10^{-7} mole per min. from (2) and (5)
and 2.9×10^{-7} mole per min. from (2) and (6)

On the other hand, if it is assumed that lead dimethyl and tellurium dimethyl are formed, the values of n are 2.1×10^{-7} mole per min. and 2.0×10^{-7} mole per min. from (1) and (2) respectively, and the rates of removal of radicals by both mirrors are:

1.9×10^{-7} mole per min. from (1) and (3)
1.8×10^{-7} mole per min. from (1) and (4)
1.9×10^{-7} mole per min. from (2) and (5)
and 2.4×10^{-7} mole per min. from (2) and (6).

Comparison of the two sets of calculated values would appear to favor the assumption that lead dimethyl, rather than lead tetramethyl, was formed in the experiments. Alternately, it might be assumed that tellurium tetramethyl and lead tetramethyl were formed, but there appears to be no evidence in the literature for the existence of tellurium tetramethyl, while some dialkyls of lead have been reported (2).

The high value of 2.4×10^{-7} mole per min. for the rate of removal of radicals with a lead–tellurium combination of mirrors might be due to reaction between unstable lead dimethyl and the tellurium mirror:

$$Pb(CH_3)_2 + Te \longrightarrow Te(CH_3)_2 + Pb.$$

Occurrence of such a reaction would correspond to an apparent increase in rate of removal of radicals by the two mirrors.

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THE SYNTHESIS OF AMINO ACIDS FROM 2, 3-DIHYDROFURAN DL-ORNITHINE, DL-PROLINE, AND DL-α-AMINO-δ-HYDROXYVALERIC ACID[1]

By Roger Gaudry

Résumé

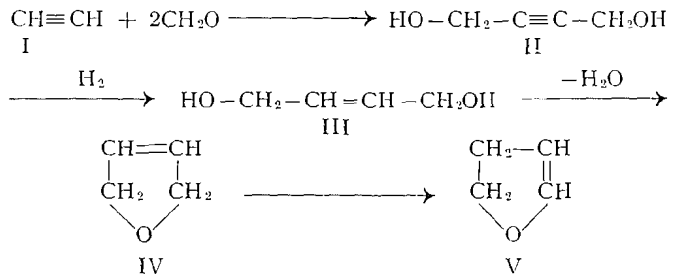
Le γ-hydroxybutanal obtenu par hydrolyse acide du 2, 3-dihydrofuranne est traité par le chlorure d'ammonium, le cyanure de potassium et le carbonate d'ammonium pour être transformé en 5-γ-hydroxypropylhydantoïne: l'hydrolyse de ce composé par l'hydroxyde de baryum sous pression donne l'acide α-amino-δ-hydroxyvalérianique ou pentahomosérine. La 3-phényl-5-γ-hydroxypropylhydantoïne est obtenue par traitement de la pentahomosérine avec l'isocyanate de phényle et chauffage en milieu acide. En y faisant barbotter HCl sec à chaud, il se forme la 3-phényl-5-γ-chloropropylhydantoïne qui, en milieu alcalin donne la 3-phényl-1, 5-triméthylenehydantoïne ou 3-phénylhydantoïne de la proline. Mais en cherchant à préparer la phénylhydantoïne bromée correspondante, la 3-phénylhydantoïne de la proline s'obtient spontanément. De plus, la 5-γ-hydroxypropylhydantoïne est transformée par HCl en 5-γ-chloropropylhydantoïne qui, par amination et hydrolyse, donne l'ornithine, et par hydrolyse acide sous pression et traitement alcalin, donne la proline.

Introduction

In a previous paper (1), we showed that 2,3-dihydropyran is an excellent starting material for the synthesis of DL-lysine and DL-α-amino-ε-hydroxycaproic acid, a lysine antagonist in mammals (4).

We have now applied the same series of reactions to 2,3-dihydrofuran (V), and studied the possibilities of the method for the preparation of DL-ornithine (XIII), DL-proline (X) and DL-α-amino-δ-hydroxyvaleric acid (XIV), which was needed for biological investigations.[2]

2,3-Dihydrofuran (V) has been prepared by the reaction of tetrahydrofurfuryl alcohol vapor over a nickel catalyst (10); by high temperature decomposition of vapors of tetrahydrofuronitrile and of methyl tetrahydrofuroate (11); and by heating 2-alkoxy-3-chlorotetrahydrofuran with sodium (3). Recently, it was shown that it could readily be prepared in large quantities in the following way: by condensation with two moles of formaldehyde, acetylene (I) is transformed into butynediol (II) which is catalytically hydrogenated to butenediol (III), followed by dehydration into 2,5-dihydrofuran (IV) (7). Isomerization of this compound in alkaline solution gives 2,3-dihydrofuran (V) (5).



I II III IV V

[1] *Manuscript received March 15, 1951.*
Contribution from the Department of Biochemistry of the Faculty of Medicine, Laval University, Quebec, Que.

[2] *The biological properties of this amino acid to which the name "pentahomoserine" has been given, will be reported elsewhere.*

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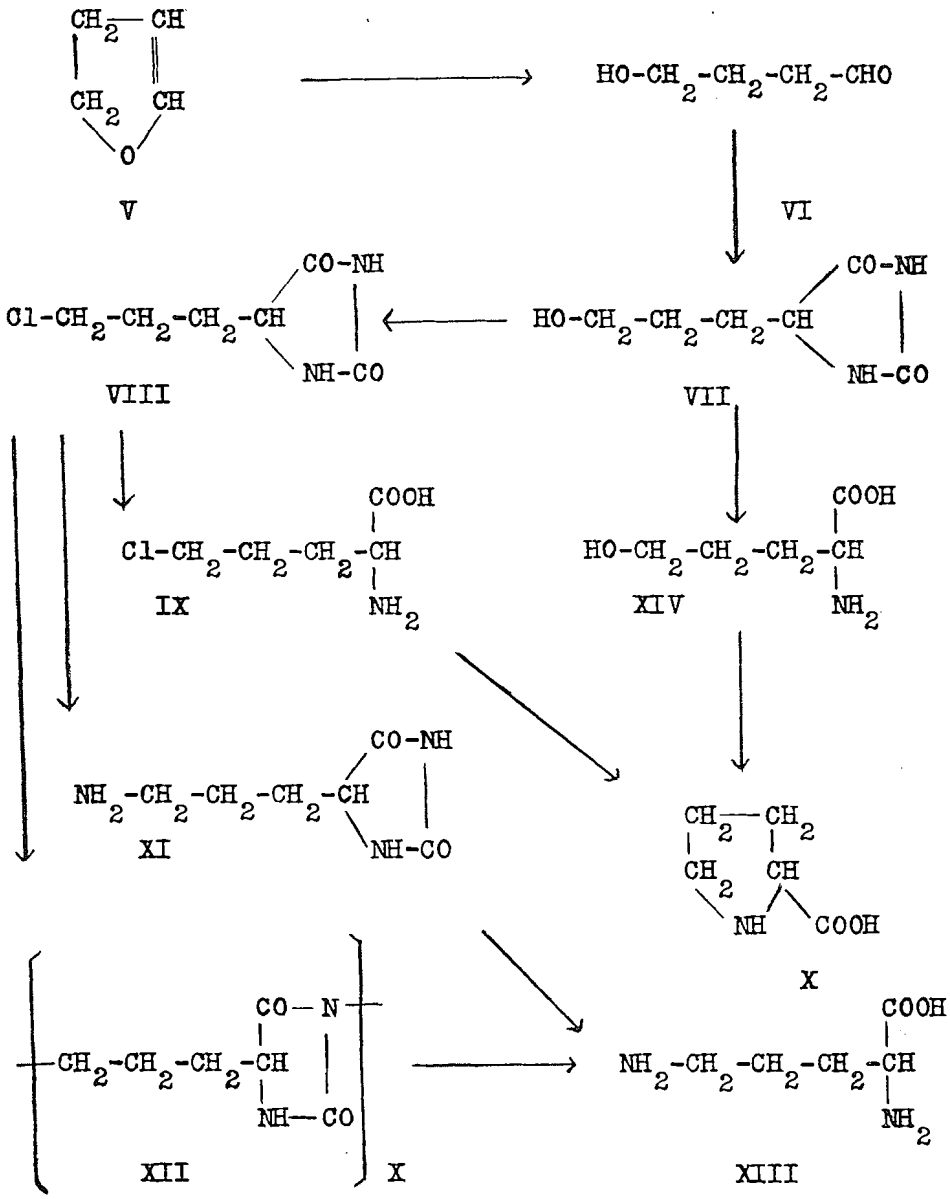
In aqueous acid solution, 2,3-dihydrofuran (V) hydrolyzes to γ-hydroxybutyraldehyde (VI) which is allowed to react, first with ammonium chloride and sodium cyanide to give the corresponding aminonitrile and then with ammonium carbonate to give 5-γ-hydroxypropylhydantoin (VII). This hydantoin is difficult to crystallize because of its extreme solubility in water and alcohol. It was therefore immediately hydrolyzed wth barium hydroxide under pressure to give a 55 to 60% over-all yield of DL-α-amino-δ-hydroxyvaleric acid (XIV). This amino acid has already been prepared by hydrolysis and decarboxylation of δ-acetoxy-α-phthalimidopropylmalonic ester (9) and by



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reductive amination of α-keto-δ-valerolactone (6), but these methods are impractical for its preparation in large quantities.

By treating this amino acid with potassium cyanate, followed by hydrochloric acid under reflux, it has been possible to obtain in a nearly pure state 5-γ-hydroxypropylhydantoin (VII) which crystallizes out slowly when most of the water in which it was dissolved has evaporated. This crystalline hydantoin, or the crude one obtained directly from 2,3-dihydrofuran (V) is transformed into the corresponding 5-γ-bromo- and 5-γ-chloropropylhydantoins (VIII) by heating it with concentrated hydrobromic acid, or by bubbling gaseous hydrochloric acid into the dry, fused hydroxypropylhydantoin (VII). These halogenated hydantoins, when treated with an excess of ammonium hydroxide, give 5-γ-aminopropylhydantoin (XI), which on hydrolysis yields DL-ornithine (XIII). In spite of various attempts to increase the yield of ornithine (XIII), it never exceeded 32% calculated from the chloro- or bromopropylhydantoin (VIII). One reason for this seems to be that during the amination reaction, some of the halogenated hydantoin cyclizes to the hydantoin of proline.

If the crude or the pure 5-γ-chloropropylhydantoin (VIII) is hydrolyzed under pressure in a sealed tube in the presence of concentrated hydrochloric acid, the hydrochloride of DL-α-amino-δ-chlorovaleric acid (IX) is obtained, which, by standing at room temperature in the presence of alkali, cyclizes to DL-proline (X).

A 33% over-all yield of pure DL-proline (X) from 2,3-dihydrofuran (V) was obtained when the reactions were carried out without isolation of any intermediate compound.

DL-Proline (X) has also been made directly from α-amino-δ-hydroxyvaleric acid (XIV) (6) in an 85% yield by heating its hydrochloride at 170°C. for two hours, which means an approximately 47% over-all yield if calculated from 2,3-dihydrofuran (V).

Attempts to make DL-ornithine by fusing the γ-halogenated hydantoins with sodium carbonate according to the method developed by Rogers *et al.* for the synthesis of lysine (8) were not very successful, apparently also because of the ease with which these hydantoins cyclize to a proline derivative.

When α-amino-δ-hydroxyvaleric acid (XIV) is treated with phenylisocyanate and the corresponding ureido derivative (XV) is refluxed with hydrochloric acid, 3-phenyl-5-γ-hydroxypropylhydantoin (XVI) is obtained as a white and easily recrystallized solid. When this hydroxyhydantoin is treated with gaseous hydrochloric acid, a high yield of 3-phenyl-5-γ-chloropropylhydantoin (XVII) is obtained. But when hydrobromic acid is used instead of hydrochloric acid, no brominated hydantoin can be isolated, but the phenylhydantoin of proline (XVIII) separates during the attempted recrystallization of the expected 3-phenyl-5-γ-bromopropylhydantoin. This spontaneous ring closure of 3-phenyl-5-γ-bromopropylhydantoin to form the phenylhydantoin of proline (XVIII)

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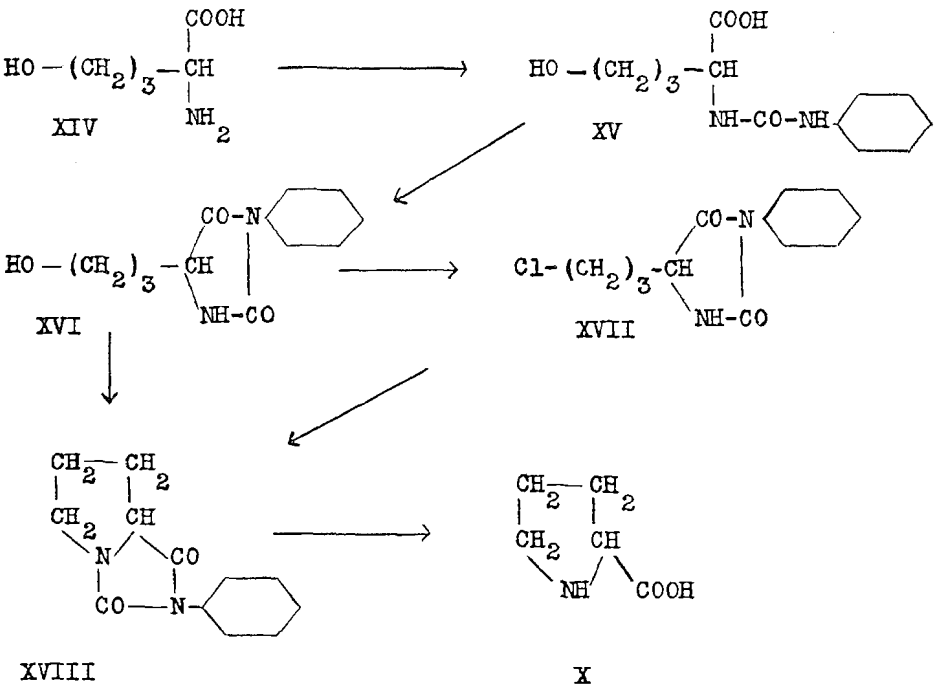

XIV XV XVI XVII XVIII X

while the corresponding chloro compound (XVII) does not behave in the same way shows again the difference in reactivity between chlorinated and brominated compounds. We have encountered a somewhat similar experience with α-dichloro-δ-benzamidovaleric acid which remains as an open chain compound while the corresponding dibromo compound spontaneously cyclizes to a derivative of α-piperidone.

It is, however, comparatively easy to cyclize 3-phenyl-5-γ-chloropropylhydantoin (XVII) to the corresponding 3-phenylhydantoin of proline (XVIII) by treating it with sodium ethylate, or ammonia, or by fusing it with sodium carbonate.

In conclusion, while 2,3-dihydrofuran (II) may not be a very good starting material for making DL-ornithine (XIII) by the method which has proved so successful for making its higher homologue, it remains the best starting material for the synthesis of DL-α-amino-δ-hydroxyvaleric acid (XIV) and also provides an excellent synthesis of DL-proline (X).

Experimental Part

DL-α-*Amino-δ-hydroxyvaleric acid (XIV)*

2,3-Dihydrofuran (40 gm., 0.5 mole of a product titrating 88%) was added to 0.2 normal hydrochloric acid (100 ml.) and the mixture was mechanically stirred at room temperature until the dihydrofuran had completely dissolved (about 10 min.). The resulting solution was then slowly added to a solution of sodium cyanide (26 gm.) and ammonium chloride (27 gm.) in water (200 ml.),

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and the mixture was stirred at room temperature for one hour. Fresh ammonium carbonate (106 gm.) was then added, and the mixture was stirred at 55–60°C. for two hours, then at the boiling point for 15 min., and evaporated to dryness *in vacuo*. The hot residue was stirred with absolute ethyl alcohol (200 ml.), the insoluble sodium chloride (28.5 gm., 98%) was filtered on a Büchner funnel, washed on the filter with a little absolute alcohol, and the alcoholic solution was evaporated to dryness *in vacuo*. The residue was dissolved in boiling water (400 ml.), the hot solution was added to a beaker containing barium hydroxide (200 gm. of the octahydrate), stirred, and the mixture was heated at 160°C. for half an hour in an autoclave. After cooling, ammonium carbonate (25 gm.) was added, and the mixture was stirred and slowly brought up to the boiling point, cooled, and filtered on a Büchner funnel. The clear solution was again taken to the boiling point, filtered hot, and evaporated to dryness *in vacuo*. The residue was slurried with cold methyl alcohol (150 ml.) and the crude amino acid was filtered and dried. Yield, 37 gm., 55%. It was recrystallized by dissolving it in boiling water (55 ml.) and adding ethyl alcohol (165 ml.). Yield, 33 gm., 50% calculated from 2,3-dihydrofuran. M.p. 215°C.[3] with evolution of gas. Lit., 223–224°C. (9), 218–220°C. (6). Calc. for $C_5H_{11}O_3N$: N, 10.52%. Found (Kjeldahl): N, 10.57%.

DL-α-*Benzamido-δ-hydroxyvaleric acid*

DL-α-Amino-δ-hydroxyvaleric acid (7.98 gm., 0.06 mole) was dissolved in aqueous sodium hydroxide (60 ml. of a normal solution), and the solution was treated simultaneously with benzoyl chloride (7.2 ml.) and a normal sodium hydroxide solution (75 ml.). After stirring at room temperature for one hour, the solution was filtered, cooled in an ice bath, and acidified slowly with concentrated hydrochloric acid (15 ml.). After standing in the cold for a few hours, the crystalline product was filtered and allowed to dry. Yield: 12.4 gm., 87%. It was recrystallized by dissolving it in hot ethyl alcohol (35 ml.), filtering, and adding ethyl ether (350 ml.) while stirring. M.p.: 141°C. with evolution of gas. Calc. for $C_{12}H_{15}O_4N$: N, 5.95%. Found: 5.74%.

5-γ-Hydroxypropylhydantoin (VII)

DL-α-Amino-δ-hydroxyvaleric acid (19.95 gm., 0.15 mole) was dissolved in water (75 ml.) and treated with potassium cyanate (13 gm.) in water (25 ml.). The mixture was kept at 65°C. for two hours and acidified with concentrated hydrochloric acid (35 ml.), and the solution was heated at 90°C. for two hours and finally evaporated to dryness *in vacuo*. The residue was stirred with hot acetone (100 ml.), the insoluble potassium chloride was filtered, and the acetone was evaporated *in vacuo*. The residue was dissolved in hot water (200 ml.), the solution was decolorized with "Norit", filtered, and evaporated to a small volume. The hydantoin crystallizes slowly at room temperature as the solution becomes more and more concentrated. A nearly pure product is obtained if the solid is filtered before the mixture becomes too thick. M.p.: 112–113°C. Yield, 10.9 gm., 46%. Calc. for $C_6H_{10}O_3N_2$: N, 17.72%. Found: N, 17.15%.

[3] *Melting points are not corrected.*

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5-γ-Chloropropylhydantoin (*VIII*)

The residue obtained by evaporating the acetone solution of 5-γ-hydroxypropylhydantoin (see paragraph above) was heated in an oil bath at 110–120°C. and gaseous hydrochloric acid was bubbled through it for two hours while the oil bath was maintained at the same temperature. On cooling, a brown crystalline compound was obtained. It was dissolved in boiling water (150 ml.) decolorized with "Norit", filtered, and evaporated to dryness. The residue was dissolved in boiling water (20 ml.) and the solution was left in the ice box. The pale yellow crystalline product was filtered and dried at room temperature. Yield, calculated from 19.95 gm. of α-amino-δ-hydroxyvaleric acid: 15.1 gm., 57%. M.p.: 119–120°C. Calc. for $C_6H_9O_2N_2Cl$: N, 15.86%. Cl, 20.11%. Found: N, 15.68%. Cl, 19.59%.

5-γ-Bromopropylhydantoin

The residue obtained by evaporating the acetone solution of 5-γ-hydroxypropylhydantoin (see paragraph above) was treated with 48% hydrobromic acid (100 ml.) and the solution was kept at 90°C. for two hours and was evaporated to dryness *in vacuo*. Hot water (150 ml.) was added, the solution was filtered, decolorized with "Norit", evaporated to a small volume, and allowed to cool. The crystalline residue was filtered and allowed to dry. Yield, 9.5 gm., 28%. M.p.: 135–137°C. Calc. for $C_6H_9O_2N_2Br$: N, 12.67%. Found, 12.60%.

DL-*Ornithine* (*XIII*)

In a pressure bottle was placed 5-γ-bromopropylhydantoin (2.21 gm., 0.01 mole) and concentrated ammonia (100 ml.). The bottle was closed and heated at 60°C. for 60 hr. The solution was evaporated to dryness, the residue was dissolved in hot water (100 ml.), barium hydroxide (7.8 gm. of the octahydrate) was added with stirring, and the solution was heated in an autoclave at 160°C. for half an hour. After cooling, ammonium carbonate (3 gm.) was added with stirring. The mixture was heated to the boiling point, filtered, and the solution was evaporated to a small volume. Picric acid (2.6. gm.) dissolved in hot water (150 ml.) was added, the solution was filtered hot and allowed to stand overnight in the cold. The crystalline precipitate was filtered and recrystallized from a little hot water. Yield of ornithine dipicrate: 1.5 gm., 25%. M.p.: 198–199°C., unaffected by mixture with an authentic sample.

DL-*Proline* (*X*)

5-γ-Chloropropylhydantoin (3.53 gm.) was heated in a sealed tube with concentrated hydrochloric acid (8 ml.) and water (12 ml.) at 150°C. for five hours. The solution was evaporated to dryness, and the residue was dissolved in hot water (50 ml.), decolorized with "Norit", and again taken to dryness. The residue was dissolved in an excess of aqueous sodium hydroxide (50 ml. of a 30% solution) and the solution was allowed to stand overnight at room temperature. It was then carefully neutralized to pH 7 with dilute hydrochloric acid, and boiled under reflux for one hour with an excess of cupric car-

bonate. The hot solution was filtered, the excess cupric carbonate on the filter was washed with boiling water, and the filtrate and the washings were combined and taken to dryness *in vacuo*. The residue was dissolved in boiling water (15 ml.) and allowed to crystallize in the cold. The blue copper prolinate was filtered and dried in the oven at 160°C. for one hour. Yield, 2.91 gm. 56%. Calc. for $C_{10}H_{16}O_4N_2Cu$: N, 9.62%. Found: N, 9.5%.

α-Phenylureido-δ-hydroxyvaleric acid (*XV*)

DL-α-Amino-δ-hydroxyvaleric acid (3.99 gm., 0.03 mole) was dissolved in a solution of sodium hydroxide (1.2 gm.) in water (50 ml.), and phenylisocyanate (3.6 gm., 0.3 mole) was added dropwise into the solution at room temperature. After stirring very efficiently for 15 min., the solution was cooled in an ice bath and slowly acidified with concentrated hydrochloric acid (3.5 ml). The precipitate was stirred in the cold for a few minutes, filtered in a Büchner funnel and allowed to dry. Yield, 7.0 gm., 92%. It was recrystallized from dilute alcohol. M.p., 124–6°C. with evolution of gas. Calc. for $C_{12}H_{16}O_4N_2$: N, 11.11%. Found: N, 11.13%.

3-Phenyl-5-γ-hydroxypropylhydantoin (*XVI*)

DL-α-Amino-δ-hydroxyvaleric acid (28 gm.) was dissolved in a solution of sodium hydroxide (8.4 gm.) in water (350 ml.) and treated as described in the previous paragraph with phenylisocyanate (25 gm.). The solution was then acidified with concentrated hydrochloric acid (100 ml.) and heated in a boiling water bath for one hour. The solution was evaporated to dryness in a vacuum and the residue was recrystallized from dilute alcohol. Yield, 42 gm., 89%. M.p.: 134–5°C. Calc. for $C_{12}H_{14}O_3N_2$: N, 11.96%. Found: N, 11.76%.

3-Phenyl-5-γ-chloropropylhydantoin (*XVII*)

3-Phenyl-5-γ-hydroxypropylhydantoin (11.7 gm., 0.05 mole) was melted in a wax bath at 135°C. and dry gaseous hydrochloric acid was bubbled through it for two hours while the bath was kept at 125°C. Hot, 50% aqueous alcohol (50 ml.) was added to the residue while still warm and the solution was kept overnight in the cold. The crystals were filtered and allowed to dry. Yield, 9.8 gm., 77%. The product was recrystallized from dilute alcohol. M.p.: 102–3°C. Calc. for $C_{12}H_{13}O_2N_2Cl$: N, 11.08%, Cl, 14.0%. Found: N, 11.13%, Cl, 13.4%.

3-Phenyl-1,5-trimethylenehydantoin (*XVIII*)

(*A*) *From 3-Phenyl-5-γ-hydroxypropylhydantoin*

3-Phenyl-5-γ-hydroxypropylhydantoin (11.7 gm., 0.5 mole) was heated at 90°C. for two hours with 48% hydrobromic acid (300 ml.). The solution was evaporated to dryness in a vacuum. The residue was dissolved in boiling water (1800 ml.), decolorized with "Norit", filtered, concentrated to a small volume, and cooled. The precipitate was filtered and allowed to dry. Yield, 7.7 gm., 71%. It was recrystallized three times from 50% aqueous alcohol. M.p.: 114–116°C. Lit. 117°C. corr. Calc. for $C_{12}H_{12}O_2N_2$: N, 12.96%. Found: N, 12.88%.

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(*B*) *From 3-Phenyl-5-γ-chloropropylhydantoin*

3-Phenyl-5-γ-chloropropylhydantoin (2.2 gm.) was refluxed for two hours in a solution of sodium (0.22 gm.) in absolute ethyl alcohol (50 ml.). The solution was filtered from the insoluble sodium chloride and evaporated to dryness in a vacuum. The residue was recrystallized from hot water. Yield: 1 gm., 46%. M.p.: 114–115°C. unchanged when mixed with the sample prepared as in "*A*".

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ANALYSIS OF MIXTURES OF SIMPLE ALIPHATIC ALCOHOLS BY PARTITION CHROMATOGRAPHY

By A. C. Neish

Abstract

Mixtures of methanol, ethanol, isopropanol, *n*-butanol, and isoamyl alcohol were resolved by partition chromatography on Celite–water columns, using carbon tetrachloride and chloroform as developing solvents, each alcohol being determined quantitatively by dichromate oxidation of the fractions thus obtained. Only 0.5 ml. of an aqueous solution containing 1–5 mgm. of each alcohol was required for an analysis. The method was used successfully in the analysis of a mixture of volatile fermentation products containing *n*-butanol, isopropanol, ethanol, acetoin, diacetyl, and acetone.

Introduction

The determination of *n*-butanol in the presence of ethanol has received a considerable amount of study because they occur together in certain fermentation solutions. Methods based on their separation by distillation are time consuming and not applicable to small amounts of solution. Some of the simplest procedures are based on differential dichromate oxidation with measurement of the dichromate reduced (1, 2) or measurement of the acetic and butyric acids formed (4, 8). Advantage has been also taken of the differing solubilities of ethanol and butanol (2), the aqueous distillate being oxidized with dichromate before and after partitioning with a definite proportion of carbon tetrachloride. This suggests use of partition chromatography for the complete separation of these and possibly other alcohols. The present paper describes a chromatographic method for the quantitative separation and determination of some of the simpler alcohols, particular attention being paid to those likely to be formed in fermentation solutions.

Experimental

Reagents

(*1*) *Purified Celite.*—Celite 535 was digested with concentrated hydrochloric acid at room temperature for 20–22 hr. After having been washed with distilled water, twice by decantation and then in a Büchner funnel until free of acid, it was dried at 150°–170°C.

(*2*) *Developing solvents.*—Reagent grade carbon tetrachloride was washed twice with an equal volume of water and filtered through a dry filter paper. Washed chloroform was prepared in the same way except that six or seven washings were required to remove the alcohol added as a preservative. The carbon tetrachloride–chloroform (50%) mixture was made by mixing equal volumes of the washed solvents and then filtering the mixture. Washed chloroform is not very stable and should be prepared the same day that it is used.

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(*3*) *Oxidizing reagent.*—Potassium dichromate (0.04 *N*) in 18.6 *N* sulphuric acid.

(*4*) *Alcohol solutions.*—Commercial absolute ethanol was further purified by treatment with magnesium followed by distillation. The other alcohols were used as received. The methanol was Canadian Industrial Alcohol Co. C.P. Grade; isopropanol, Nichols Purified (98%); *n*-propanol, Eastman Kodak Reagent No. 848; *n*-butanol, Baker and Adamson Reagent Grade; and isoamyl alcohol, Eimer and Amend C.P. Grade. Standard solutions were prepared by weighing in stoppered volumetric flasks.

Separation of Alcohols by Chromatography

The chromatographic technique was the same as that used for separation of 2, 3-butanediol and glycerol (5, 6). Three grams of dry Celite was mixed thoroughly with 2.5 ml. of distilled water, slurried in washed carbon tetrachloride, and poured into a 300 × 15 mm. O.D. Pyrex chromatogram tube fitted with a porous porcelain plate and a filter paper disc. The Celite was compressed to give a column about 8 cm. long by inserting another filter paper disc and forcing it down with a glass ramrod. An 0.5 gm. portion of dry Celite was slurried in washed carbon tetrachloride and packed on top of this in a similar fashion. Any excess solvent was decanted and an 0.5 ml. aliquot of an aqueous solution containing the alcohols (about 1–5 mgm. of each) pipetted on top of the column, care being taken to prevent any from getting on the glass tube except for 2–3 mm. above the top of the packing. While the sample was being absorbed by the layer of dry Celite a 50 ml. graduate was placed in position to receive the effluent solvent. The sample was washed in by two 1 ml. portions of washed carbon tetrachloride and development started using this solvent. The solvents were forced through the column by gentle air pressure to give four to five drops of effluent per second. When the developing solvents were changed, any of the solvent left in the tube was decanted before the new one was added. Five successive fractions were collected:

(*a*) 20 ml. of CCl_4; contained *n*-butanol and higher alcohols, also diacetyl and acetone.

(*b*) 22 ml. of CCl_4–$CHCl_3$ (50%); contained *n*-propanol isopropanol, and acetoin.

(*c*) 25 ml. of $CHCl_3$; contained ethanol.

(*d*) 15 ml. of $CHCl_3$; did not contain any alcohols.

(*e*) 40 ml. of $CHCl_3$; contained methanol.

It was possible to divide the first fraction in such a way that isoamyl alcohol and *n*-butanol were separated. The isoamyl alcohol was in the first 9–12 ml. of carbon tetrachloride while the *n*-butanol was in the remainder of this fraction. In order to be sure that the proper separation point was chosen four successive 1 ml. fractions were collected and analyzed separately in the region between 9–12 ml. of carbon tetrachloride. The other alcohols gave bands separated widely enough to permit collection of fractions of predetermined size, one for each alcohol.

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Determination of Alcohols by Dichromate Oxidation

The alcohols can be determined quantitatively by oxidation with dichromate in the presence of the developing solvent. Each fraction obtained by chromatography was transferred to a separate 250 ml. glass stoppered Erlenmeyer using 5–10 ml. of carbon tetrachloride to rinse out the graduate. Ten ml. of the oxidizing reagent, accurately measured by a syringe, was added and the flasks allowed to stand 30 min. at room temperature (22°–24°C.). During this period they were shaken vigorously for about 10 sec., at least five times. Controls containing the developing solvents and some *n*-butanol standards were run at the same time. When the oxidation was finished, 100 ml. of distilled water was added and then 1–2 gm. of potassium iodide crystals. The iodine released was titrated by standard sodium thiosulphate, using starch indicator, until vigorous shaking of the flask for 15–20 sec. no longer resulted in appearance of the blue starch–iodine complex in the aqueous phase. The milliequivalents of dichromate reduced by the alcohol in any sample was calculated from the difference between its titer and that of the blank containing an equal amount of the same developing solvent. Isopropanol, ethanol, and methanol reduced 2, 4, and 6 equivalents of oxidant per mole, as expected for oxidation to acetone, acetic acid, and carbon dioxide, respectively. The amount reduced by *n*-butanol or isoamyl alcohol is empirical, the proper factors being obtained from standard solutions oxidized at the same time. The factor for *n*-butanol is usually about 4.5 equivalents per mole.

Analysis of a Complex Mixture of Volatile Fermentation Products

The volatile neutral fraction of a fermentation solution can be expected to contain *n*-butanol, isopropanol, ethanol, acetoin, diacetyl, and acetone. If this mixture is chromatographed as above to give the alcohols in three separate fractions the acetone and diacetyl will be recovered quantitatively in the butanol fraction and the acetoin in the isopropanol fraction. Acetone will not interfere in the determination of the alcohols since it is not appreciably oxidized by dichromate but acetoin and diacetyl must be determined and corrections made. Diacetyl was determined on a separate aliquot of the neutral volatile fraction by condensation with hydroxylamine and urea (10, 6) and the sum of acetoin plus diacetyl on another aliquot by reaction with creatine and alkaline α-napthol (9, 6) for one hour. The *n*-butanol was calculated after correction for the dichromate reduced by diacetyl (determined on a standard solution) and the isopropanol after correction for the dichromate reduced by the acetoin (four equivalents per mole). Acetone was determined in another aliquot by condensation with salicylaldehyde (6, 7) to complete the analysis of this fraction. This colorimetric method for acetone is preferable to the more precise volumetric method employing alkaline iodine (3, 6) since it is much more specific; even acetoin and diacetyl do not interfere if present in equal amounts. Isopropanol can also be determined by oxidation to acetone followed by microdiffusion into alkaline salicylaldehyde (6); none of the other alcohols mentioned above interfere, hence this procedure can be used for estimation of isopropanol in the presence of *n*-propanol.

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Results and Discussion

The rates of oxidation of individual alcohols by the oxidizing reagent, in the presence and absence of solvents, are shown in Table I. The solvent does not interfere in the determination of the alcohols by this method. The oxidations were complete in 30 min. or less. Judging from the amount of dichromate reduced, methanol was oxidized to carbon dioxide, ethanol to acetic acid, and isopropanol to acetone. Butanol does not seem to be oxidized according to any simple equation although the oxidations practically stopped after 15 min.

TABLE I

RATE OF OXIDATION OF ALCOHOLS BY DICHROMATE AT ROOM TEMPERATURE
One ml. of an aqueous solution of the alcohols and 10 ml. of the oxidizing reagent used

Alcohol	Solvent	Dichromate (m.e.) reduced per mM. of alcohol with oxidation times of:					
		5 min.	10 min.	15 min.	20 min.	25 min.	30 min.
Methanol	30 ml. $CHCl_3$	4.70	5.20	5.53	5.75	5.92	5.98
Ethanol	None	3.89	....	4.01	....	3.94	....
Ethanol	30 ml. of $CHCl_3$ + CCl_4(50%)	....	3.85	....	4.05	....	4.05
Isopropanol	None	2.00	2.00	1.97	....	....	....
Isopropanol	30 ml. of $CHCl_3$ + CCl_4(50%)	1.86	2.00	1.98	....	....	....
n-Butanol	None	4.96	....	5.12	....	5.06	5.19
n-Butanol	30 ml. of $CHCl_3$ + CCl_4(50%)	4.10	....	4.92	....	4.78	5.06

The results in Table II show the effect of using varying amounts of butanol and water. In these experiments the standard butanol solution was made up in carbon tetrachloride. The factor is reasonably constant but seems to become lower as more water is added. This is not serious since no water, except the small amount dissolved in the developing solvents, is added when the chromatographic technique is used.

TABLE II

OXIDATION OF *n*-BUTANOL BY DICHROMATE AT ROOM TEMPERATURE
Each oxidation run 20 min. at room temperature in presence of 30 ml. of washed CCl_4

No.	Mgm. *n*-butanol	Ml. of water added	Dichromate reduced, m.e.	Dichromate (m.e.) reduced per mM. of butanol
1	1.05	Nil	0.064	4.50
2	3.15	Nil	0.191	4.52
3	4.20	Nil	0.256	4.51
4	5.25	Nil	0.326	4.56
5	2.10	1.0	0.126	4.66
6	2.10	2.0	0.121	4.42
7	2.10	3.0	0.117	4.30
8	2.10	4.0	0.117	4.30

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A number of mixtures made from standard solutions of various alcohols in water were chromatographed and the fractions analyzed as outlined above (see Experimental Section). The results are shown in Table III. The amount found was usually within 3% of the amount added even with fairly complex mixtures. The sensitivity of the method is different for various alcohols since it depends on their dichromate-reducing power. One milligram of methanol reduces 5.6 times as much dichromate as 1 mgm. of isopropanol, hence a correspondingly greater amount of isopropanol must be added to the column to obtain the same accuracy for the titration.

TABLE III

SEPARATION OF ALCOHOLS BY PARTITION CHROMATOGRAPHY*

Mixture No.	Mgm. of alcohol									
	Methanol		Ethanol		Isopropanol		*n*-Butanol		Isoamyl alcohol	
	Added	Recovered	Added	Recovered	Added	Recovered	Added	Recovered	Added	Recovered
1	–	–	3.04	3.07	5.15	5.08	2.36	2.34	–	–
2	–	–	3.33	3.34	3.30	3.21	3.33	3.21	–	–
3	–	–	–	–	–	–	5.00	5.05	2.65	2.59
4	–	–	–	–	–	–	2.00	2.02	4.24	4.35
5	–	–	2.50	2.45	4.96	4.90	2.50	2.44	–	–
6	–	–	2.50	2.54	2.48	2.50	5.00	5.00	–	–
7	–	–	2.50	2.45	2.44	2.40	2.71	2.66	–	–
8	–	–	1.25	1.28	2.47	2.50	2.71	2.71	–	–
9	–	–	4.48	4.36	3.31	3.36	4.18	4.22	–	–
10	–	–	2.50	2.43	7.45	7.47	2.71	2.70	–	–
11	–	–	3.38	3.33	7.45	7.35	–	–	–	–
12	–	–	3.38	3.35	7.45	7.41	5.02	5.00	–	–
13	1.30	1.28	2.50	2.46	2.48	2.45	2.46	2.42	–	–
14	1.44	1.41	3.75	3.70	–	–	–	–	–	–
15	0.362	0.363	3.75	3.64	–	–	–	–	–	–
16	1.24	1.22	2.75	2.75	2.54	2.53	2.53	2.54	2.48	2.56
17	1.24	1.19	2.75	2.70	2.54	2.60	2.53	2.52	2.48	2.49

* *In an additional experiment 2.35 mgm. of n-propanol was added and 2.33 mgm. recovered, all in the isopropanol fraction. One millimole of n-propanol reduced 3.94 m.e. of dichromate.*

Special attention has been given to the analysis of mixtures of ethanol, isopropanol, and *n*-butanol since these are the alcohols most likely to be found in fermentation solutions. A complex mixture of volatile fermentation products containing all three of these alcohols as well as acetone, diacetyl, and acetoin was analyzed, as outlined in the Experimental Section, with good results (see Table IV).

Application of this procedure to the volatile neutral fraction from an *Aerobacter aerogenes* fermentation has shown, as expected, that ethanol is the only alcohol present except for a trace of higher alcohols.

When fermentation solutions are analyzed for alcohols (6), the volatile neutral fraction is used. The total dichromate-reducing power of an aliquot is measured first. An appropriately diluted sample is then chromatographed, but

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TABLE IV

ANALYSIS OF A MIXTURE OF VOLATILE FERMENTATION PRODUCTS

Compound	Mgm. per ml. of mixture		
	Added	Found*	% Recovery
n-Butanol	4.21	4.20	99.8
Isopropanol	4.22	4.20	99.6
Ethanol	4.57	4.52	99.2
Acetoin	3.34	3.30	98.8
Diacetyl	1.92	1.93	100.5
Acetone	3.59	3.59	100.0

* *Average of duplicates agreeing within 2%.*

only the first three fractions of effluent are collected since methanol is not an expected product. The percentage recovery from the chromatogram is calculated from the sum of the dichromate-reducing values of the separate fractions. If an appreciable amount of alcohol is found in the propanol fraction, isopropanol can be determined by a more specific method (6) on another aliquot of the volatile neutral fraction and *n*-propanol calculated by difference.

2, 3-Butanediol, which may be found in small concentrations in the volatile neutral fraction of fermentation solutions does not interfere in the determination of the alcohols by chromatography since it remains on the column even if the full development procedure is used.

This technique of partition chromatography on Celite should also prove useful for the purification of small amounts of alcohols prior to formation of crystalline derivatives, particularly when it is desirable to work on a small scale, as in radiotracer experiments. The method using the solvent system outlined above would not be useful for monohydric alcohols with five carbons or more since their sparing solubility in water would cause them to move together rapidly down the column and the unfractionated mixture would appear in the first 10 ml. of effluent.

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A NEW APPARATUS FOR RAPID CARBON DETERMINATION BY WET COMBUSTION[1]

By J. A. Thorn and Ping Shu

Abstract

A simple, compact apparatus has been designed for the estimation of carbon in organic materials by a wet combustion procedure employing the Van Slyke–Folch oxidation liquid. Oxidation of the sample and absorption of the resultant carbon dioxide take place under reduced pressure. The carbon dioxide is transferred from the oxidation flask by diffusion and is absorbed in stirred sodium hydroxide, the excess alkali being determined by titration with hydrochloric acid after addition of barium chloride. Samples containing from 0.3 mgm. to 15 mgm. of carbon may be analyzed with a probable error of 0.35%. Volatile compounds in aqueous solution may also be analyzed. Sulphur, nitrogen, and halogens do not interfere. Determinations were made on the following compounds: sucrose, succinic acid, cysteine hydrochloride, cholesterol, stearic acid, and acetone. An analysis requires from 20 to 25 min.

Several methods are described in the literature for the determination of carbon by wet combustion. The methods differ essentially in the manner in which measurement of carbon dioxide is made, and may be classified as manometric, gravimetric, or volumetric. The manometric method (8), although providing excellent results, suffers from the complexity normally associated with manometry. Gravimetric methods (5, 6) involve the quantitative isolation of carbon dioxide as barium carbonate, a procedure which can become difficult when small amounts of precipitate are encountered. The volumetric methods contain undesirable features such as the need to titrate in flasks other than the carbon dioxide absorption flask (3, 4) or the need to use multistep determinations of the precipitated carbonate (2).

Lindenbaum, Schubert, and Armstrong (5) described an apparatus in which combustion of the sample and absorption of carbon dioxide occurred under reduced pressure. However, their apparatus was designed for the gravimetric method of carbon dioxide determination and is not suitable for rapid analyses. Also, it is suitable only for the analysis of nonvolatile samples. A similar apparatus was designed by Barker (1).

The purpose of this paper is to describe an apparatus with which both volatile and nonvolatile samples may be analyzed with considerable speed. The apparatus is compact and requires only simple manipulation. It may be used for submicroanalyses with 0.3 to 1 mgm. of carbon, for microanalyses with 1 to 8 mgm., and for macroanalyses with 8 to 15 mgm. The probable error is 0.35%. The method is suitable for analysis of samples commonly encountered in biochemical studies. Nitrogen, sulphur, and halogens do not interfere. An analysis requires between 20 and 25 min.

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Experimental

Reagents

(1) Combustion Fluid (5)

This was prepared by adding to 12 gm. of chromium oxide (chromic acid) in a glass-stoppered flask 66 ml. of syrupy phosphoric acid and 134 ml. of fuming sulphuric acid. The mixture was heated to 160°C. and held at a temperature between 140° and 160°C. for 15 min. It was stirred occasionally with a thermometer in order to facilitate solution of the chromic acid and the escape of carbon dioxide evolved from contaminating organic material. The neck of the flask was then covered with an inverted beaker and, after the combustion fluid had cooled to room temperature, the flask was stoppered and again protected from dust by the beaker.

(2) Potassium iodate, powdered crystalline.

(3) Barium chloride, saturated aqueous solution.

(4) Hydrochloric acid, 0.1 *N*, 0.05 *N*, and 0.01 *N*.

(5) Sodium hydroxide (carbonate-free), 0.5 *N*, 0.2 *N*, and 0.1 *N*.

(6) Phenolphthalein and/or thymol blue, alcoholic solutions.

Apparatus

The apparatus is shown in Fig. 1. The ground joints, A, B, and C, as well as stopcock D, are lubricated with syrupy phosphoric acid. Other joints and the second stopcock are lubricated with ordinary stopcock grease. When the combustion unit for volatile samples is employed, its ground joints and stopcock are lubricated with phosphoric acid.

The acid and iodine trap is packed with zinc turnings and with potassium iodide granules (10 mesh). A few zinc turnings placed at the lower end of the trap prevent the inlet from being plugged by potassium iodide. The trap is repacked with fresh materials when either the zinc becomes tarnished or the potassium iodide is quite yellow from absorbed iodine. A single packing will suffice for several analyses.

The position of the thermometer well should allow immersion of the thermometer bulb in the reaction mixture (6 to 10 ml.) and, at the same time, it should be placed sufficiently high that carbon dioxide cannot be trapped in the well by the reaction mixture.

The carbon dioxide absorption flask is a standard 125 ml. Erlenmeyer flask with a ⧩ 24/40 ground joint. The inlet tube extends to within 2 cm. of the bottom of the flask and is not immersed in the sodium hydroxide. Thus, except for the rare occasion when it is splashed owing to uneven stirring of the alkali, the inlet tube does not need to be washed down with each analysis.

Procedure

The sample, which may contain 0.5 ml. of water, is placed in the combustion flask with about 300 mgm. of potassium iodate. The flask is connected to the

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apparatus, and the thermometer is inserted. Sodium hydroxide is pipetted into the absorption flask which contains a glass-coated magnet. The apparatus is then evacuated by means of a water pump to a pressure of 20 to 30 mm. of mercury. Combustion liquid is placed in the reservoir. When the desired evacuation is attained, the stopcock leading to the water pump is closed, and the combustion fluid is allowed to enter the combustion flask, care being taken that air does not enter the flask.

The magnetic stirrer is started, and heat is applied to the bottom of the combustion flask by means of a microburner. When the temperature of the reaction mixture reaches 210°C. (about seven to nine minutes are required), the flame is removed and a period of 10 min. is allowed for absorption of carbon dioxide by the stirred sodium hydroxide. At the end of this time, the vacuum in the apparatus is released by opening the stopcock between the combustion fluid reservoir and the combustion flask. Stirring is stopped, the absorption flask removed, and the excess alkali is titrated with hydrochloric acid (after addition of barium chloride). A blank is run. Phenolphthalein indicator was satisfactory for titrations when samples containing from 1 to 15 mgm. of carbon were analyzed. For smaller samples, thymol blue gave more distinct end points.

The amounts and concentrations of the reagents employed for analyses of samples containing different amounts of carbon are given below.

Sample carbon, mgm.	Combustion fluid, ml.	Sodium hydroxide		$BaCl_2$ solution, ml.	Hydrochloric acid concn.
		Ml.	Concn.		
8–15	10	10	0.5 *N*	5	0.1 *N*
1–8	5	10	0.2 *N*	2	0.05 *N*
0.3–1	5	5	0.1 *N*	1	0.01 *N*

When volatile samples are to be analyzed, the accessory combustion unit is employed. The small sample tube is charged with potassium iodate and the sample, and then is placed in position with stopcock E closed. Combustion fluid (10 ml.) is placed in the upper combustion chamber and the apparatus is evacuated. Stopcock E is then carefully opened, thus releasing air from the sample tube, and combustion fluid allowed to enter the tube. Heat from a microburner is then applied to the sample tube for 6 to 10 min., after which an additional period of 10 min. is allowed for absorption of carbon dioxide. Before releasing the vacuum in the apparatus, stopcock E is closed, thus preventing the sample tube from slipping off.

Results and Discussion

Table I shows the results obtained when analyses were made on samples of sucrose containing from 0.3 mgm. to 15 mgm. of carbon. Two examples are given for the top and bottom of each of the three ranges of sample size. Recoveries of carbon were uniformly good.

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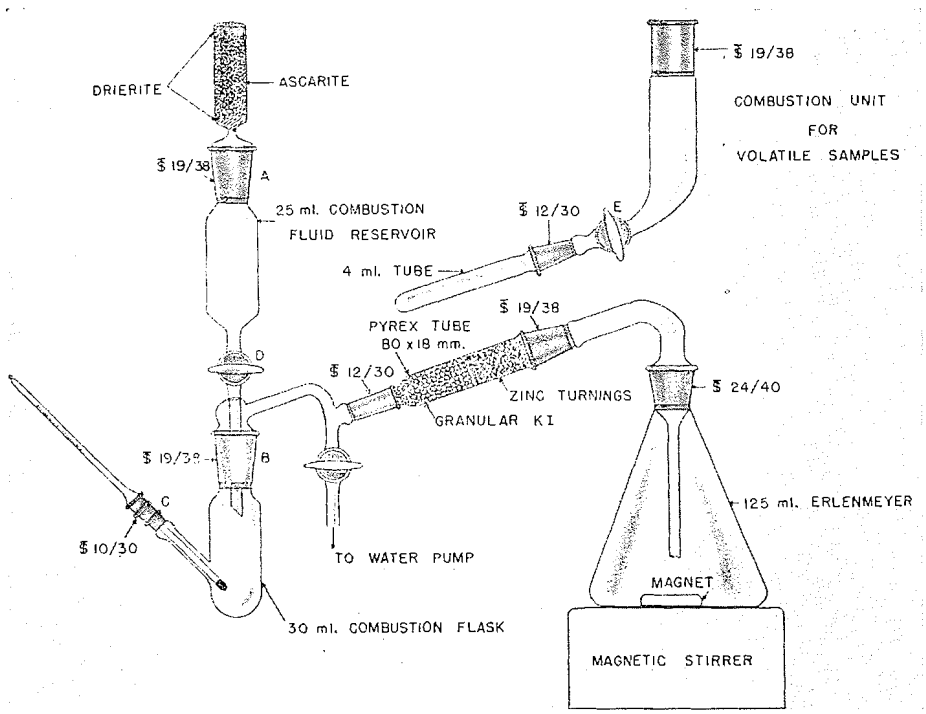

FIG. 1. *Apparatus for wet combustion.*

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TABLE I

ANALYSES OF SUCROSE SAMPLES CONTAINING FROM 0.3 TO 15 MGM. OF CARBON

Submicroanalyses			Microanalyses			Macroanalyses		
Carbon			Carbon			Carbon		
Taken, mgm.	Found, mgm.	Recovered, %	Taken, mgm.	Found, mgm.	Recovered, %	Taken, mgm.	Found, mgm.	Recovered, %
0.302	0.302	100.0	1.00	0.98	98.0	9.70	9.61	99.1
0.302	0.302	100.0	1.00	1.00	100.0	10.00	9.97	99.7
1.208	1.190	98.5	8.00	7.96	99.5	15.17	15.16	99.9
1.208	1.201	99.4	8.00	7.94	99.3	14.50	14.48	99.9

Table II shows the results of analyses of a number of representative types of compounds commonly encountered in biochemical research. Data are shown also for analyses conducted on samples of sucrose containing considerable sodium nitrate. This amount of acid-forming salt, far greater than one would expect to have in samples, had little, if any, effect on the analyses. Hockenhull (3) stated that 0.2 ml. of aqueous sample could be analyzed for carbon. We found that successful analyses could be done with samples as large as 0.5 ml., but did not determine whether larger samples could be employed. Dr. Neish of this laboratory has successfully determined succinic acid–carbon in the presence of 2 ml. of water when 10 ml. of oxidizing reagent was employed (7).

TABLE II

ANALYSES OF SEVERAL COMPOUNDS

Substance	Carbon			Substance	Carbon		
	Taken, mgm.	Found, mgm.	Recovered, %		Taken, mgm.	Found, mgm.	Recovered, %
Sucrose	0.604	0.612	101.3	Cholesterol	4.08	4.04	99.1
	0.604	0.609	100.8		4.08	4.08	100.0
	0.906	0.912	100.7		4.08	4.06	99.5
	0.906	0.902	99.6		8.42	8.42	100.0
	2.00	1.98	99.0		8.42	8.36	99.3
	2.00	2.01	100.5		8.42	8.40	99.7
	4.00	4.00	100.0	Stearic acid	4.19	4.23	100.9
	4.00	4.00	100.0		4.19	4.21	100.3
	4.00	3.98	99.5		4.19	4.18	99.8
	10.00	10.00	100.0		7.65	7.71	100.7
	10.00	10.11	101.1		7.65	7.68	100.4
Cysteine hydrochloride	4.66	4.63	99.3		7.65	7.68	100.4
	4.66	4.67	100.2	Succinic acid	4.00	4.01	100.3
	4.66	4.62	99.3		4.00	4.00	100.0
	10.06	10.06	100.0		4.00	4.00	100.0
	9.57	9.65	100.8	Acetone (0.5 ml. of 1.3% aqueous solution)	3.91	3.86	98.7
Sucrose + 26 mgm. sodium nitrate	10.00	10.13	101.3		3.91	3.88	99.2
	10.76	10.77	100.1		3.91	3.87	99.0

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The degree of evacuation of the apparatus and the length of time allowed for absorption of carbon dioxide were both critical factors in the determinations. Stirring of the alkali also was found necessary under the conditions employed. Using stirred alkali and an initial pressure of 20 to 30 mm. of mercury in the apparatus, complete absorption was obtained in eight minutes after cessation of heating. Incomplete absorption occurred in six minutes. A 10 min. period is recommended in order to allow for variations of absorption rate.

Only 80% of the carbon dioxide was recovered when the initial pressure in the apparatus was 32 cm. of mercury and a 10 min. absorption period was used. When the initial pressure was 14 cm., 95% of the carbon dioxide was recovered. Since it was convenient to evacuate to the full vacuum allowed by the water pump (20 to 30 mm. of mercury), the effect of initial pressure was not studied further.

Acknowledgment

The authors wish to thank Mr. Wm. Hogg for constructing the apparatus for this work.

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THE INFLUENCE OF CATION RADIUS AND SALT CONCENTRATION IN THE SALTING OUT OF ETHYL ETHER FROM AQUEOUS NITRATE SOLUTIONS AT 25°C.[1]

By H. G. Heal

Abstract

The solubility of ethyl ether in aqueous solutions of the nitrates of the alkali metals, the alkaline earths and magnesium, and ammonium, tetramethyl, tetraethyl, and tetra-*n*-propyl ammonium has been measured with high precision. The salting out at infinite dilution of salt, estimated by extrapolation from data for salt concentrations below 0.1 molal, conforms in a general way to the Debye theory, with some discrepancies. Data for high salt concentrations are also given.

Introduction

In this paper are presented the results of some measurements of salting out at salt concentrations between 0.01 and 0.1 molal, and also some data for higher concentrations. The purpose of the investigation was to obtain accurate enough values for the salting out at low salt concentrations to enable an extrapolation to infinite dilution of salt to be made, with the aid of Gross's extension (4, 5) of the Debye theory of salting out (2). In this way the salting out powers of the cations Li^+, Na^+, K^+, Rb^+, and Cs^+; NH_4^+, NMe_4^+, NEt_4^+, and $Nn\text{-}Pr_4^+$; and Mg^{++}, Ca^{++}, $Sr,^{++}$ and Ba^{++} have been compared. They tend to follow the predictions of the Debye theory, with discrepancies for which qualitative explanations are suggested. The variation of salting out with salt concentration has been studied empirically, up to nearly saturating concentration in some cases.

A precision of 0.06% in the solubility measurements has been attained and the present data are believed to be the most accurate of their kind hitherto published. Such data are needed in order to determine the extent of validity of the Debye theory of salting out, since the theory deals with phenomena at infinite dilution of salt and reliable extrapolations to infinite dilution can only be made from salt concentrations of the order of 0.1 molal downwards, where the amount of salting out is small. The reasons for this are given in the Discussion part of the paper.

Experimental

In attempting to use changes in the solubility of a liquid nonelectrolyte such as ether, as a measure of salting out, one must have regard to the risk that the activity of the nonelectrolyte in the saturating phase may vary from one salt solution to another, because of a variation in the amounts of water and salt passing into this phase. This would give rise to a variation of solubility entirely

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unconnected with the salting out effect. There is no variation of this kind of any importance in any of the systems described here. The concentration of salt in the ether phase was shown, by analysis of this phase in equilibrium with concentrated solutions of all the salts, to be less than 0.01% in every case. The concentration of water in the ether phase in equilibrium with dilute salt solutions is the same, for practical purposes, as in equilibrium with pure water; with concentrated salt solutions it is somewhat lower. By application of the Gibbs–Duhem equation to the ether phase, it can be shown that the variation in water concentration in this phase leads to changes in the activity of ether comparable with the experimental error in the solubility measurements for concentrated salt solutions, but entirely negligible for dilute ones. It is therefore sufficiently accurate to equate s_0/s, the ratio of molal solubilities of ether in pure water and in the salt solution, to γ/γ_0, the inverse corresponding ratio of molal activity coefficients, and to regard the change of solubility as a true measure of the salting out.

The solubility of ether in each salt solution was measured by equilibrating ether, in slight excess over the amount required to saturate the solution at 25°C., with the salt solution, and measuring the volume of ether remaining undissolved. The special vessel (Fig. 1) of capacity 28 ml. was employed. It has a neck of 4 mm. inside diameter, calibrated for volume per centimeter along its whole length. There is a closure consisting of a threaded Lucite cylinder (*a*) cemented on to the neck, with a Lucite screw cap (*b*). When screwed down this cap presses a piece of 0.05 mm. thick annealed platinum foil (*c*) against the opening of the neck, the pressure being transmitted via a 1 mm. thick Tygon washer (*d*). The rim of the neck has been ground off square and carefully firepolished. This arrangement constitutes an easily removable and practically airtight seal, the leakage through which was shown to be incapable of causing an error greater than 0.02% in the solubility measurements. About 27 ml. of the salt solution was run into the vessel from an ungreased

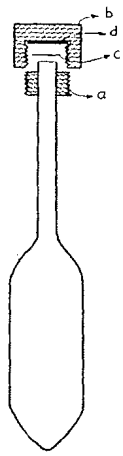

FIG. 1. *Solubility apparatus.*

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burette and weighed. The required quantity of ether, 0.03 to 0.10 gm. in excess of that required to saturate the salt solution at 25°C., was added from a drawn out pipette, and weighed. The closure was screwed up tightly and the vessel cooled to 15°C. or so and shaken vigorously to dissolve the ether. The vessel was centrifuged in order to drive down liquid caught high in the neck, then hung in a water bath regulated to 25.00°C. within 0.02° (by standard thermometer) with a variation of less than 0.01° either way. The whole solution became turbid. The turbidity than rose leaving a clear solution beneath, separated from it by a sharp boundary. In less than two hours the whole solution became clear. The excess ether was mostly in the neck above the aqueous phase, while a few droplets clung to the walls of the vessel. As many of these as possible were released by sharply twisting the vessel. The phase separation was completed by centrifugation, which also served to drive down ether condensed high in the neck. Careful tests showed that the quantity of ether found in the separated phase was independent of (*a*) the temperature of the centrifuge as long as this was below 25°C., (*b*) the speed of the centrifuge (radial accelerations between 200 g. and 400 g.), (*c*) the duration of centrifugation, up to more than two minutes. This is to be expected, since the solubility of ether increases with falling temperature and increasing hydrostatic pressure, while the densities of aqueous ether solutions decrease with increasing ether concentration. Under the conditions of the experiment, the redissolution of appreciable quantities of ether during centrifugation was impossible. Moreover, the result of a solubility measurement was shown not to depend upon how long the vessel was left in the bath, so long as it was left long enough to allow the turbidity to clear completely. In practice, the vessel was usually left in the bath for about two hours, and centrifuged at 300 g. for about twenty seconds, with the centrifuge at 22–24°C. The vessel was then replaced in the bath, and the distance between the ether–air and ether–water menisci measured to 0.05 mm. with a cathetometer.

Weighing corrections were applied for air displaced by the liquids, by ether vapor in the neck of the vessel, and by the weights. The mass of ether vapor present in the neck at the end of a measurement was estimated and included in the measured excess. The concentration of ether in the ether phase was taken as 0.705 gm. per ml., a value calculated from Hill's figure for the solubility of water in ether (6), and was assumed constant, though in reality it varies to an extent too slight to cause any error of consequence.

Materials

The ether was treated with a particular view to the removal of impurities which might affect the solubility results. The most objectionable impurities in this respect are those which strongly favor the ether phase in their distribution between ether and water, for this phase, in the method used, was small in volume compared with the original amount of ether added. Consequently, an impurity present in traces in the original ether might attain considerable concentration in the ether phase in equilibrium with the aqueous solutions, so

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lowering the activity of ether in this phase and leading to a low result for the solubility. Commercial reagent grade ether was, in fact, shown to contain such an impurity, probably isoamylene, which could not easily be removed by distillation. Its presence was revealed by a systematic variation in the measured solubility of ether in water with the amount of ether in excess, from which it was deduced that the ether must have contained about 0.03% of the impurity. The following procedure was adopted in order to remove it. Two liters of water were shaken with one liter of reagent grade ether. The ether layer, which contained almost all of the impurity, was rejected. Most of the ether dissolved in the water phase was distilled out, dried over sodium hydroxide pellets, and then refluxed for 24 hr. with a series of additions of bright sodium shavings, in all-glass apparatus. The final additions of sodium did not react at all, even on prolonged standing. The ether was distilled off the sodium through a two plate column; only the middle two-thirds of the distillate was retained. This was stored in the dark in a desiccator. Each batch was used for a week. Analysis by the acid potassium iodide method showed that the concentration of ether peroxide built up in this period did not exceed 0.005%. Small traces of water-soluble impurities, such as ether peroxide, are not objectionable, because they accumulate in the aqueous phase and there give rise to a constant amount of salting out or salting in, which may slightly affect the absolute value of the measured solubility, but cannot significantly change the measured salting out due to the ions. The solubility in water of the ether samples prepared in this way did not vary outside the experimental error ($\pm$ 0.06%) when the excess of ether used in the determination was varied between 0.02 gm. and 0.2 gm., nor when the final distillation of the preparation was repeated, nor during the period of storage of the samples.

Water for the recrystallization of salts and the preparation of solutions was made by redistilling ordinary distilled water from alkaline permanganate in an all-Pyrex still.

Tetramethyl, tetraethyl, and tetra-*n*-propyl ammonium nitrates were made by grinding the iodides (Eastman Kodak) with water and the exact equivalent of silver nitrate. The resulting suspensions were filtered and the filtrate evaporated to dryness *in vacuo* at room temperature. The salts were recrystallized several times, the methyl compound from a mixture of acetone and methanol, the ethyl compound from acetone alone, and the propyl compound from acetone mixed with carbon tetrachloride. Any traces of the solvents remaining after air-drying were removed by powdering the product finely and pumping on them in a high vacuum at room temperature for several hours. The propyl compound was also washed with ether after powdering. The purified salts gave no test for silver or iodide ion. All other nitrates were purified by recrystallizing reagent grade material several times from water. Lithium nitrate was dissolved in water and the solution washed with ether before recrystallizing to remove organic matter. The lithium nitrate was crystallized as the trihydrate, which was dehydrated first over sodium hydroxide *in vacuo*, and finally at 110°C. All

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the alkali nitrates, strontium, barium, and ammonium nitrates were weighed anhydrous. Magnesium and calcium nitrates were made up into concentrated solutions which were analyzed by ignition both to oxide and sulphate, and diluted as required.

Results and Discussion

The solubility of ether in water (s_0) at 25.00°C. was found to be 0.8599 molal, or 5.99 gm. per 100 gm. solution. This is the mean of 15 results, none of which deviated more than 0.06% from the mean. This value is slightly lower than those given by Hill (6) and Bennett and Philip (1), namely 6.027 and 6.03 gm. per 100 gm. solution. The fact that these authors did not employ the centrifuge and hence failed to achieve complete separation of the phases, may well explain the difference, as we have established by comparing results obtained with and without centrifugation.

The first column under each salt in Table I gives the number of moles of salt (m) per 1000 gm. water, and the second the corresponding number of moles of ether (s) in the ether-saturated solution. The probable error for low m values is about ± 0.03%.

The Influence of Cation Radius at Infinite Dilution

At infinite dilution of salt, the proportional change of molal solubility of ether should be a linear function of the salt molality:

$$\frac{s_0 - s}{s_0} = \mu m$$

The aim of this investigation was to determine values of μ for the different salts by means of reliable extrapolations from the experimental data; μ should be additive for the cation and anion, i.e.

$$\mu = \mu_+ + \mu_- \text{ for 1-1 nitrates}$$
$$\mu = \mu_+ + 2\mu_- \text{ for 2-1 nitrates}$$

The measurements provide no indisputable basis for estimating μ_+ and μ_- separately, but such a subdivision will be made on apparently reasonable grounds.

The assumptions made in the Debye theory of salting out are almost perfectly fulfilled in regions where the ionic field is weak, but may be very inaccurate where it is strong. Thus, at distances of, say, 7–10 Å and upwards from a singly charged ion, dielectric saturation phenomena are practically absent. There is little or no difference in structure between the solvent in this region and that in regions where the field strength is zero, and the dielectric constant varies with concentration of the nonelectrolyte almost exactly as it does in macroscopic measurements. On the other hand, at distances of, say, less than 5 Å from such an ion, the solvent structure is completely disrupted, and the dielectric constant of the medium may be more than a factor of 10 lower than

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TABLE I

MOLAL SOLUBILITIES OF ETHYL ETHER (s) IN AQUEOUS NITRATE SOLUTIONS OF MOLALITY m

$LiNO_3$		$NaNO_3$		KNO_3		$RbNO_3$		$CsNO_3$	
m	s	m	s	m	s	m	s	m	s
0.0250	0.8557	0.0253	0.8525	0.0250	0.8525	0.0250	0.8526	0.0250	0.8536
0.0501	0.8521	0.0502	0.8458	0.0514	0.8468	0.0487	0.8478	0.0514	0.8486
0.0749	0.8491	0.1003	0.8327	0.0996	0.8337	0.1012	0.8341	0.1003	0.8385
0.0998	0.8460	0.2004	0.8060	0.2014	0.8073	0.1484	0.8231	0.1503	0.8266
0.1527	0.8391	0.3006	0.7806	0.3002	0.7832				
0.2486	0.8275	0.8221	0.6568	0.3980	0.7594				
0.510	0.7988	1.249	0.5700	1.046	0.6132				
1.037	0.7326	1.689	0.4941	2.188	0.4250				
2.135	0.6212	2.141	0.4256	3.187	0.3235				
3.320	0.5194	3.329	0.2906						
4.575	0.4297	4.618	0.1918						
5.94	0.3542	6.013	0.1323						
9.09	0.2409	7.551	0.0886						
		9.40	0.0588						

NH_4NO_3		Me_4NNO_3		Et_4NNO_3		Pr_4NNO_3	
m	s	m	s	m	s	m	s
0.0253	0.8565	0.0216	0.8584	0.0251	0.8630	0.0250	0.8670
0.0500	0.8531	0.0471	0.8575	0.0550	0.8667	0.0490	0.8727
0.1008	0.8461	0.1002	0.8565	0.0941	0.8718	0.0750	0.8802
0.5140	0.7977	0.1504	0.8553				
1.054	0.7347						
2.223	0.6178						
3.533	0.5079						
5.009	0.4182						
6.688	0.3400						
10.86	0.2283						
20.3	0.1319						

$Mg(NO_3)_2$		$Ca(NO_3)_2$		$Sr(NO_3)_2$		$Ba(NO_3)_2$	
m	s	m	s	m	s	m	s
0.0388	0.8487	0.0220	0.8521	0.0100	0.8545	0.0123	0.8537
0.0797	0.8377	0.0462	0.8439	0.0265	0.8479	0.0250	0.8479
0.1535	0.8167	0.0927	0.8290	0.0500	0.8385	0.0499	0.8374
0.2159	0.8206	0.1861	0.8006	0.0738	0.8286	0.0751	0.8267
0.3046	0.7806	0.2802	0.7724	0.1002	0.8184	0.1016	0.8149
0.4484	0.7496	0.4709	0.7165	0.1490	0.7997	0.1491	0.7950
		0.991	0.574	0.1998	0.7805	0.2002	0.7734
		1.385	0.491	0.2497	0.7613	0.2999	0.7331
		1.750	0.410	0.3003	0.7420		
		2.149	0.347	0.3988	0.7058		
		2.661	0.277				
		3.30	0.218				
		3.81	0.183				

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in weak fields, while the variation of the electrical field energy with nonelectrolyte concentration bears little relation to that calculated on Debye's assumptions. In typical cases, such as that of ether in water, about half of the total salting out takes place in each of these somewhat arbitrarily distinguished regions. Hence we can expect the salting out in such cases to be composed of two contributions of comparable magnitude, one of which, that associated with regions far from the ions, conforms well to the Debye theory, while the other, associated with the immediate neighborhood of the ion, may not conform to the theory at all well. At finite concentrations of salt the ionic atmosphere creates a potential around each ion additional to the simple coulombic potential assumed in Debye's theory of salting out. From the expression developed for this potential in the Debye–Hückel electrolyte theory, it can be shown that its contribution to the electrical field strength at small distances is negligible compared with the contribution of the ion itself. At moderate distances, however, ($\backsim$ 20 Å in the case of a singly charged ion in 0.05 molal solution), the two are comparable. Consequently we may expect the chief effect of varying salt concentration to be upon the salting out in the 'outer' region, where the Debye theory is obeyed. This will be true when the parameter $1/\kappa$ of the Debye–Hückel theory is decidedly larger than the distance $\backsim$ 5 Å for singly charged ions, marking the boundary between the regions where the Debye salting out theory is valid and where it is not; i.e. at low enough salt concentrations. It should, in fact, be true in about the same range of salt concentration as that in which the Debye–Hückel theory of activity coefficients gives good results, since similar factors determine the limits of validity in both cases. This means up to about 0.1 molal for 1-1 electrolytes, and about 0.03 molal for 2-1 electrolytes.

Gross's salting out theory utilizes the Debye–Hückel potential to calculate the effect of ionic atmospheres on the salting out. The argument just given shows that the difference between $\frac{s_0 - s}{s_0 m}$ at infinite dilution and the same function at small finite concentration, calculated by the Gross theory, should be correct, even if the absolute value of the function, calculated by the Debye theory, is wrong (owing to the departure of salting out in the inner region from Debye theory values).

The values of μ given in Table II were accordingly calculated in the following steps:

(1) Experimental values of $\frac{s_0 - s}{m s_0}$ were determined for the various salts from the graphs (Figs. 2 to 5) at $m = 0.05$ for 1-1 nitrates and $m = 0.025$ for 2-1 nitrates. These concentrations were chosen so as to come sufficiently within the range of validity of the Debye–Hückel electrolyte theory, at the same time giving reasonable accuracy of measurement of the salting out. The values of this salting out function are given under μ' in Table II.

TABLE II

Cation	μ'	μ	μ_+ (experimental)	μ_+ (Debye theory)
Li^+	0.181	0.229	0.142	0.142
Na^+	0.326	0.374	0.287	0.140
K^+	0.302	0.350	0.263	0.136
Rb^+	0.288	0.336	0.249	0.134
Cs^+	0.256	0.304	0.217	0.131
NH_4^+	0.158	0.206	0.119	0.139
NMe_4^+	0.058	0.105	0.018	0.080
NEt_4^+	−0.144	−0.099	−0.186	0.058
NPr_4^+	−0.302	−0.258	−0.345	0.045
Mg^{++}	0.336	0.481	0.307	0.401
Ca^{++}	0.412	0.557	0.383	0.400
Sr^{++}	0.526	0.671	0.497	0.399
Ba^{++}	0.558	0.703	0.529	0.396

(2) Gross's equations were used to calculate differences between μ and μ'. Debye's value of the characteristic salting out length R for the ether–water system, 2.49 Å was employed. In the Gross theory, (a') was set equal to R for the monatomic ions and to the ionic radius for the substituted ammonium ions. The difference between molal and molar concentrations is here of no importance for accuracies of the order aimed at, and was ignored. The nitrate ion was treated as a small singly charged ion for the purpose of this calculation.

(3) These differences were added to experimental values of μ' to give the values of μ in Table II.

The figures for μ_+ given in Table II were arrived at by the following reasoning. Since Li^+ is a very small ion, and is believed to fit well into water without disrupting its tetrahedrally co-ordinated structure, it seems reasonable to suppose that the salting out due to this ion approaches more nearly to the Debye theory value than does that caused by most other ions. Moreover, NH_4^+, which is tetrahedral itself, and probably likewise fits well into the water structure, has about the same μ_+ as Li^+, since the μ values for the two nitrates are approximately equal. It was therefore assumed that μ_+ for $Li^+ = 0.142$, the Debye theory value. This fixes μ_- for the nitrate ion at 0.087, from which the μ_+ values for all the other cations given in Table II were calculated. The possible experimental error in the tabulated values of μ', μ, and μ_+ is about $\pm$ 0.008 for the 1-1 nitrates and $\pm$ 0.016 for the 2-1 nitrates.

Debye theory values for μ_+, calculated assuming crystallographic radii for the monatomic ions, and estimated over all radii for the others, are given in the last column of Table II.

The following are the principal conclusions emerging from a study of these figures.

(1) The experimental μ_+ values for the alkali cations other than Li^+ are anomalously high.

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(2) The experimental μ_+ values for the bivalent cations are of the expected order of magnitude, but increase with increasing cation radius instead of diminishing slightly as expected.

(3) The experimental μ_+ values for the ammonium ions display approximately the expected falling off with increasing cation radius between ammonium and tetramethylammonium, but thereafter decrease very rapidly to large negative values, corresponding to strong salting in. These conclusions are not affected if a somewhat different value is adopted for μ_+ for the lithium ion.

The hypothesis of Frank and Evans (3) to the effect that the larger alkali and alkaline earth cations in aqueous solution are surrounded, outside their first solvation layer, by a region of unusually structureless or "depolymerized" water suggests an explanation for (1) and (2). These changes in the water structure may give rise to a salting out effect additional to the electrostatic one, and most pronounced for the larger ions. The salting in caused by the large substituted ammonium ions is undoubtedly due to the long alkyl chains, which project out of the region where electrical forces are strong, and would on general grounds be expected to favor the solution of ether. The significant fact about the results obtained with the ammonium series of nitrates is simply that electrical forces give way to other influences when the radius exceeds 2–3 Å, as they should according to the Debye theory.

Absolute μ_+ and μ_- values could be determined experimentally for all ions if the value for any one ion were known. Unfortunately, Debye theory values

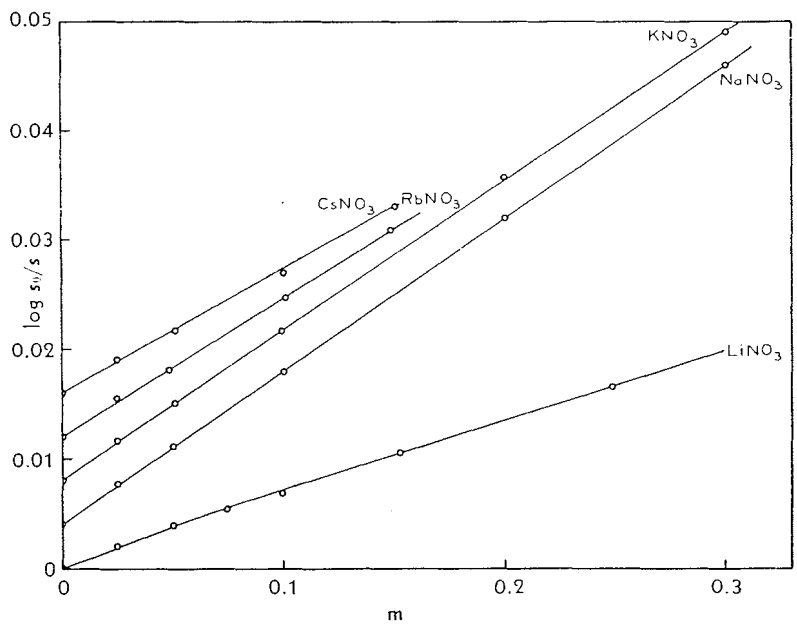

FIG. 2. *Salting out of ether from alkali nitrate solutions at low concentrations. (These curves should all pass through the origin—the upper four of them have been moved bodily upward in order to avoid confusion.)*

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cannot safely be assumed for large ions because of molecule–molecule type interaction with the nonelectrolyte, nor for small ions because of dielectric saturation effects and changes in the solvent structure. Structural changes might be less important with some nonaqueous solvents.

The Influence of Salt Concentration

The best simple empirical equation for representing the results is:

$$\log \frac{s_0}{s} = km.$$

The data are accordingly plotted in Figs. 2 to 5 in the form of graphs of $\log \frac{s_0}{s}$ against m. The above equation, however, does not exactly fit the results in

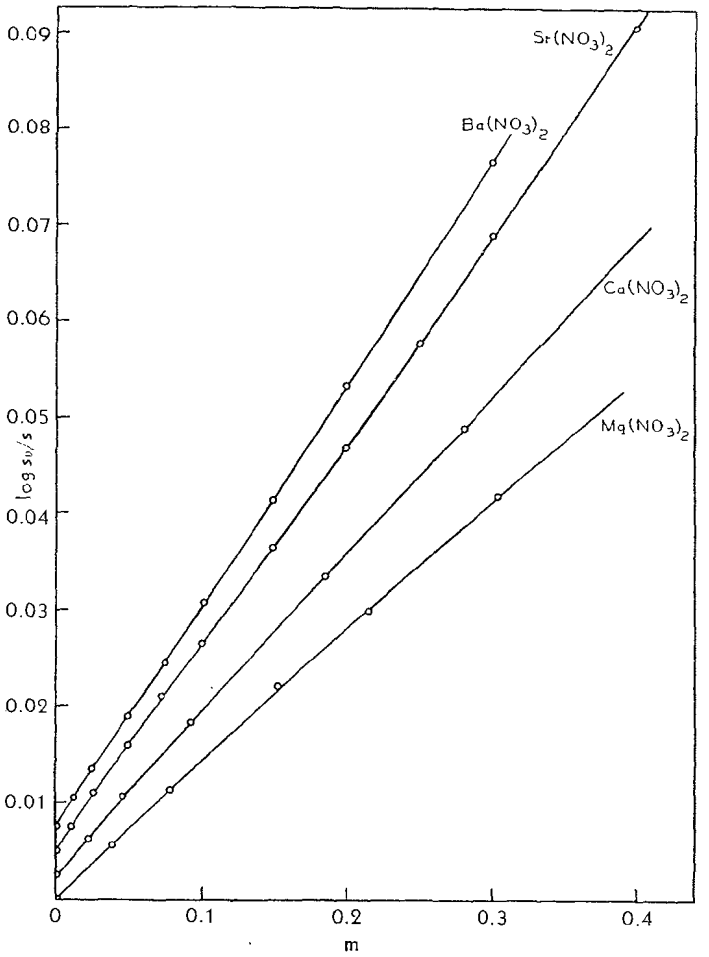

FIG. 3. *Salting out of ether from solutions of magnesium and the alkaline earth nitrates at low concentrations. (All curves should pass through the origin—the upper three have been moved bodily upward in order to avoid confusion.)*

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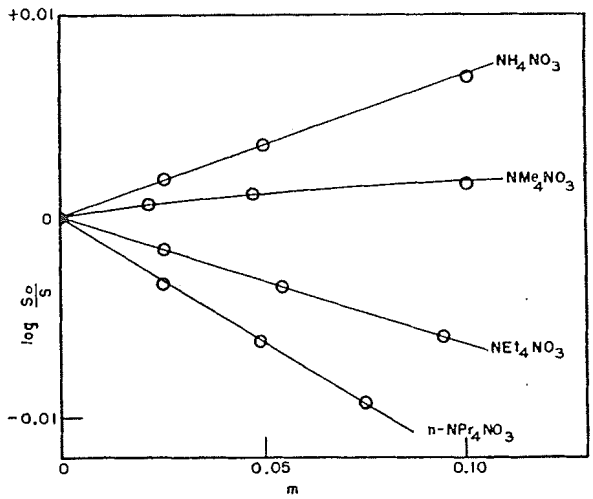

FIG. 4. *Salting out of ether from solutions of ammonium and substituted ammonium nitrates at low concentrations.*

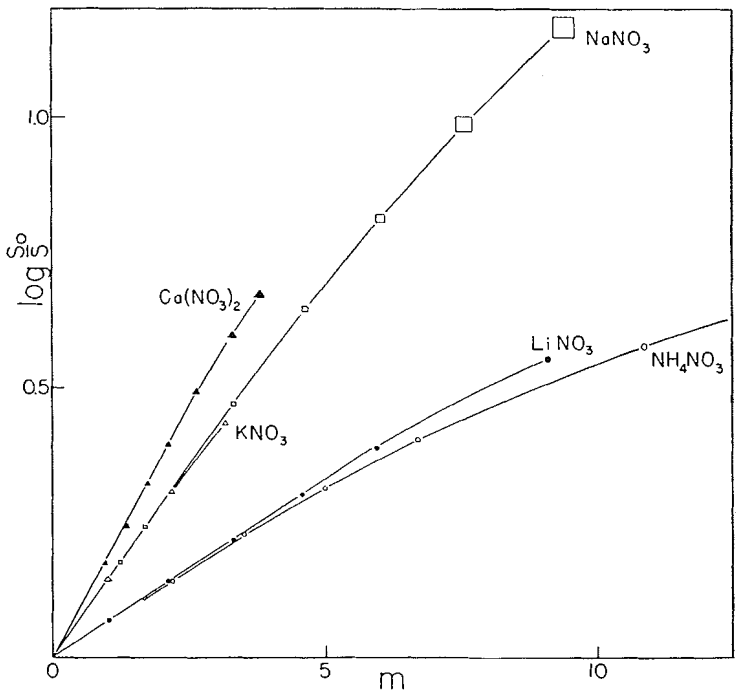

FIG. 5. *Salting out of ether from solutions of lithium, sodium, potassium, ammonium, and calcium nitrates at high concentrations.*

any single case. It works best at moderate concentrations. Below 0.3 molal, the lines for the alkaline earth nitrates are slightly S-shaped, the slope first diminishing, and then increasing again as the concentration rises. A similar effect is perceptible in the curves for the alkali nitrates except lithium, but is

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smaller than the experimental error in these cases. With magnesium, lithium, and tetramethylammonium nitrates the slope declines continuously with increasing concentration at low concentrations. These results were checked and confirmed. At very high concentrations the salting out falls below the amount given by the equation just quoted in all cases studied.

The data are not accurate enough at very low concentrations to enable Gross's equations to be satisfactorily tested, but the tendency of the first one or two experimental points for each salt is compatible with the concentration dependence predicted by Gross's equations.

The alkaline earth nitrates are believed to be associated in aqueous solutions at moderate to high concentrations (7). At 0.01 molal, the degree of association is about 2% for calcium nitrate and 8% for barium nitrate, with strontium nitrate intermediate. This association, if it occurs, does not cause any marked diminution in the salting out caused by these salts.

Acknowledgments

I wish to acknowledge a stimulating correspondence on this subject with Drs. J. O'M. Bockris and H. Egan of Imperial College, London, England, and to thank Miss H. Fleming for assistance in making up the solutions.

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THE CHEMISTRY OF ETHYLENE OXIDE

II. THE KINETICS OF THE REACTION OF ETHYLENE OXIDE WITH AMINES IN AQUEOUS SOLUTION[1]

By A. M. Eastham, B. deB. Darwent, and P. E. Beaubien

Abstract

The kinetics of the reaction of ethylene oxide in dilute aqueous solution at 25°C. with di- and tri-ethylamines, aniline, and pyridine have been investigated over a wide range of hydrogen and hydroxyl ion concentrations. The rates for all four amines were found to be very similar and were accurately expressed by the simple second order equation $-d\,\text{oxide}/dt = k(\text{oxide})(\text{amine})$. The results indicate that basic catalysis does not occur and that catalysis by hydrogen or ammonium-type ions, if it occurs at all, is of no significance in the pH range 4-14.

The work of Bronsted, Kilpatrick, and Kilpatrick (1) has shown that ethylene oxide reacts readily with many nucleophilic reagents to give both spontaneous (uncatalyzed) and hydrogen ion-catalyzed reactions. There is no evidence that the acid catalysis is of the general type, nor does basic catalysis in the usual sense seem to occur, since most of the so-called basic catalyses reported in the literature may be attributed to direct nucleophilic attack by anions (6). Further information on the nature of these catalyses is necessary if the reaction mechanisms are to be established. Accordingly, a study of the reactions between ethylene oxide and amines has been undertaken since these reactions are capable of being investigated over a wide range of hydrogen and hydroxyl ion concentrations and since they can also be examined for catalysis by weak cation acids of the ammonium ion type.

It was observed by Knorr (5) in 1899 that ethylene oxide reacts with amines only in solvents such as water and ethanol. His observations led him to suggest that in such solutions ammonia ionizes not only to ammonium (NH_4^+) ions, but also to NH_2^- ions, and that these NH_2^- ions react with ethylene oxide to give the ethanolamines. Such an explanation is inadequate, however, because tertiary amines react equally as well as primary or secondary amines with ethylene oxide and hence one might expect that in all cases the hydroxyl group is formed from ethylene oxide by the addition of a proton derived from a source other than the amine. The over-all reaction would then be represented by the following equations:

$$NH_3 + \underset{\diagdown O \diagup}{CH_2-CH_2} + H^+ \rightarrow \overset{+}{N}H_3-CH_2-CH_2OH \rightarrow NH_2-CH_2CH_2OH + H^+$$

$$R_3N + \underset{\diagdown O \diagup}{CH_2-CH_2} + H^+ \rightarrow R_3\overset{+}{N}-CH_2CH_2OH$$

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Since the reaction requires a proton and since ethylene oxide reactions are known to be susceptible to hydrogen ion catalysis, a kinetic study might be expected to increase our knowledge of the mechanism of this reaction. Smith (10) attempted such a study but his analytical methods were not sufficiently precise to detect small changes in rate. Other studies (3, 8) are still more limited and serve only to indicate that in aqueous solution the reaction is bimolecular. Smith's data do show that no simple relation exists between reaction rate and amine structure or basicity. This might suggest a rate controlling step not involving the amine, but such a view is not compatible with the observed first order dependence upon the concentration of amine.

Experimental

In the present work the rates of reaction of ethylene oxide in aqueous solution with aniline, pyridine, and di- and tri-ethylamine have been measured dilatometrically. Since this method is adaptable only to first order reactions, all experiments have been performed in a large excess of amine. Under these conditions the reaction exhibits pseudo- first order kinetics. The ethylene oxide concentration was generally between 0.01 and 0.03 *M*. The temperature was controlled to about 0.001°C. at 25.0°C.

Rates were usually calculated by Guggenheim's method (4) and showed good reproducibility. In a few cases, where the oxide–amine ratio was high, the rates were estimated graphically from the initial rates of contraction.

Reaction mixtures were prepared by mixing standard solutions of the amine and perchloric acid to give the desired concentrations and pH. The ionic strength was kept constant by the addition of sodium perchlorate. The buffering action of these solutions was generally sufficient to maintain the pH within 0.1 pH unit during the course of the reaction. In those cases in which a quaternary base was formed during the reaction, the perchloric acid concentration was always kept higher than the initial oxide concentration to prevent formation of a mixture of quaternary base and quaternary salt. This was particularly necessary in the reactions with pyridine, since the free quaternary bases of this amine are unstable (7, 9).

All pH values and amine concentrations reported were calculated from the recorded concentration dissociation constants on the assumption that the amines reacted completely with perchloric acid. The pH values measured by a glass electrode were in fair agreement with those calculated.

In aqueous solution and especially in acidic or strongly alkaline solution, ethylene oxide reacts with water to form glycol and it is therefore necessary to correct the observed rates to obtain the rate of the amine reaction. Since under the conditions of the experiments all rates are of the first order with respect to ethylene oxide, the following expression will hold:

$$k_{obs} = k_a\,(\text{amine}) + k_g$$

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where k_a is the second order rate constant for the reaction between ethylene oxide and amine and where k_g is the rate of glycol formation which is given by the expression

$$k_g = k_0 + k_{H^+}(H^+) + k_{OH^-}(OH^-)$$

The value of k_0 at 25°C. was calculated from the data of Bronsted *et al.* (1) to be 4.0×10^{-5}; the values for k_{H^+} and k_{OH^-}, which had been previously determined by other workers (1, 6) at 20°C. were measured at 25°C. in these laboratories and found to be:

$$k_{H^+} = 0.537 + 0.55c, \text{ where } c = \text{anion concentration}$$
$$k_{OH^-} = 7.5 \times 10^{-3}.$$

Analyses for glycol were made occasionally by a periodate method (2) and always agreed with the calculated values to 5% or better. The analysis could not be applied to aniline solutions however, because of the reducing action of this amine. As far as possible reaction conditions were chosen such that the rate of the amine reaction was much greater than that of glycol formation.

Analyses for ethanolamine formation were made only in those cases where the product was a quaternary base and could be determined by titration at the end of the reaction. Such analyses after correction for glycol formation always indicated essentially quantitative conversion of oxide to ethanolamine. The only probable side reaction other than glycol formation is the reaction of the product with a second molecule of oxide. However, since the amine was in large excess with respect to the oxide and since the rates of the reactions of ethylene oxide with amines and with the corresponding ethanolamines are not far different, no serious error should arise from this source.

All the amines used in this work were reagent grade. They were carefully distilled through a 20 plate Stedman column after standing for some days over solid potassium hydroxide. Solutions were prepared in ordinary distilled water which had been boiled to remove carbon dioxide. Sodium perchlorate solutions were prepared by neutralizing standard perchloric acid solutions with sodium hydroxide. All titrations were performed electrometrically.

The reaction mixtures were brought to the temperature of the bath and a weighed sample of ethylene oxide broken into the solution (2). A few minutes were allowed for mixing and the solution was then forced into the dilatometer. A period of five minutes was allowed for thermal equilibrium to be attained before readings were taken. Usually 20–30 readings were made over a period of about 1.5 half lives, followed by a second set of readings after an interval of two to three half lives. In some experiments the readings were taken during three or four instead of 1.5 half lives, but in no case was appreciable deviation from first order observed.

In the study of the reactions of aniline and pyridine a series of experiments was made at each of several pH values. To do this, mixtures of amine and perchloric acid were prepared and diluted with sodium perchlorate solution to

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constant ionic strength. Since the pH is determined by the ratio of free amine to aminium ion, any such series of dilutions should have a constant pH and experimentally this was found to be true.

Results

The results of these experiments are given in the accompanying tables and figures. The following calculation of a typical run will serve to clarify the tabulated data.

Run 90 (Table I)

A solution was prepared to contain 0.300 moles per liter diethylamine and 0.135 moles per liter of perchloric acid. From the ionization constant of diethylamine (1.0×10^{-3}) it may be calculated that the aminium ion concentration

TABLE I

REACTION OF ETHYLENE OXIDE WITH DIETHYLAMINE*

Run	Free amine (moles/l.)	Amine perchlorate (moles/l.)	$NaClO_4$ (moles/l.)	Oxide (moles/l.)	pH	k_{obs} 10^2 min.$^{-1}$	k_g 10^2 min.$^{-1}$	k_a (amine) 10^2 min.$^{-1}$	$10^2 k_a$ l.mol.$^{-1}$ min.$^{-1}$
A. Experiments at constant ionic strength									
92	.283	....	.250	.0191	12.2	1.81	.02	1.79	6.53
98	.248	.052	.197	.0289	11.7	1.57	.008	1.56	6.68
97	.195	.105	.149	.0159	11.3	1.26	.009	1.25	6.69
90	.165	.135	....	.0201	11.1	1.08	.005	1.08	6.96
91	.100	.200	.050	.0206	10.7	0.574	.004	0.570	6.34
93	.084	.216	.033	.0209	10.6	0.420	.004	0.416	5.66
94	.052	.248	....	.0243	10.3	0.287	.004	0.283	(7.1)
96	.020	.280	....	.0208	9.85	0.08	.004	0.08	(8.)
89	.283	....	....	.0200	12.2	1.83	.02	1.81	6.63
95	.300	....	(NaOH) (.264)	.0213	....	2.05	.21	1.84	6.37
									Av. 6.48×10^{-2}
B. Experiments at varying ionic strength									
89	0.283		0.0	.0200	12.2	1.83	0.02	1.81	6.63
92	0.283		0.25	.0191	12.2	1.81	0.02	1.79	6.53
112	0.259		0.25	.0299	12.2	1.74	0.02	1.72	7.05
111	0.259		0.50	.0163	12.2	1.88	0.02	1.86	7.41
110	0.283		1.0	.0201	12.2	2.34	0.02	2.32	8.50
109	0.259		2.0	.0187	12.2	2.38	0.02	2.36	9.44

* *Concentrations and pH values calculated from an ionization constant of* 1.0×10^{-3}.

TABLE II

REACTION OF ETHYLENE OXIDE WITH TRIETHYLAMINE*

Run	Free amine (moles/l.)	Amine perchlorate (moles/l.)	$NaClO_4$ (moles/l.)	Oxide (moles/l.)	pH	k_{obs} 10^3 min.$^{-1}$	k_g 10^3 min.$^{-1}$	k_a (amine) 10^3 min.$^{-1}$	$10^2 k_a$ l.mol.$^{-1}$ min.$^{-1}$
102	.062	.253	....	0.0177	10.1	1.17	.04	1.13	(1.82)
103	.112	.203	.050	0.0161	10.5	3.56	.04	3.52	3.14
104	.163	.152	.100	0.0270	10.8	4.97	.04	4.93	3.05
105	.188	.127	.125	0.0254	10.9	5.48	.05	5.43	2.89
106	.214	.101	.150	0.0153	11.1	6.38	.05	6.33	2.96
107	.264	.051	.200	0.0148	11.5	8.54	.06	8.48	3.21
108	.302	....	.250	0.0137	12.1	9.89	.14	9.75	3.29
									Av. 3.09×10^{-2}

* *Concentrations and pH values calculated from an ionization constant of* 5.5×10^{-4}.

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is essentially that of the perchloric acid (0.135 moles per liter) and hence that the free amine concentration is 0.165 moles per liter. On reaction of this solution with 0.0209 moles per liter of ethylene oxide, free amine is consumed and a new amine, diethyl ethanolamine, produced. The composition of the final mixture must be affected by the basic strength of this new amine since the hydrogen ions are distributed according to the basic strengths and concentrations of all amines present. Usually, however, the ethanolamines are considerably weaker bases than diethylamine and it is therefore assumed that the diethylaminium ion concentration remains essentially unchanged throughout the reaction. Under these conditions the free amine concentration at the end of the reaction is (0.165–0.0209) = 0.144 moles per liter, and the average free amine concentration during the reaction becomes 0.155 moles per liter.

The observed reaction rate in this solution was 1.08×10^{-2} min.$^{-1}$ and represents the sum of the rates of glycol and ethanolamine formation. Since the aminium ion and free amine concentrations are known, the hydrogen and hydroxyl ion concentrations may be calculated. These were found to be 8.2×10^{-12} and 1.2×10^{-3} moles per liter respectively. From the rate constants for glycol formation given above, it is apparent that no significant amount of glycol will be formed by hydrogen ion catalysis but that the rates corresponding to the uncatalyzed and to the hydroxyl ion catalyzed reactions will be 0.004×10^{-2} and 0.001×10^{-2} min.$^{-1}$ respectively. The rate of reaction of ethylene oxide with amine in this solution is therefore $(1.08 - .004 - .001) \times 10^{-2} = 1.08 \times 10^{-2}$ min.$^{-1}$. The specific rate constant is obtained by dividing this value by the average amine concentration obtained above–i.e. $1.08 \times 10^{-2}/0.155 = 6.96 \times 10^{-2}$ l. mol.$^{-1}$ min.$^{-1}$.

It should be noted that triethylamine and pyridine, being tertiary amines, yield quaternary ammonium bases as products and the over-all reaction is given by the following equations:

$$R_3N + (CH_2)_2O + H_2O \rightarrow R_3\overset{+}{N}CH_2CH_2OH + OH^-$$
$$R_3NH^+ + OH^- \longrightarrow R_3N + H_2O$$
$$\overline{R_3NH^+ + (CH_2)_2O \longrightarrow R_3\overset{+}{N}CH_2CH_2OH}$$

It is therefore aminium ion and not free amine which disappears and the above calculations have been modified accordingly when applied to the tertiary amines.

Discussion

The data for diethylamine and triethylamine are best interpreted by reference to Fig. 1, where values of (amine), (amine) (aminium ion), and (amine) (hydroxyl ion) have been plotted against the corresponding pH. These three curves correspond respectively to the uncatalyzed, aminium ion catalyzed, and hydroxyl ion catalyzed addition of amine to ethylene oxide and hence a plot of observed rates against pH should constitute a rather sensitive test of the type

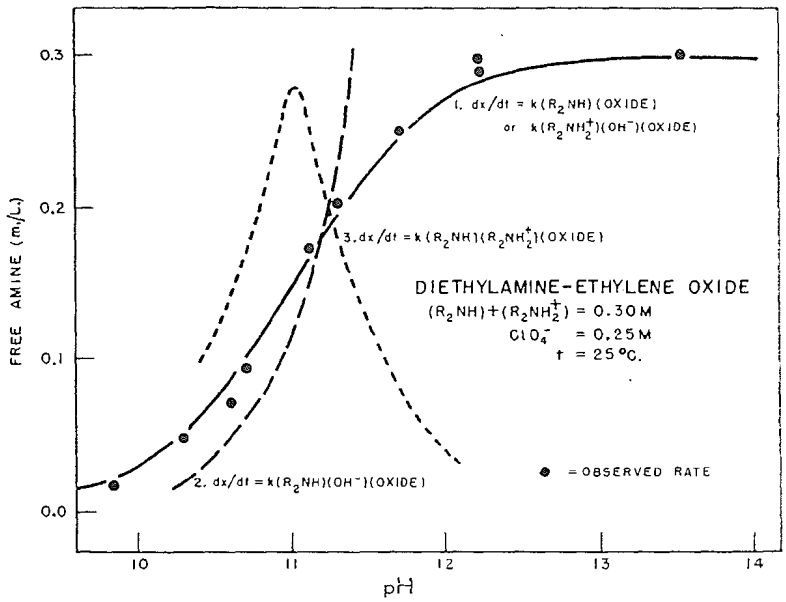

FIG. 1

of mechanism or mechanisms involved. The curve for the expression (amine) (hydrogen ion) corresponding to specific hydrogen ion catalysis has not been shown but is roughly the reciprocal of the curve for the uncatalyzed reaction.

It is seen that the results for diethylamine correspond very closely to the curve for the uncatalyzed reaction. Essentially similar data were obtained for triethylamine. These results show conclusively that no hydroxyl ion catalysis exists and it is also apparent that any aminium ion catalysis must be very small indeed, since there is no indication of the inflection in the pH range 11-12, which would occur if catalysis by aminium ions was important.

Very basic amines such as diethylamine are not suitable for the detection of hydrogen ion catalysis because no appreciable hydrogen ion concentration may be maintained in their presence. Calculations suggest that an amine having an ionization constant of about 10^{-12} would be best suited for this purpose but for reasons of solubility, availability, etc., it has been necessary to work with aniline and pyridine (ionization constants 4.6×10^{-10} and 1.7×10^{-9} respectively). Preliminary experiments with aniline (Table III) showed similar results to those in Fig. 1, but gave some indication of a trend towards higher rates as the hydrogen ion concentration was increased. Since such a trend could be due to catalysis by hydrogen or anilinium ions, the reaction was further investigated under more rigorous conditions.

If both hydrogen and anilinium ion catalysis are present together with an uncatalyzed reaction, the over-all rate will be given by the expression

$$\frac{-d\,\text{oxide}}{dt} = k_1\,(\text{aniline})\,(\text{oxide}) + k_2\,(\text{aniline.H}^+)\,(\text{aniline})\,(\text{oxide}) + k_3(\text{H}^+)$$

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TABLE III

PRELIMINARY EXPERIMENTS WITH ANILINE AND ETHYLENE OXIDE*

Run	Free aniline (moles/l.)		Oxide (moles/l.)	pH observed	$10^3 k_{obs}$ min.$^{-1}$	$10^3 k_g$ min.$^{-1}$	$10^3 k_a$ (amine) min.$^{-1}$	$10^2 k_a$ l.mol.$^{-1}$ min.$^{-1}$
131	.327		.0251	8.3	5.90	.04	5.86	1.85
121	.355		.0245	8.25	6.15	.04	6.11	1.79
118	.309		.0257	8.10	5.91	.04	5.87	1.98
		Trace						
122	.355	NaOH	.0161	12.1	6.54	.19	6.35	1.83
125	.345	"	.0227	12.1	6.53	.19	6.34	1.89
130	.327	"	.0268	10.2	6.37	.04	6.33	2.00
		$HClO_4$ (moles/l.)		pH (calc.)				
128	.252	.033	.0250	5.5	4.25	.04	4.21	1.75
129	.191	.093	.0268	5.0	3.37	.05	3.37	1.85
119	.211	.098	.0480	5.0	4.06	.05	4.01	2.10
117	.191	.118	.0255	4.9	3.95	.05	3.90	2.15
126	.121	.164	.0244	4.5	2.47	.06	2.44	2.19
127	.094	.187	.0115	4.35	2.09	.07	2.02	2.25
124	.074	.216	.0281	4.2	1.61	.08	1.53	2.45
120	.071	.275	.0155	4.1	1.81	.10	1.71	2.63
123	.030	.258	.0315	3.75	(1.04)	.12	.94	(5.9)

* *All calculations made as described for diethylamine; ionization constant taken as* 4.6×10^{-10}.

(aniline) (oxide). Under the conditions of the experiments the reactions are of the first order with respect to oxide and, since at any pH the ratio (aniline.H^+)/(aniline) is constant, then at that pH the following expression will describe the dependence of k_{obs} on the concentration of free aniline and hydrogen ion

$$k_{obs} = k_1(\text{aniline}) + ck_2(\text{aniline})^2 + k_3(H^+)\ (\text{aniline})$$
$$\text{where } c = (\text{aniline})/(\text{aniline}.H^+).$$

Thus, if k_{obs} is plotted against the free aniline concentration, a straight line will be obtained only if no anilinium ion catalysis is present, and the slope of this line will be equal to $k_1 + k_3(H^+)$. It follows that in the presence of hydrogen ion catalysis and in the absence of anilinium ion catalysis, a series of lines of increasing slope should be obtained as the pH is decreased.

Our results for such an experiment with aniline are shown in Table IV and Fig. 2, and it is apparent that the results—particularly at low concentrations—show some divergence from the single straight line corresponding to an uncatalyzed reaction. The divergence is, however, in the opposite direction to that which might be expected from hydrogen and anilinium ion catalyses and we are able to account for it only as an experimental error. Errors may arise from faulty corrections for glycol, reaction of the product with a second molecule of oxide, or from small errors in the calculated free amine concentration. However, although a number of these experimental errors disappear when pyridine is substituted for aniline, essentially similar experimental results are obtained with both amines (Table V, Fig. 3).

It must be concluded then that, under the conditions of our experiments, the reaction between amines and ethylene oxide is essentially uncatalyzed. Catalysis by aminium and hydroxyl ions in which the rate is given by an equation of the type

$$\frac{-d\,\text{oxide}}{dt} = k(\text{oxide})(OH^-)(NH_4^+)$$

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TABLE IV

REACTION OF ANILINE WITH ETHYLENE OXIDE*

Run	Free amine (moles/l.)	Amine perchlorate (moles/l.)	$NaClO_4$ (moles/l.)	Oxide (moles/l.)	pH	10^3k_{obs} min.$^{-1}$	10^3k_s min.$^{-1}$	10^3k_a (amine) min.$^{-1}$	10^5k_a l.mol.$^{-1}$ min.$^{-1}$
143	.344	.055	.295	.0177	5.46	6.10	.04	6.06	1.81
144	.275	.044	.306	.0285	5.46	5.09	.04	5.05	1.93
145	.207	.033	.317	.0162	5.46	3.99	.04	3.95	1.92
146	.172	.028	.322	.0273	5.46	3.34	.04	3.30	2.05
147	.115	.018	.332	.0173	5.46	2.37	.04	2.33	2.18
									Av. 2.00
138	.381	.330	....	.0141	4.72	7.18	.06	7.12	1.89
139	.305	.264	.070	.0167	4.72	5.53	.06	5.47	1.83
140	.229	.198	.139	.0159	4.72	4.25	.06	4.19	1.89
141	.190	.165	.175	.0186	4.72	3.44	.06	3.38	1.85
142	.116	.110	.233	.0136	4.72	2.36	.06	2.30	2.09
									Av. 1.94
163	.192	.350	....	.0136	4.40	3.67	.07	3.60	1.94
164	.153	.280	.070	.0147	4.40	3.01	.07	2.94	2.00
165	.115	.210	.140	.0202	4.40	2.35	.07	2.28	2.15
166	.096	.175	.175	....	4.40	1.89	.07	1.82	2.12
167	.064	.117	.233	.0182	4.40	(1.42)	.07	1.35	(2.40)
									Av. 2.12
148	.172	.338	....	.0135	4.38	3.27	.07	3.20	1.92
149	.138	.270	.069	.0181	4.38	2.82	.07	2.75	2.08
150	.103	.203	.138	.0152	4.38	2.25	.07	2.18	2.22
151	.086	.169	.175	.0183	4.38	2.04	.07	1.97	2.46
152	.057	.113	.233	.0222	4.38	1.59	.07	1.52	3.04
									Av. 2.34
		NaOH							
153	.325	.034	.306	.0133	ca 13	6.02	.29	5.73	1.80
154	.260	.027	.316	.0147	ca 13	5.00	.25	4.75	1.89
155	.195	.020	.327	.0245	ca 13	3.65	.19	3.46	1.89
156	.163	.017	.333	.0198	ca 13	3.08	.16	2.92	1.91
									Av. 1.87
170	.125	Trace	.350	.0218	ca 9	2.37	.04	2.33	2.04
169	.094	"	.350	.0154	ca 9	1.80	.04	1.76	2.05
168	.078	"	.350	.0200	ca 9	1.53	.04	1.49	2.19
									Av. 2.09

* *All calculations made as for diethylamine and based on an ionization constant of* 4.6×10^{-10}.

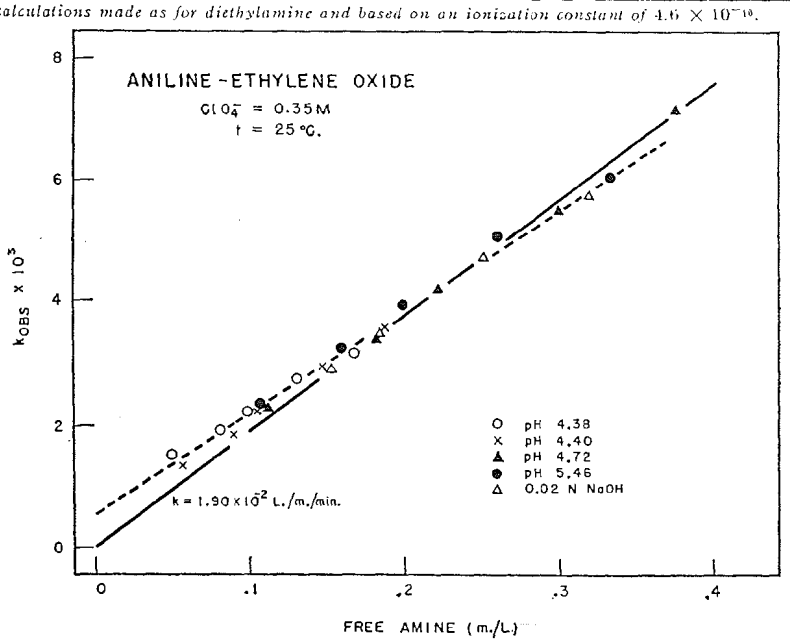

FIG. 2

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TABLE V

REACTION OF ETHYLENE OXIDE WITH PYRIDINE*

Run	Free pyridine (moles/l.)	Pyridinium perchlorate (moles/l.)	$NaClO_4$ (moles/l.)	Oxide (moles/l.)	pH	10^3k_{obs} min.$^{-1}$	10^3k_g min.$^{-1}$	10^3k_a (amine) min.$^{-1}$	10^3k_a l.mol.$^{-1}$ min.$^{-1}$
188	.600	.665	....	.0178	5.2	6.95	.04	6.91	1.15
189	.360	.399	.270	.0170	5.2	4.53	.04	4.49	1.25
190	.240	.266	.404	.0177	5.2	3.21	.04	3.17	1.32
191	.150	.166	.503	.0217	5.2	2.28	.04	2.24	1.49
									Av. 1.30
183	.954	.497	.173	.0200	5.5	10.8	.04	10.8	1.13
184	.572	.298	.370	.0251	5.5	7.05	.04	7.01	1.22
185	.381	.199	.470	.0160	5.5	4.97	.04	4.93	1.29
186	.239	.124	.546	.0168	5.5	3.20	.04	3.16	1.32
187	.0954	.0497	.620	.0173	5.5	1.55	.04	1.51	1.58
									Av. 1.31
178	.934	.333	.333	.0197	5.7	11.0	.04	11.0	1.18
179	.560	.200	.467	.0197	5.7	7.37	.04	7.33	1.32
180	.374	.133	.533	.0173	5.7	4.75	.04	4.71	1.26
181	.234	.0833	.584	.0169	5.7	3.21	.04	3.17	1.35
182	.110	.0394	.630	.0200	(5.7)	1.58	.04	1.54	1.40
									Av. 1.30
		NaOH							
200	.184	.0705		.0212		2.90	.54	2.36	1.32
199	.138	.0705		.0218		2.27	.54	1.73	1.30
198	.115	.0705		.0193		1.96	.54	1.42	1.29
202	.092	.0705		.0426		(1.69)	.54	1.15	(1.32)
201	.0460	.0705		.0400		(1.16)	.54	0.62	(1.47)
									Av. 1.30
177	.250	Trace		.0172	11	2.91	.08	2.83	1.15
173	.250	Trace		0.173	12	2.96	.09	2.89	1.18
176	.250	Trace		0.150	10.5	2.84	.07	2.77	1.12
									Av. 1.15
113	.580	....		.0209		6.87	.06	6.81	1.20
171	.500	....		.0187		5.11	.06	5.05	1.03
									Av. 1.12

* *All calculations made as for triethylamine: ionization constant taken as* 1.7×10^{-9}.

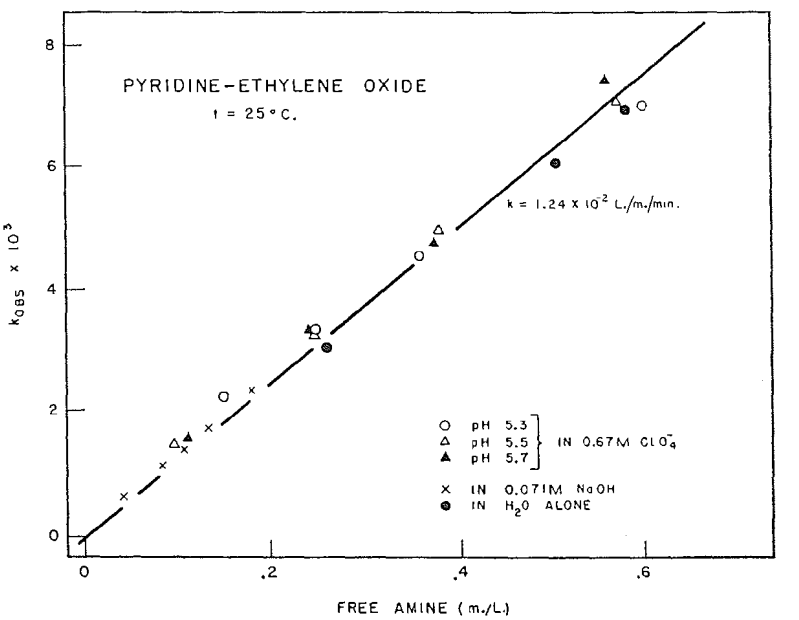

FIG. 3

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would be kinetically indistinguishable from the simpler form, but there seems to be no justification for considering so complicated a mechanism when the simple second order equation

$$\frac{-d\,\text{oxide}}{dt} = k(\text{oxide})(\text{amine})$$

adequately describes the rate.

The results obtained in these experiments, together with some data obtained by Smith (10) at 20°C., are summarized in Table VI. Surprisingly, there appears to be no relationship between the reaction rate and either the structure or the basicity of the amines.

TABLE VI

Amine	Ionization constant	$k_{25°}$	$k_{20°}$ (Smith)
Diethylamine	1.0×10^{-3}	6.5×10^{-2}	2.3×10^{-2}
Triethylamine	5.5×10^{-4}	3.1×10^{-2}	1.3×10^{-2}
Pyridine	1.9×10^{-9}	1.2×10^{-2}	6.5×10^{-3}
Aniline	4.6×10^{-10}	1.9×10^{-2}	.....
Trimethylamine	6.5×10^{-5}	.....	6.1×10^{-1}
Ammonia	1.8×10^{-5}	.....	3.8×10^{-3}

A more detailed discussion of the mechanism of these reactions has been reserved for a subsequent paper.

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THE CHEMISTRY OF ETHYLENE OXIDE

III. REACTION OF ETHYLENE OXIDE IN AMINE SOLUTION[1]

By A. M. Eastham and B. deB. Darwent

Abstract

A kinetic study has been made of the reaction of ethylene oxide in pyridine solution in the presence of strong acids. The rate has been found to be dependent upon the concentration of acid and of oxide over a wide range of concentrations at 25°C. The specific rate constant, however, varies markedly with the nature of the acid anion and appears to decrease with increasing basic strength of the anion. The absence of large salt effects seems to indicate that the anion effect is of a physical rather than chemical nature and the results are therefore tentatively attributed to the nature of solutions of electrolytes in solvents of low dielectric constant.

Introduction

The results of some experiments on the reaction of ethylene oxide with amines in aqueous solution were reported in a previous paper (3). It was shown that in water the rate is a function of the concentrations of amine and oxide only, although the reaction must take the general form

$$R_3N + (CH_2)_2O + HX \rightarrow R_3\overset{+}{N}\text{–}CH_2CH_2OH + X^-$$

which, when R = H, becomes

$$NH_3 + (CH_2)_2O + HX \rightarrow H_3\overset{+}{N}\text{–}CH_2CH_2OH + X^- \rightarrow H_2N\text{–}CH_2CH_2OH + HX$$

However, in spite of the fact that the reaction proceeds through a proton transfer, no appreciable hydrogen ion or aminium (R_3NH^+) ion catalysis occurs over a very wide range of experimental conditions. Basic catalysis is also absent and the rate is given very closely by the equation

$$\frac{d \text{ product}}{dt} = k(\text{amine})\ (\text{oxide})$$

where the amine concentration is that of the free or unionized amine present in the solution. Apparently then, in aqueous solution water is the principal source of protons.

In view of the above results it was of interest to study this reaction in aprotic solvents where the concentration of proton-supplying substances could be controlled. In this paper we present the results of some experiments carried out with pyridine as both solvent and reactant, together with a few results obtained in diethylamine solution. Pyridine was chosen for most of the work because it is an excellent solvent for its own salts and because the formation of a pyridonium base permits the reaction to be followed accurately by simple acid–base titration. Unfortunately, however, pyridine cannot be used to study the

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catalytic activity of water or other weakly acidic compounds because the pyridonium base formed in the reaction is stable only as the salt of a fairly strong acid (6). Accordingly, a few experiments were performed in diethylamine solution to obtain some idea of the catalytic activity of water.

Experimental

1. Materials

(*a*) Ethylene oxide—a commercial product having a purity of 99.5% or better was used without further purification. It was weighed in small sealed ampoules which were broken into the reaction mixture (4).

(*b*) Amines—all amines with the exception of pyridine were purified by careful fractional distillation after standing some days over solid potassium hydroxide.

(*c*) Pyridine—most of the pyridine used was purified by distillation, first from sodium hydroxide, then from aluminum chloride, and finally by careful fractionation (1, 2). Some of the dilatometric measurements were made, however, with pyridine carefully fractionated after standing over potassium hydroxide and barium oxide. There is some indication that the more rigorous purification gives slightly higher rates, but the differences unless otherwise noted are too close to the experimental error to be of much significance. In general, pyridine purified with barium oxide was used for the dilatometric experiments, while pyridine distilled from aluminum chloride was used for the experiments in which the reaction was followed by titration.

(*d*) Pyridinium salts were prepared by adding concentrated aqueous acids to a slight excess of pyridine and filtering the crystalline mass. The product was then dried over sulphuric acid in a vacuum desiccator at a few millimeters pressure, recrystallized from a suitable solvent, and finally dried again over sulphuric acid or phosphorus pentoxide. The acid content of the product was determined by potentiometric titration against standard sodium hydroxide and in all cases was found to be in excellent agreement with the theoretical value. In a few cases, where the pyridinium salts were too hygroscopic to be handled conveniently, solutions were prepared by adding the acid to the pyridine and titrating to establish the concentration. Thus, hydrogen chloride and hydrogen bromide solutions were prepared from the dry gaseous acids; sulphuric acid solutions were prepared by adding a few drops of concentrated acid to pyridine and assuming that the small amount of water present could be neglected.

2. Methods

All experiments were performed at 25°C. in a bath controlled to ± 0.002°. All titrations were made electrometrically with a Beckmann Model G pH meter.

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The reaction appears to be very clean since, when it is run to completion, analyses for quaternary base are essentially in quantitative agreement with the theoretical yields calculated from the ethylene oxide used. In pyridine solution the reaction was found to be of the second order, obeying the rate expression $d(\text{product})/dt = k(\text{oxide})(\text{acid})$; it was followed by a dilatometric method at acid concentrations above 0.1 *M* and by an analytical method below this concentration.

(*a*) *Dilatometric Method*

This method was essentially the same as that previously described (3). Dilatometers are suitable for use only with first order reactions and hence in pyridine solution were used only in the presence of a large excess of acid relative to ethylene oxide. For this reason the method was limited to those experiments in which the acid concentrations were above 0.1 *M*. In diethylamine solution the reaction is pseudo first order, since the proton required is regenerated and hence the concentration restrictions do not apply. Unfortunately, however, anhydrous diethylamine is a very poor solvent for its own salts and it was therefore necessary to restrict the experiments with this solvent to a few runs in which a small amount of water was added to the diethylamine. It was necessary to provide mercury seals for the dilatometers in these runs because no stopcock grease was found that would resist this solvent.

(*b*) *Analytical Method*

The reaction, in pyridine solution, actually consumes the acid "catalyst" so may be followed by determining the unreacted acid at intervals during the reaction. A sample of the reaction mixture was removed and quickly transferred to a small flask. This flask was fitted with a removable condenser to act as a spray trap and this in turn was connected to a vacuum system capable of reducing the pressure below one millimeter. The ethylene oxide and pyridine were rapidly distilled off at room temperature and the stable residue, consisting of pyridinium and pyridonium salts, was set aside for titration.

The condenser and flask were rinsed with water and the resulting solution titrated against a standard solution of sodium hydroxide using the internal electrodes of a Beckmann Model G pH meter. Conditions were usually chosen so that a sample of the initial acid solution required about 5 to 7 cc. of sodium hydroxide and titrations were accurate to about 0.01 cc. However, at low acid concentrations the end point of the titrations becomes poor with the result that the method is unsatisfactory for use with solutions less concentrated than 0.005 *M*. This is particularly true in the case of periodic acid which in water is a fairly weak acid. As a result the data for this acid are slightly more erratic than those for the stronger acids.

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Generally, four samples were taken on each run between 10% and 50% total reaction. In some cases reactions were carried close to completion but in no case was appreciable deviation from second order observed. It was assumed that one mole of ethylene oxide disappears with one mole of acid and the results so obtained were plotted against time using one of the usual second order rate expressions. The recorded rate was that given by the best straight line through the four points and was usually within 1–2% of the values calculated from the individual points.

3. Reaction Mixtures

Wherever possible, reaction mixtures were prepared by weighing the pyridine salt into a volumetric flask and making up to volume with pyridine. The solution was transferred to a vessel designed for filling the dilatometers or for withdrawing samples, and brought to the temperature of the bath. A weighed bulb of ethylene oxide was then broken into the mixture in the usual fashion.

Solutions of various amine perchlorates in pyridine were prepared by dissolving weighed quantities of pyridine perchlorate and amine in pyridine. The amount of amine added was slightly greater than that calculated as being necessary to transfer 98% of the protons from the pyridine. The calculations were based on the assumption that the distribution of the protons between the amines is given by the ionization constants of the amines as determined in dilute aqueous solution, and by the relative concentration of the amines.

Solutions in diethylamine were prepared by dissolving weighed amounts of water and of pyridine salt in the diethylamine. The more basic diethylamine was assumed to take up the protons, leaving a small amount of free pyridine in solution. The effect of this free pyridine should be very small in view of the large excess of diethylamine.

Results

The results obtained with the various acids in pyridine and diethylamine solution are shown in the accompanying tables and figures. Detailed results are given only for perchloric acid (Table I), since this acid was studied over the widest range of concentrations; the data show good agreement between the dilatometric and analytical methods and, more important, show that the rate constant holds over a very wide range of concentrations.

Essentially similar results, but with different values for the rate constant, were obtained with other acids. The data are illustrated graphically in Fig. 1 and the average values for the rate constants are given in Table II. It was not possible to study the catalytic activity of the halogen acids in this work because their reactions are complicated by the formation of halohydrins. In Table III are shown the data for sulphuric acid. For reasons given below, the rates for this acid have been calculated from both the normality and molarity of the acid.

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TABLE I

REACTION OF ETHYLENE OXIDE IN PYRIDINE SOLUTIONS OF PERCHLORIC ACID

Run	$HClO_4$ (moles/l.)	Oxide (moles/l.)	k_{obs} (min.$^{-1}$)	$k_{obs}/(H^+)$ (l.mol.$^{-2}$ min.$^{-1}$)
A. Dilatometric method				
265	1.65	0.0422	4.93×10^{-2}	2.98×10^{-2}
264	1.17	0.0581	2.71	2.31
262	0.778	0.0345	1.81	2.33
260	0.648	0.0360	1.49	2.30
300	0.614	0.0353	1.39	2.26
259	0.455	0.0384	1.01	2.20
276	0.411	0.0307	0.960	2.33 (contains 0.175 *M* $NaClO_4$)
301	0.302	0.0270	0.681	2.25
263	0.201	0.0210	0.428	2.14
266	0.200	0.0154	0.458	2.29
235	0.109	0.0374		(2.1) (Estimated only)
233	0.0750	0.0367		(2.7) (" ")
234	0.0555	0.0354		(2.6) (" ")
k average (dilatometric) = 2.27 × 10^{-2} between 1.2–0.2 M $HClO_4$				
B. Analytical method				
379	0.120	0.0969		2.47×10^{-2}
371	0.0911	0.0719		2.47
374	0.0710	0.0564		2.35
385	0.0500	0.0500		2.40
378	0.0305	0.0212		2.38
384	0.0155	0.0155		2.45
370	0.0153	0.0124		2.40
382	0.0100	0.0120		2.46
377	0.0101	0.00906		2.31
381	0.0100	0.00792		2.43
376	0.00815	0.00785		2.22
375	0.00502	0.00501		2.30
383	0.00334	0.00259		3.11
k average (analytical) = 2.39 × 10^{-2} between 0.1–0.005 M $HClO_4$				

TABLE II

CATALYTIC ACTIVITY OF STRONG ACIDS ON THE REACTION OF ETHYLENE OXIDE IN PYRIDINE

Acid	*k* (dilatometric) (l.mol.$^{-1}$ min.$^{-1}$)	*k* (analytical) (l.mol.$^{-1}$ min.$^{-1}$)	Solubility of acid in pyridine at 25°C. (moles/l.)
$HClO_4$	22.7×10^{-3}	23.9×10^{-3}	*ca.* 2.0
HIO_4	22.4	24.4	*ca.* 2.0
H_2SO_4		8.9 (?)	0.032
$C_6H_5SO_3H$		8.25	0.19
p-$C_7H_7SO_3H$	7.08	7.62	0.80
HNO_3	7.18	7.41	0.36

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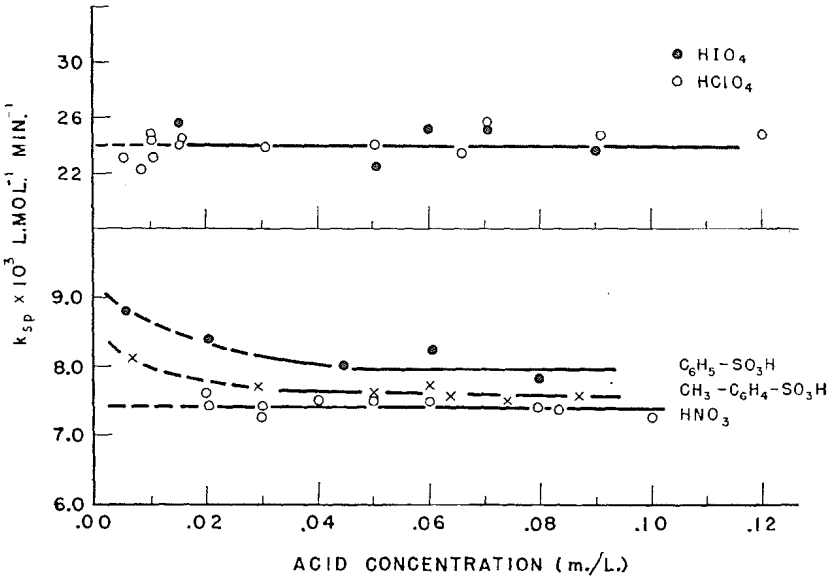

FIG. 1. *Rate of reaction of ethylene oxide in pyridine in the presence of strong acids (Analytical Method).*

TABLE III

REACTION OF ETHYLENE OXIDE IN PYRIDINE SOLUTIONS OF SULPHURIC ACID

Run	H_2SO_4 (moles/l.)	Oxide (moles/l.)	k_N*	k_M*
Analytical method				
427	0.0162	0.0256	4.0×10^{-3}	8.8×10^{-3}
428	0.00802	0.0122	4.2	8.9

* *k_N calculated from normality, k_M from molarity of H_2SO_4; all measurements made in the initial stages of the reaction only.*

The effect of sodium perchlorate on the perchloric acid catalyzed reaction is shown in Table IV. Salt effects are seen to be small.

Table V shows the results of some experiments in which small amounts of water were added to the pyridine–acid systems. The data are too limited to be of much significance but seem to indicate that the effect of water on the rate is small. As already mentioned, the catalytic activity of water alone cannot be studied in pyridine solution because the product is an unstable pyridonium hydroxide which undergoes further reaction. Some idea of the catalytic activity of water was obtained, however, in diethylamine solutions with the results shown in Table VI. Diethylamine in the absence of water is a very poor solvent for its own salts, so the studies were extended to include rate measurements in the system diethylamine–water–perchloric acid. The results shown in Fig. 2,

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TABLE IV

SALT EFFECT ON THE PERCHLORIC ACID CATALYZED REACTION

Run	$HClO_4$ (moles/l.)	$NaClO_4$ (moles/l.)	ClO_4^- (moles/l.)	Oxide (moles/l.)	k (l. mol.$^{-1}$ min.$^{-1}$)
Analytical method					
426	0.01023	0.0877	0.0979	0.0192	25.8×10^{-3}
425	0.01023	0.0438	0.0540	0.0204	25.0
424	0.01023	0.0175	0.0277	0.0209	24.5
423	0.01023	0.0088	0.0190	0.0218	23.5
422	0.01023	none	0.0120	0.0219	23.6

TABLE V

EFFECT OF WATER ON THE ACID INDUCED REACTION OF ETHYLENE OXIDE WITH PYRIDINE

Run	Acid	Acid conc. (moles/l.)	Oxide (moles/l.)	Added H_2O (moles/l.)	k (l. mol.$^{-1}$ min.$^{-1}$)
396	$HClO_4$	0.0713	0.0713		2.40×10^{-2} (analytical method)
397	$HClO_4$	0.0713	0.0713	0.10	2.32 "
398	$HClO_4$	0.00517	0.00517	1.0	2.78 "
399	$HClO_4$	0.00811	0.00811	1.0	2.51 "
400	$HClO_4$	0.0119	0.0119	1.0	2.17 "
286	HNO_3	0.711	0.0312	1.0	8.03×10^{-3} (dilatometric method)
282	HNO_3	0.711	0.0410	1.0	8.40 "
284	HNO_3	0.213	0.0275	0.3	7.70 "
All runs	HNO_3				7.20 "
269	*p*-toluene sulphonic	0.528	0.0263	0.5	7.33 "
All runs	"				7.08 "

TABLE VI

REACTION OF ETHYLENE OXIDE IN DIETHYLAMINE SOLUTION IN THE PRESENCE OF WATER (DILATOMETRIC)

H_2O (moles/l.)	k_{obs}(min.$^{-1}$)
8.0	1.6×10^{-2} . . average of three runs
7.0	1.3 . . . . . average of three runs
6.0	0.9 . . . . . average of two runs
5.6	1.0 } by extrapolation
4.2	0.4 } to zero $HClO_4$
1.4	0.04 } (see Fig. 2)

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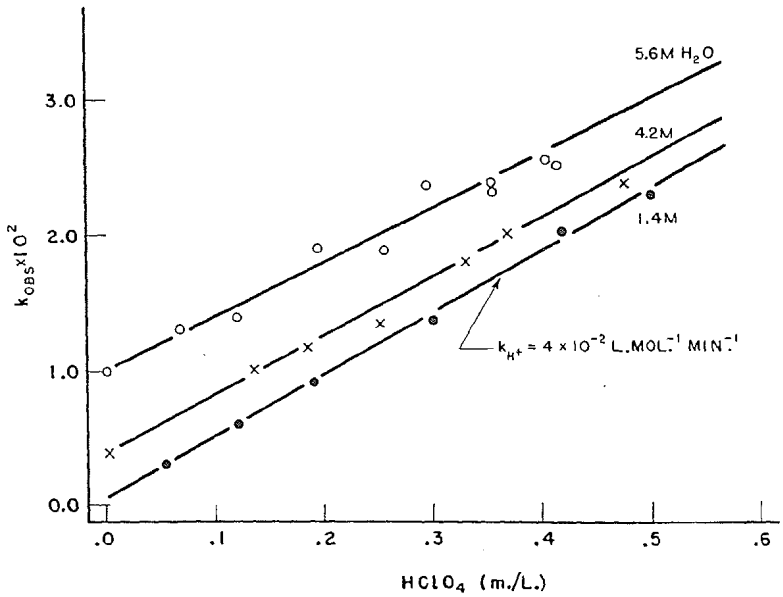

FIG. 2. *Reaction of ethylene oxide in diethylamine solution in the presence of both water and perchloric acid (Dilatometric Method).*

TABLE VII

EFFECT OF VARIOUS AMINES ON THE ACID INDUCED REACTION OF ETHYLENE OXIDE IN PYRIDINE SOLUTION (DILATOMETRIC)

Run	Acid	Acid conc. (moles/l.)	Amine	Amine conc. (moles/l.)	Oxide (moles/l.)	k_{obs} (min.$^{-1}$)	k_{obs}/acid (l. mol.$^{-1}$ min.$^{-1}$)
	$HClO_4$		Pyridine				2.27×10^{-2}
294	$HClO_4$	0.705	Triethyl-	0.788	0.0321	1.86×10^{-3}	2.64×10^{-3}
292	$HClO_4$	0.526	amine	0.563	0.0322	1.47	2.80
291	$HClO_4$	0.423		0.450	0.0280	1.20	2.83
296	$HClO_4$	0.836	Ammonia	0.836	0.0322	2.75	3.28
293	$HClO_4$	0.644		0.644	0.0319	1.90	2.95
297	$HClO_4$	0.418		0.418	0.0342	1.14	2.73
278	$HClO_4$	0.658	Benzylamine	0.757	0.0224	2.18	3.01
279	$HClO_4$	0.508		0.565	0.0340	1.72	3.37
277	$HClO_4$	0.333		0.389	0.0306	1.14	3.42
287	$HClO_4$	0.878	Diethanol-	0.934	0.0328	2.96	3.38
288	$HClO_4$	0.526	amine	0.560	0.0312	1.31	2.50
295	$HClO_4$	0.351		0.374	0.0330	0.797	2.70
	HNO_3		Pyridine				7.20×10^{-3}
298	HNO_3	0.870	Ammonia	0.870	0.0309	1.61×10^{-3}	1.85×10^{-3}
299	HNO_3	0.500		0.500	0.0259	0.87	1.74

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although rather erratic, suggest that the catalysis by perchloric acid is not greatly affected by the presence of small amounts of water. Water itself gave very low rates at concentrations below about 2.0 *M*, presumably owing to a reduction of its effective concentration through association with diethylamine.

Since in the pyridine – perchloric acid system the proton source is presumably the pyridinium ion, it was of interest to examine the effect of the addition of small amounts of more basic amines in the reaction mixture. It might be expected that the rate of the reaction would be reduced in proportion to the basicity of the added amine, since the protons would be transferred to, and more firmly bound by, the more basic amines. The data of Tables VII and VIII indicate that the more basic amines do indeed reduce the rate but to about the same extent in all cases. It is possible, however, that the basic strengths of amines in pyridine solutions are not directly related to the ionization constants of the amines in water (7).

TABLE VIII

EFFECT OF THE VARIOUS AMINES ON THE ACID INDUCED REACTION OF ETHYLENE OXIDE IN PYRIDINE (SUMMARY)

Acid	Amine	Amine ionization constant	k (l. mol.$^{-1}$ min.$^{-1}$)
$HClO_4$	Pyridine	1.7×10^{-9}	2.3×10^{-2}
	Diethanolamine	7.6×10^{-7}	2.8×10^{-3}
	Benzylamine	2.0×10^{-5}	3.3
	Ammonia	1.9×10^{-5}	3.0
	Triethylamine	5.5×10^{-4}	2.8
HNO_3	Pyridine	1.7×10^{-9}	7.2×10^{-3}
	Ammonia	1.9×10^{-5}	1.8×10^{-3}

Discussion

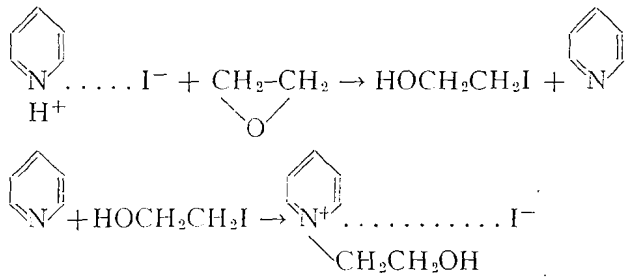
In the previous paper it was shown that the reaction of ethylene oxide with amines probably occurs according to the equation:

$$R_3N + \underset{\diagdown O \diagup}{CH_2{-}CH_2} + HA \rightarrow R_3\overset{+}{N}{-}CH_2CH_2OH + A^-$$

where R_3N = amine and HA a source of protons (acid). It is therefore not surprising that in pyridine solution the rate of the reaction has been found to be dependent upon the concentrations of oxide and of acid.

However, the results have also shown quite clearly that the rate constant for the reaction is sensitive to the nature of the acid anion present in the solution. This might suggest that the reaction in pyridine, like the reaction of ethylene oxide with neutral salts in water, is actually independent of the proton concentration, and proceeds through anion attack. Qualitative support for such a view is found in the hydriodic acid "catalyzed" reaction of ethylene oxide

in pyridine; this reaction is too complex for study at the present time but some results obtained during the course of this investigation indicate that the reaction probably proceeds, at least in part, according to the equations:

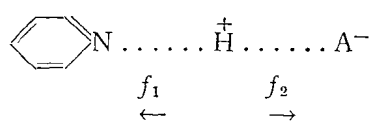


In the case of hydriodic acid the second step is slower than the first; in the case of an acid such as perchloric, however, the second step might well be very rapid and the over-all rate could conceivably be determined by the concentrations of oxide and of anion. There is, however, little reason to believe that anions such as perchlorate and nitrate actually do add to ethylene oxide and this view is supported by the very small increase obtained when sodium perchlorate is added to the perchloric acid catalyzed reaction (Table IV). For these reasons and from considerations of mechanisms, we at present prefer to regard the rate of the reaction as being determined by the concentrations of the oxide and of the proton source, and believe that the anion effect is due to the peculiarities of solutions of electrolytes in solvents of low dielectric constant. This view is amplified in the following paragraphs.

It is obvious that, because of the basicity of amine solvents, any strong acid, and even quite weak acids, may be expected to react completely to give, in pyridine, the pyridinium salt. The dependence of the rate constants upon the nature of the anion may be explained if we assume, in agreement with current theory, that in these solutions the pyridinium ion and the anion remain in more or less loose association.

$$Py + HA \rightarrow PyH^+ \ldots\ldots\ldots A^-$$

If this is true then it is obvious that in reaction with ethylene oxide, the proton is removed, not from the free pyridinium, but from the $PyH^+ \ldots A^-$ complex and the anion may then play a significant part in the case of proton transfer. This view is at least in qualitative agreement with the experimental data but requires that the proton be rather loosely bound in the complex



since, if the attractive force f_1 is large with respect to f_2, it would be impossible for the anion to exert so large an effect upon the rate. In support of the view that f_1 is small, it may be noted that Burgess and Kraus (1) have found that

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the pyridinium ion has an exceptionally high conductance, a fact which they attribute to the transfer of protons through the solvent. Furthermore, Fuoss *et al.* (5) have presented some evidence for the view that in toluene solution, amine picrates may exist in an equilibrium of the form

$$\begin{array}{ccc} R_3H.HPi & \rightleftharpoons & R_3NH^+.Pi^- \\ \downarrow\uparrow & & \downarrow\uparrow \\ R_3N + HPi & & R_3NH^+ + Pi^- \end{array}$$

Experimentally we have found that the rate constants are, qualitatively, in the orders of the strengths of the catalyzing acids, and this is further support for the hypothesis that the protons are removed from ion pairs, since the value of f_2 will increase as the acid strength decreases.

It may be noted that the rate constants for the sulphonic acids seem to increase significantly at low concentrations (Fig. 1). This increase may possibly be due to an increase in the dissociation of the ion pairs in the system. Burgess and Kraus (1) have found a value of 5×10^{-5} for the dissociation constant of pyridinium nitrate ions which is so low that one would not expect any deviations from linearity with nitric acid at the concentration used here. However, they point out that the dissociation constants are determined largely by the diameters of the ions and hence it is likely that pyridinium benzene sulphonate, with its large ions, may be so much more highly dissociated than the nitrate that dilution effects become important at the concentration used in this work.

The cases of sulphuric and periodic acids merit some attention. Periodic acid in water appears to be very much weaker than perchloric acid—probably due to hydration to give H_3IO_5—but kinetically, in pyridine where no hydration is possible, it appears to be quite as strong as perchloric acid. Analyses of the pyridine salt of this acid show it to have the composition $C_5H_5N.HIO_4$.

The rate constant for sulphuric acid has been assigned the value of 8.9×10^{-3} and this value is based on the assumption that it behaves as a monobasic acid in pyridine. The conclusion that sulphuric acid acts as a monobasic acid is supported by the following data, which were obtained in the course of this investigation:

(*a*) Pyridinium acid sulphate may be recovered unchanged by recrystallization from pyridine, and all our efforts at preparing the dipyridinium salt were unsuccessful.

(*b*) The acid sulphates of sodium, tetramethylammonium, and benzyltrimethylammonium are exceedingly insoluble in pyridine; when ethylene oxide reacts with pyridine solutions of sulphuric acid, precipitation of a reaction product occurs very early in the reaction.

It is evident from the foregoing discussion that the reaction of ethylene oxide in amine solutions is too complex to permit any definite conclusions on the reaction mechanism to be made at the present time. For the present our knowledge of the reaction may be summarized as follows:

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(*a*) Since all amines behave essentially similarly, regardless of whether or not they have hydrogen attached to nitrogen, the reaction must take the general form

$$R_3N + \underset{\diagdown O \diagup}{CH_2\text{–}CH_2} + HA \rightarrow R_3\overset{+}{N}\text{–}CH_2CH_2OH + A^-$$

(*b*) In aqueous solution the reaction is largely independent of the source of hydrogen ions and takes the kinetic form

$$\frac{-d\ \text{oxide}}{dt} = k(\text{oxide})(\text{amine})$$

No basic catalysis exists; acid catalysis is not impossible but if it exists will only be found under conditions such that appreciable amounts of free amine and oxonium ion will be present together in the solution.

(*c*) In pure amine solution the reaction is dependent upon, and rather sensitive to, the source of hydrogen ion; the reaction rate is given by the equation

$$\frac{-d(\text{oxide})}{dt} = k(\text{oxide})(\text{HA})$$

(*d*) In both aqueous and amine solution salt effects are small, suggesting the existence of an uncharged intermediate.

(*e*) The reaction rates, particularly in aqueous solution, show no relation to amine structure or basicity.

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CONTRIBUTION TO THE THEORY OF DIFFUSION FLAMES[1]

By R. J. Cvetanović and D. J. Le Roy

Abstract

In order to evaluate the rate constant for the reaction of atomic sodium with halides using the diffusion flame method, Hartel and Polanyi introduced three simplifying assumptions: that the mass flow of the carrier gas could be neglected, that there was a spherical distribution of sodium vapor in the reaction zone, and that the halide concentration was constant throughout the reaction zone. In an attempt to maintain the validity of the third assumption previous workers limited their experimental determinations to cases in which the collision yield was considerably less than unity. In the present contribution equations are developed which remove this restriction and permit the evaluation of the rate constant without assuming a constant halide concentration. On carrying out the computation for a relatively slow reaction ($Na + C_2H_5Cl$) it was found that the error introduced by the third assumption was only of the order of 20%. The error for fast reactions would be considerably larger but can always be evaluated from the equations given. In some cases an approximate value of the error can be obtained without carrying out the complete computation.

Introduction

A great amount of experimental work on the reactions of alkali metal atoms with different organic and inorganic halides has been carried out in the past two decades, following the development of suitable experimental techniques by M. Polanyi and his collaborators (7). The view has been expressed that this work provides one of the most complete chapters in reaction kinetics (1).* While undoubtedly a very valuable contribution has been made, there seems to be some uncertainty as to the order of validity of some of the evaluations and deductions made. This is not surprising in view of the experimental and theoretical difficulties involved.

Most of the experiments were based on the "diffusion flame" method developed in 1930 by Hartel and Polanyi (5). This method has the advantage over the earlier method of "highly dilute flames" (2) in the wider applicability and especially in the fact that no wall reaction interferes with the chemical reaction under investigation. A third method, the "life period method", developed by Frommer and Polanyi in 1934 (3), was based on essentially similar experimental conditions to those used in the diffusion flame method, but the evaluation of the reaction rate constants did not involve a knowledge of the spacial distribution and the rate of diffusion of the alkali metal. For these reasons the life period method is frequently regarded as more accurate than the diffusion method. Polanyi himself has expressed some doubts as to the degree of approximation involved in the evaluation of rate constants by the diffusion flame method (3).

[1] *Manuscript received March 27, 1951.*
Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont. This paper was presented at the Annual Meeting of the Royal Society of Canada, Montreal, June, 1951.

* *A review on the sodium "flame" reactions by W. E. Warhurst has just been published in Quart. Reviews, 5: 44. 1951.*

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A critical investigation of the possible errors of the diffusion flame method was made by Heller (6), who described the experimental conditions for which he estimated that the determined reaction rates would not differ from the absolute values by more than a factor of about two. The experimental conditions imposed by Heller limited the method to reactions having collision yields between 1/50 and 1/5000. In order to apply the method to faster reactions, with collision yields as large as 1/10 or even 1/5, Haresnape, Stevels, and Warhurst (4) suggested a modification of the experimental conditions which consisted, essentially, in reducing the ratio of the concentration of the alkali metal to that of its reaction partner.

Although the diffusion flame method has been widely used, the possibility of a complete and exact mathematical treatment of the method would seem to be rather remote. It has, however, been considered desirable to attempt to derive expressions which would allow an evaluation of the degree of approximation involved in some of the original simplifying assumptions made by Hartel and Polanyi (5).

The Treatment of Hartel and Polanyi

In the diffusion method a carrier gas, such as nitrogen or hydrogen, is used to introduce the vapor of the alkali metal, usually sodium, through a nozzle into the reaction zone. From the nozzle mouth the sodium (Reactant 1) spreads through the reaction zone encountering, as it diffuses, the vapor of the halide (Reactant 2). The rate of reaction is given by the expression

$$-dc_1/dt = -dc_2/dt = kc_1c_2, \tag{1}$$

in which c_1 and c_2 are the concentrations of the reactants and k is the rate constant. When a steady state is reached the values of c_1 and c_2 at any point in the reaction zone will be determined by the rates of diffusion of the two reactants, the rate of the chemical reaction, and the mass velocity of the carrier gas.

It is generally accepted that in the steady state the over-all process can be described by an equation of the form

$$D_1\Delta c_1 + v \text{ grad } c_1 - kc_1c_2 = 0, \tag{2}$$

in which D_1 is the diffusion coefficient of sodium vapor and v is the mass velocity of the carrier gas. In order to solve Equation (2), Hartel and Polanyi introduced the following simplifying assumptions:

1. The term v grad c_1 can be neglected.
2. There is a spherical symmetry in the distribution of sodium vapor in the reaction zone.
3. The halide concentration, c_2, is constant throughout the reaction zone.

Under these conditions Equation (2) reduces to

$$D_1\left(d^2c_1/dr^2 + \frac{2}{r}dc_1/dr\right) - kc_1c_2 = 0. \tag{3}$$

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Provided c_2 is constant and c_1 vanishes when $r = \infty$, the solution of (3) is

$$c_1 = (A/r) \exp (-r\sqrt{kc_2/D_1}). \tag{4}$$

The boundary conditions are

$$c_1 = c_1^i \text{ when } r = r_1$$
$$\text{and} \quad c_1 = c_1^0 \text{ when } r = R.$$

The quantity r_1 represents the radius of a small sphere around the origin, the surface of which is a surface of constant initial sodium concentration, c_1^i; it is assumed to be equal to the radius of the nozzle. The concentration c_1^i is identified with the concentration corresponding to the vapor pressure of sodium in the saturator through which the carrier gas passes before reaching the nozzle. The quantity R is the radius of the 'flame' made visible when the reaction zone is illuminated with sodium resonance radiation; c_1^0 is the sodium concentration at R, corresponding to the visibility limit. The rate constant k can therefore be expressed in terms of observable quantities,

$$k = \frac{(\ln c_1^i/c_1^0 - \ln R/r_1)^2 D_1}{(R - r_1)^2 c_2}. \tag{5}$$

The Present Approach

In the present approach an attempt is made to eliminate the third of the simplifying assumptions of Hartel and Polanyi by taking into account the fact that Reactant 2 also diffuses and is consumed in the reaction so that its concentration is a function of r. The other simplifying assumptions are retained. Equation (3) must then be replaced by the following two equations,

$$D_1 \left(\delta^2 c_1/\delta r^2 + \frac{2}{r} \delta c_1/\delta r \right) - kc_1c_2 = 0 \tag{6}$$

$$D_2 \left(\delta^2 c_2/\delta r^2 + \frac{2}{r} \delta c_2/\delta r \right) - kc_1c_2 = 0 \tag{7}$$

where D_2 is the diffusion constant of the Reactant 2.

By subtracting (7) from (6) and making the substitution

$$u = c_1D_1 - c_2D_2 \tag{8}$$

the following relation is obtained

$$d^2u/dr^2 + \frac{2}{r} du/dr = 0. \tag{9}$$

The solution of (9) is

$$u = -A/r + B = c_1D_1 - c_2D_2. \tag{10}$$

In order to determine the constants A and B in (10) the following boundary conditions are imposed:

$$\text{for } r = \infty, c_1 = 0, c_2 = c_2^i, \text{ and hence } B = -c_2^iD_2 \tag{11}$$

$$\text{for } r = r_1, c_1 = c_1^i, c_2 = c_2^0, \text{ and hence}$$
$$A = -r_1 \{c_1^iD_1 + (c_2^i - c_2^0)D_2\}. \tag{12}$$

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Thus, in the steady state,

$$c_1D_1 - c_2D_2 = (r_1/r)\{c_1^iD_1 + (c_2^i - c_2^0)D_2\} - c_2^iD_2. \tag{13}$$

In this treatment r_1 is defined in the same manner as before. Under ideal conditions c_2^0 should be equal to zero; only under these conditions can c_1^i be identified with the concentration corresponding to the vapor pressure of sodium in the saturator. Actual measurements carried out by Heller (6) showed that for a definite range of experimental conditions c_2^0 is very small, even in the absence of sodium, as a result of the distortion produced by the inflow of carrier gas. The assumption that c_2^0 is negligible can therefore be considered justifiable; it will, in fact, allow for the greatest part of the distortion effect resulting from the finite mass velocity of the carrier gas as it leaves the nozzle. (An alternative would be to select a value for c_2^0 based on Heller's experiments.)

By solving Equation (10) or (13) for c_2 and making the substitution in (6), the following equivalent relations are obtained:

$$d^2c_1/dr^2 + \frac{2}{r}dc_1/dr - \frac{k}{D_2}c_1^2 - \frac{kA}{D_1D_2}\frac{c_1}{r} - \frac{kc_2^i}{D_1}c_1 = 0 \tag{14a}$$

$$d^2c_1/dr^2 + \frac{2}{r}dc_1/dr - \frac{k}{D_2}c_1^2 + \frac{kc_1^ir_1}{D_2r}c_1 + \frac{k(c_2^i - c_2^0)r_1}{D_1r}c_1 - \frac{kc_2^i}{D_1}c_1 = 0 \tag{14b}$$

Equation (14*b*) reduces to the simplified equation (3), used by Hartel and Polanyi, if it is assumed that $D_2 = \infty$ and $c_2^0 = c_2^i$. In principle the rate constant k may be evaluated from (14) provided c_1^i, c_1^0, c_2^i, c_2^0, D_1, D_2, r_1, and R are known and the condition that c_1 vanishes when $r = \infty$ is imposed.

Unfortunately, an analytical solution of (14) could not be found. However, a value of k for a given set of experimental data was determined by the Computation Centre of the University of Toronto, using Milne's method for the numerical solution of a differential equation. As values for the parameter k and for the quantity dc_1/dr at one end of the range (r_1 or R) are required in the application of the method, the particular set of the two for which the curve $c_1(r)$ passes through the points (c_1^i, r_1) and (c_1^0, R) and at the same time approaches the value $c_1 = 0$ as r approaches infinity, had to be found by the trial and error method. The computation is tedious, although it can always be carried out to any desired degree of approximation. However, some conclusions can be drawn from (14) without actually solving it.

By introducing the relation $v = c_1r$, Equation (14*b*) is altered to

$$\frac{1}{k}d^2v/dr^2 = \frac{1}{D_2}\frac{v^2}{r} - \frac{r_1c_1^i}{D_2}\frac{v}{r} - \frac{r_1(c_2^i - c_2^0)}{D_1}\frac{v}{r} + \frac{c_2^i}{D_1}v \tag{15}$$

If the Hartel and Polanyi Equation (3) is treated in a similar manner, by making the substitution $v_P = c_1r$, writing $c_2 = c_2^i$, and denoting the corresponding value of k by k_P, the following relation is obtained,

$$\frac{1}{k_P}d^2v_P/dr^2 = \frac{c_2^i}{D_1}v_P. \tag{16}$$

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From (15) and (16) it follows that

$$k_P = k\left\{\frac{v}{v_P} - \frac{D_1 c_1^i}{D_2 c_2^i}\frac{v}{v_P}\left(\frac{r_1}{r} - \frac{v}{r c_1^i}\right) - \left(1 - \frac{c_2^0}{c_2^i}\right)\frac{r_1}{r}\frac{v}{v_P}\right\}\frac{d^2v_P/dr^2}{d^2v/dr^2} \qquad (17)$$

Since $v = v_P = c_1^0 R$, when $r = R$,

$$\text{then } k_P = k\left\{1 - \frac{D_1 c_1^i}{D_2 c_2^i}\left(\frac{r_1}{R} - \frac{c_1^0}{c_1^i}\right) - \left(1 - \frac{c_2^0}{c_2^i}\right)\frac{r_1}{R}\right\}\alpha, \qquad (18)$$

$$\text{in which } \alpha = \frac{(d^2v_P/dr^2)_{r=R}}{(d^2v/dr^2)_{r=R}}$$

The functions v_P and d^2v_P/dr^2 may be readily calculated. These functions, together with the values of the functions v and d^2v/dr^2 for the particular set of conditions for which the numerical computations were carried out, are plotted in Fig. 1. Under the conditions chosen it is evident that α is a positive number somewhat less than unity. Also, since $r_1/R > c_1^0/c_1^i$, and $c_2^0/c_2^i < 1$, it follows that $k > k_P$. This conclusion might be anticipated from a consideration of Equation (5), since in all experiments the effective value of c_2 will always be less than c_2^i, the value used in the Hartel and Polanyi treatment. Although the computations for the extreme limiting cases for which the diffusion flame method has been used have not, as yet been carried out, it seems reasonable to assume that α will, in general, be a positive number somewhat less than unity and that, in consequence, k will always be greater than k_P.

Some approximate deductions can be made from Equation (18) by assuming, as a first approximation, that α is equal to unity. The second term in the co-

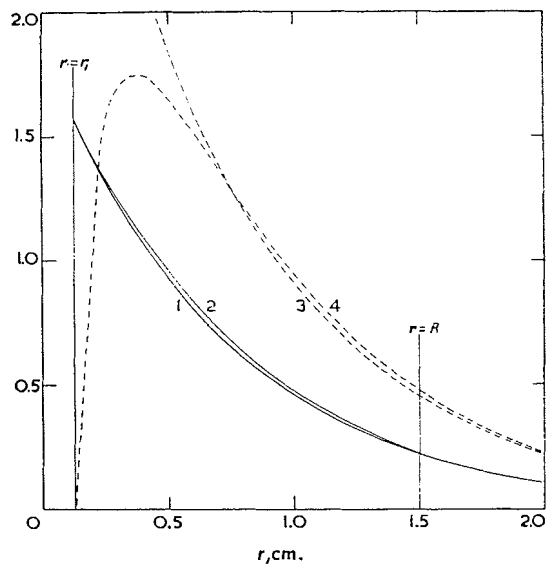

FIG. 1. *The functions v_P (1), v (2), d^2v_P/dr^2 (3), and d^2v/dr^2 (4), for the reaction $Na + C_2H_6Cl = NaCl + C_2H_5$ at 260°C. The ordinate scale has been reduced by a factor of 10^{12}.*

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efficient of k would then indicate under what conditions the ratio of the two diffusion coefficients may appreciably affect the value of k. For 'slow' reactions, for which c_2^i must be considerably greater than c_1^i in order to confine the flame diameter to the usual range of 3 to 4 cm. it is evident that this term will be negligibly small. For 'fast' reactions, in which c_2^i is made only slightly greater than c_1^i, and especially if D_1 is considerably greater than D_2, the contribution of this term might become quite appreciable.

The third term in the coefficient of k vanishes when $c_2^0 = c_2^i$ and has its maximum value when $c_2^0 = 0$. It represents, therefore, the contribution of the impoverishment in c_2 at $r = r_1$; it is appreciable under all usual experimental conditions.

By assuming $\alpha = 1$, Equation (18) may be used to obtain an approximate lower limit for k when k_P is known. In one of a series of experiments in which ethyl chloride was used as component 2 the value of k_P was found to be 39.8×10^{-15} cm.^{3} molecules^{-1} sec.$^{-1}$. For the conditions used, assuming $\alpha = 1$, the value of k calculated from (18) was 43.4×10^{-15}. The numerical solution of Equation (14), which was carried out for this same set of experimental conditions gave a value of k lying between the limits $46.5 \times 10^{-15} < k < 47.5 \times 10^{-15}$. For this experiment α was, of course < 1, as shown by Fig. 1. A better approximation was obtained in this case, and would undoubtedly be obtained in a number of other cases, by assuming that for $r = (r_1 + R)/2$, $d^2v/dr^2 = d^2v_P/dr^2$ and $v = v_P$. Equation (17) is then reduced to

$$k_P/k = 1 - \frac{D_1 c_1^i}{D_2 c_2^i}\left\{1 - \exp\left(\frac{r_1 - R}{2}\sqrt{k_P c_2^i/D_1}\right)\right\}\frac{2r_1}{R + r_1} - (1 - c_2^0/c_2^i)\frac{2r_1}{R + r_1}. \qquad (19)$$

The value of k calculated from (19) was 47.2×10^{-15}. In this case the value of c_2^i was several hundred times greater than c_1^i, while the ratio D_1/D_2 was estimated to be of the order of 2. The diffusion term was therefore negligibly small, and the difference between k and k_P was caused entirely by the impoverishment term. This value of k was very close to that calculated from Equation (5) after allowance was made for the over-all impoverishment on the basis of Heller's measurements (6).

Discussion

From the foregoing considerations it is evident that, if the first two assumptions of Hartel and Polanyi are valid, and if the reaction is moderately slow so that the ratio c_2^i/c_1^i is considerably greater than unity, the value of the rate constant calculated from the simplified equation of Hartel and Polanyi (Equation (5)) will be smaller than the true value and will differ from it, in the case of flames of about 3 cm. diameter, by a factor of about 0.8. For any particular experiment the difference can be evaluated by computing k from Equation

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(14), or can be calculated approximately from Equation (18) or (19). In many cases a correction for the average over-all impoverishment based on Heller's measurements will give a very close value. For very fast reactions, however, in which c_2^i and c_1^i become comparable in magnitude, and especially when D_2 is small compared to D_1, the true rate constant will be dependent on the value of D_2.

In order to obtain an accurate value of k it will be necessary to ascertain the values of c_1^i, c_1^0, c_2^i, D_1, and R (and for very fast reactions, D_2). As a rule, this can be done with reasonable certainty for all of the quantities except c_1^i. While the maximum possible value of c_1^i can always be obtained, its actual value will depend on the amount of back diffusion of the second component into the jet; as a result of this a certain fraction of the alkali metal, which it is difficult to estimate, will be consumed before reaching r_1. Until a more complete mathematical treatment is developed, or until an experimental method is found for measuring c_1 at r_1, it is suggested that the experimental conditions should always be arranged so that back diffusion is negligible; these conditions have been discussed at some length by Heller (6).

Some of the conclusions presented here are based on the single numerical computation which was carried out. It is anticipated that further computations will be carried out with the object of determining the factor α (Equation (18)) for widely different experimental conditions. It is believed, however, that the present treatment will help to lessen the uncertainty that has existed regarding the order of validity of the deductions made from diffusion flame experiments. At the same time it is evident that the present treatment is only a step in the direction of a complete mathematical solution of the problem.

Acknowledgment

The authors are grateful for the assistance afforded by Prof. C. C. Gotlieb and Dr. J. H. Chung of the Computation Centre, University of Toronto. This work was carried out with the financial support of the Associate Committee on Scientific Research of the University of Toronto and during the tenure of the Nadine Phillips Scholarship (R.J.C.).

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THE ROLE OF AMORPHOUS INTERMEDIATE PRODUCTS IN THE DEHYDRATION OF CERTAIN HYDRATED SALTS[1]

By G. B. Frost, K. A. Moon, and E. H. Tompkins

Abstract

Following the dehydration of certain hydrated salts in high vacuum, an evolution of energy occurs. X-ray studies have shown that this energy liberation is due to an amorphous to crystalline transition in the products of dehydration. Measurements have been made of the integral heats of solution of the dehydration products of copper sulphate pentahydrate and zinc sulphate hexahydrate formed at a series of low dehydration pressures. From these measurements, the fractional amounts of relatively high energy amorphous products formed at a series of low dehydration pressures have been calculated. It has been found that as the water vapor pressure near the reaction interface is increased, the fractional amount of high energy product decreases to a minimum, then increases, passes through a maximum, followed by a slow decrease. These results are interpreted in terms of a possible dehydration mechanism, and an estimation made of the effect of water vapor pressure on the over-all reaction rate. In the course of this study, the integral heats of solution of the crystalline hydrates involved have been determined. The heats of transition of the amorphous to crystalline forms of copper and zinc sulphate monohydrates are reported.

Introduction

The dehydration of a hydrated salt is an example of a type of heterophase reaction which involves the destruction of a crystal lattice and the formation of a new lattice which may sometimes differ markedly from the primary lattice in structural characteristics. In cases where there is a lack of accommodation of the two lattices at the reaction interface, the mechanism of such reactions may be quite complex, and may depend on certain variables in ways which are not clearly understood.

In 1911, Partington (11) suggested that the primary step in a salt hydrate dehydration is the collapse of the lattice to form an amorphous intermediate, this step being followed by nucleation, and the development of the new crystalline phase. For some years following this suggestion, the occurrence of such an amorphous intermediate was assumed by many workers, but it was thought that nucleation and the growth of the stable crystalline phase occurred very rapidly.

This is probably the case at moderately high dehydration pressures. In 1930, however, Slonim (13) showed that on low pressure dehydration of certain salts, an amorphous material is formed which crystallizes slowly. In 1931, Kohlschütter and Nitschmann (9) found that on dehydration in high vacuum, copper sulphate pentahydrate gave a product which did not diffract X-rays, and that lines corresponding to the crystalline monohydrate appeared only after prolonged heating. Hammel (5) obtained similar results for other dimetal sulphates, and Volmer and Seydel (19) for manganous oxalate dihydrate.

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Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.
Presented, in part, before Section III of the Royal Society of Canada, at the Royal Military College, Kingston, on June 6, 1950.

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Somewhat divergent views have been expressed regarding the nature of this X-ray amorphous intermediate, and its role in the dehydration mechanism. These views have been adequately dealt with elsewhere (2, 15), and need not be discussed here, except to say that the essential difference between them lies in the assumption of highly dispersed microcrystals of a size below the limit required for X-ray diffraction, as distinct from some type of disordered zeolitic structure, or possibly a disordered assembly of ions and water molecules.

Volmer and Seydel (19) have found that the heats of solution of the X-ray amorphous and crystalline forms of manganous oxalate were 8500 and 6500 cal. per formula weight respectively, indicating a relatively high energy character of the product obtained by dehydration *in vacuo*. Khomyakov (8) observed that an evolution of heat occurred after the low pressure dehydration of copper sulphate pentahydrate, zinc sulphate heptahydrate, and manganous sulphate tetrahydrate. From the heat of solution of samples taken before and after the heat evolution, he calculated that 5020 cal. per formula weight were evolved on the formation of crystalline copper sulphate monohydrate from the amorphous intermediate, which he regarded as zeolitic in type.

It is clear, from these results, that an X-ray amorphous intermediate results from the dehydration of certain salts at very low pressure, and that this intermediate is fairly stable and has a higher heat of solution in water than the resultant crystalline salt. However, no data are available regarding the effect of water vapor pressure in the dehydration zone on the formation of this intermediate, or as to whether or not there is a limit in pressure beyond which it does not occur. The present work was undertaken with the broad purpose of obtaining this information, which it was felt might throw light on the role of the amorphous intermediate in the reaction mechanism, and possibly contribute to the clarification of some of the other problems concerned with the nature of heterophase changes.

The experiments reported in this paper have been carried out with the hydrates of copper and zinc sulphates. The experimental method has involved the determination of the integral heats of solution of salts which have been subjected to dehydration at controlled low pressures for definite times. The results of similar experiments with other salts will be reported later, as also will be the results of kinetic measurements which may be partly interpreted in the light of the present study. Work is in progress in an attempt to correlate these results with crystal structure data.

It will be convenient to report the present work in three parts. Part I is concerned with some preliminary experiments carried out with the purpose of extending Khomyakov's finding of a heat evolution following the low pressure dehydration of certain salts. The results of these experiments are helpful in interpreting those of the later work.

In order to make quantitative use of the heat of solution method, it is necessary to know the integral heats of solution of the crystalline hydrates of copper

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and zinc sulphate with greater accuracy than is indicated by available values. These have been determined and are reported in Part II.

Part III is concerned with experiments bearing directly on the main purpose of the work as outlined above.

Part I

The Thermal Effect Following the Dehydration of Certain Salts

There are sporadic references in the literature to a heat evolution following the dehydration of certain salts, this being usually attributed to surface changes. The results reported by Khomyakov, however, indicate clearly that these effects are associated with lattice changes involved in the reaction mechanism. The following experiments are an extension of those of Khomyakov.

Experimental Method

Several types of apparatus were used, but the form shown in Fig. 1 is extremely simple and effective for qualitative observations.

In this apparatus, the hydrate was held in place in the glass inner tube by a small layer of glass wool supported by narrow aluminum strips cemented to the glass. A heating coil of constantan wire and three junctions of a copper–constantan thermel were placed, as shown, in contact with the hydrate. The other three junctions were led, by means of a closed glass tube, into a mercury

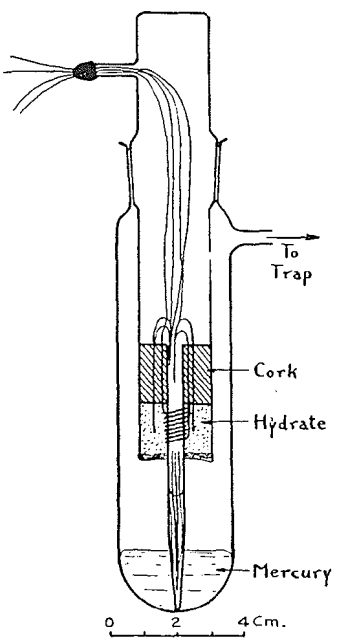

Fig. 1. *Apparatus used for observation of thermal effect following dehydration.*

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pool at the bottom of the containing vessel. Thermel e.m.f.'s were read by a Leeds and Northrup Type K-2 potentiometer with a sensitive galvanometer of suitable characteristics.

Provision was made for dehydration being conducted either under high vacuum or at a series of controlled low pressures. The traps and manometer system need not be described. In order to reduce temperature fluctuations, the whole assembly of Fig. 1 was immersed in water, up to the side arm, in a covered Dewar flask, which in turn was placed in a water bath kept approximately at the temperature of the hydrate.

The hydrate, after being ground to a suitable mesh, was placed in the apparatus and the system left for about twenty minutes to come to thermal equilibrium with the surroundings. The system was then evacuated for some definite time, energy being supplied by the heater to just compensate for the self-cooling of the hydrate due to the endothermic loss of water. The heater was then turned off, but evacuation continued for 5 to 15 min. longer depending on the dehydration rate. Dried air was then slowly admitted until the final pressure became about 90 mm. Thermel e.m.f. readings were then recorded for several hours. In most cases, X-ray powder photographs were made before and after the experiments.

Results and Discussion

The results obtained with three separate samples of copper sulphate pentahydrate are shown in Fig. 2.

These samples were all separately dehydrated for identical periods of time, at 45°C. and 0.8 mm. pressure. About ten minutes before the zero time of reading, the temperatures were lowered to 43.1°C., 33.0°C., and 28.7°C. re-

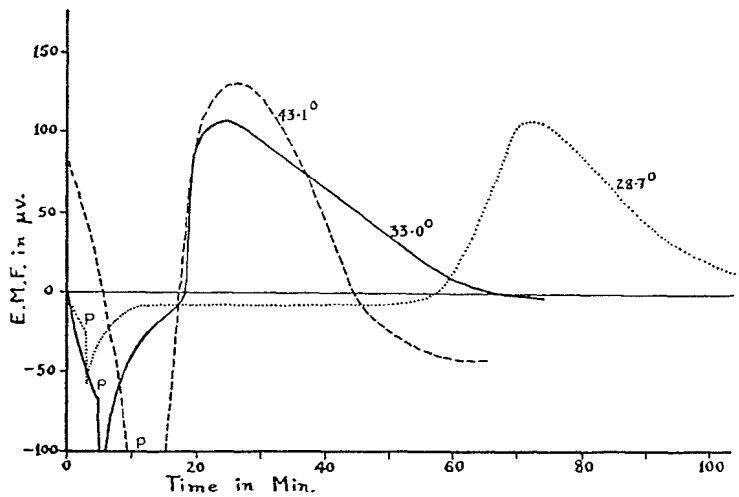

FIG. 2. *Thermal effect following the low pressure dehydration of copper sulphate pentahydrate at three temperatures.*

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spectively. For each curve shown in Fig. 2 the fall in e.m.f. from zero to the point, P, is due to the dehydration continuing after shutting off the pumps. The sudden drop at point P is due to the admission of dried air, at room temperature. It will be seen that subsequent to this drop a rapid rise in temperature occurs, after a period of time which apparently depends on the temperature of the sample. In these curves, 120 microvolts corresponds to 1°C. Samples dehydrated as above, but cooled to 25°C., showed no thermal effect, over several hours of observation.

In Fig. 3 are shown similar e.m.f.–time observations for two samples of zinc sulphate heptahydrate, the dehydration conditions being the same as those described in the foregoing, and the temperatures following dehydration being 25.7°C. and 38.8°C. respectively. It will be observed that for the sample at 25.7°C. the spontaneous evolution does not occur for over six hours after stopping the dehydration.

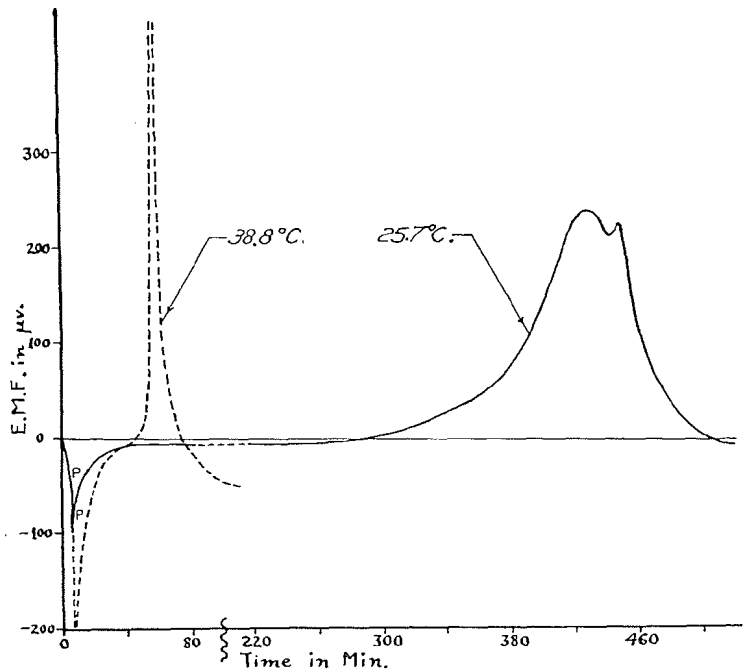

FIG. 3. *Thermal effect following the low pressure dehydration of zinc sulphate heptahydrate, at two temperatures.*

The explanation of these effects became clear when samples taken before and after the thermal evolution were studied by X-ray diffraction. Powder photographs made prior to the thermal evolution showed no lines but only a slight darkening due to small angle scattering; those made subsequent to the thermal evolution showed a distinct pattern of monohydrate and possibly some trihydrate lines. There seems to be no doubt therefore that the thermal effect is due to the crystallization of amorphous material. It is needless to say

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that the marked exothermic reaction cannot be accounted for by possible reactions between crystalline hydrates leading to thermodynamic equilibrium. It seems clear, therefore, that, on low pressure dehydration, water molecules leave the parent lattice which collapses into some sort of state which does not diffract X-rays. After varying periods of time (sometimes several hours) this collapsed lattice rearranges into the ordered crystalline state of the end product of dehydration, with the liberation of energy.

We have carried out a large number of experiments similar to those described above, in which various pressures were maintained during dehydration. These need not be reported in detail, since the relation of the formation of the amorphous intermediate to dehydration pressure is treated by a more precise method in Part III of this paper. It is important, however, to mention one important finding from these experiments. That is, that there appears to be a definite upper limit of pressure beyond which the thermal evolution does not occur. In Fig. 4, for example, is shown a time–temperature plot of the results obtained in an experiment with copper sulphate, carried out in precisely the same manner as the experiments whose results are plotted in Fig. 2, except that the dehydration pressure was 1.85 mm. instead of 0.8 mm. It will be seen that there is no evidence whatever of any thermal effect, and that therefore, presumably, the amorphous intermediate is not formed at this pressure. We shall have occasion to refer to this result, which has been substantiated by a large number of experiments, in discussing the results reported later, in Part III.

Curves similar to those shown in Figs. 2 and 3 were obtained for manganous sulphate tetrahydrate and ferrous sulphate heptahydrate. It is interesting to note, however, that no thermal evolution was observed for nickel sulphate hexahydrate, or for manganous oxalate dihydrate, although both of these salts

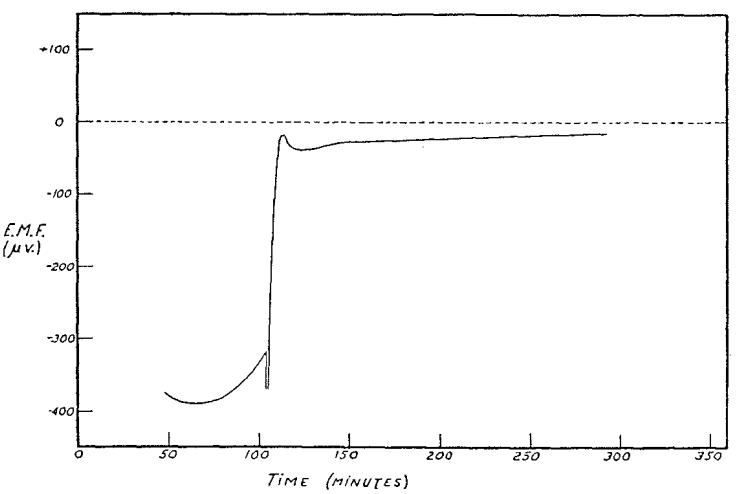

FIG. 4. *Absence of thermal effect following dehydration of copper sulphate pentahydrate at 1.85 mm.*

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are known to yield X-ray amorphous products. It is possible that the limiting pressure for these salts is very low. A slight but reproducible effect was found for cobalt chloride hexahydrate.

Part II

The Heats of Solution of Crystalline Copper and Zinc Sulphate Hydrates

Experimental Method

In order to utilize heat of solution data for the determination of the fractional amount of amorphous material formed on low pressure dehydration, it is necessary to know the heats of solution at infinite dilution of all the crystalline hydrates involved. Examination of the available data indicated too great an uncertainty in these values for this purpose. They had therefore to be obtained before the work described in Part III could be undertaken. The method used and the results obtained are reported in this section.

Reagent grade copper sulphate pentahydrate was recrystallized several times, and finally allowed to crystallize slowly at constant temperature under the vacuum of a good water aspirator. The crystals were collected and dried at room temperature in dust-free containers. The crystals were analyzed for copper by electrodeposition. The water content was found to be 36.06%. The dried crystals were screened, and the through-sixty-on-one-hundred fractions used in the calorimetric determinations.

It was found difficult to prepare samples of zinc sulphate heptahydrate of definite water content. However, it was found possible to prepare a uniform sample of the hexahydrate of the theoretical water content (40.14%) by allowing a solution of zinc sulphate to crystallize very slowly under partial vacuum at 38°C. These crystals were filtered, dried, and allowed to stand for several hours in a desiccator over calcium chloride.

Powder photographs were made of each of these hydrated salts and the lines were found to compare with tabulated wave lengths.

It is difficult to prepare samples of the lower hydrates of sufficient purity for calorimetric work. Accordingly, this was not attempted, but instead, mixtures of hydrates were prepared by dehydrating weighed samples of the pure copper sulphate pentahydrate or zinc sulphate hexahydrate, prepared as above, for various times at 100°C. and 56°C. respectively, at atmospheric pressure. Following these partial dehydrations, the loss in weight was recorded and the percentage water in the sample calculated. The dehydrations were carried out in an Abderhalden apparatus containing fused calcium chloride as a desiccant. The samples, usually less than 0.5 gm., were contained in a Pyrex thimble which could be capped for weighing. All weighings were made on a microbalance, and the weights corrected to weights *in vacuo*.

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It will be shown, from the data reported below, that in the case of copper sulphate, the products of these partial dehydrations were mixtures of either penta- and trihydrate, or, of tri- and monohydrate depending on the extent of dehydration; in the case of zinc sulphate, the products were mixtures of hexa- and monohydrate. The values of the heats of solution of the pure hydrates were obtained by extrapolating the experimental values obtained for the mixtures of known water content to the water content of the pure hydrates. For convenient reference, the percentages of water in these pure hydrates is given in the second column of Table IV.

The calorimetric assembly is shown in Fig. 5.

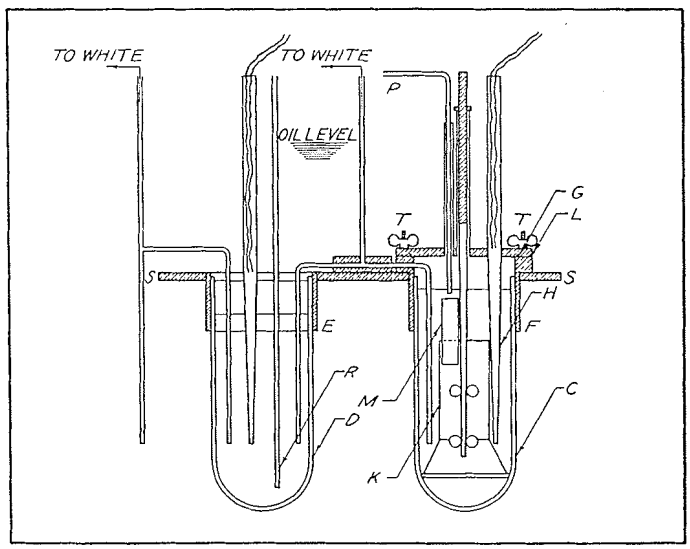

FIG. 5. *Apparatus for the determination of heats of solution.*

Two Dewar flasks were cemented in cylindrical brass supports E and F mounted in the rectangular brass frame SS. Thermel and heater leads were led into flask D through a large cork which was covered with a layer of glycerol–litharge cement and coated with sodium silicate solution.

Flask C was fitted with a removable brass lid L, secured by wing nuts. A tight fit was ensured by means of the neoprene gasket G. Rapid dissolving of the sample and efficient stirring was provided by means of a glass stirrer mounted in the inner cylinder K. The heater (H) was made of B and S 30 constantan wire in a protecting case.

A weighed sample of the salt was contained in a Pyrex cylinder closed at top and bottom by tight fitting rubber disks sealed by polystyrene. The cylinder was held in place by the brass support M, and the hydrate could be released by applying pressure by means of the rod P.

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The whole assembly could be lowered into a large oil bath maintained at constant temperature to ± 0.003°C., by means of a windlass arrangement. Water in the auxiliary flask D could be brought to the temperature of the oil bath by means of a heater or by cooling with a stream of air bubbles, as required. A four-junction copper–constantan thermel leading from flask D to the oil bath served as a means of control.

The heat of solution was determined by dissolving the weighed sample in an accurately known quantity of water in flask C, and measuring the temperature difference between flasks C and D by means of a 20-junction copper–constantan thermel. Readings of the thermel e.m.f. were made with a Leeds and Northrup White double potentiometer in conjunction with a type HS galvanometer. Current and potential readings for the determination of heat capacity were made by measuring the potential drop over calibrated standard resistances in the heater circuit, time being measured by a calibrated synchronous timer in circuit.

Calculation of the heat of solution from time–e.m.f. data was carried out according to the procedures developed by White (20).

The values of the heats of dilution required to calculate the heats of solution to infinite dilution were calculated for each experiment from the accurate data reported by Lange, Monheim, and Robinson (10).

Experimental Data

The results of these measurements, with pertinent data, are given in Tables I, II and III.

In these tables, and in all the other experimental work reported in this paper, the symbol J will be used to designate the heat of solution at infinite dilution, per gram of solute, in defined calories. The symbol c will be used to designate the per cent water of hydration in a given sample. For purposes of experimental convenience, the temperature of 20.10°C. has been taken as the standard reference temperature in this work.* In a few of the reported experiments, the value of J has been corrected by a small fraction of a calorie per gram per degree in order to compensate for slight differences in the temperature at which the determination was made.

The data of Table I pertain to copper sulphate, and include those determinations in which less than two moles of water per formula weight of pentahydrate was lost on dehydration. Experiments 3, 4, and 5 refer to the pure pentahydrate.

The data of Table II again pertain to copper sulphate and include determinations in which more than two but less than four moles of water was lost on

*The reference temperature of 20.1°C. was chosen in view of the fact that samples containing amorphous material were found to be more stable at this temperature than at 25°C. Heat of dilution values reported at 25°C. were corrected to 20.1°C. by graphical methods, using data given by Plake, Lange, Streek, Kelley, and others. At the very low molalities used, these corrections were found to be small and sometimes negligible.

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TABLE I

Experiment number	Per cent water in product = c	Calories evolved per gram	Heat of dilution	J	J from straight line equation	Powder photograph
1	25.45	15.68	1.58	17.26	17.32	Trihydrate lines
2	28.20	9.18	1.94	11.12	11.07	
3	35.90	−9.41	2.94	−6.47	−6.46	Pentahydrate lines
4	35.90	−9.40	2.94	−6.46	−6.46	Pentahydrate lines
5	36.06	−9.05	2.24	−6.81	−6.82	Pentahydrate lines

TABLE II

Experiment number	Per cent water in product = c	Calories evolved per gram	Heat of dilution	J	J from straight line equation	Powder photograph
6	10.32	54.32	2.26	56.51	56.31	
7	10.35	53.93	2.34	56.23	56.33	
8	10.38	54.32	1.98	56.25	56.25	Monohydrate lines
9	15.81	40.67	1.72	42.36	42.40	
10	16.81	38.00	1.90	39.88	39.85	
11	22.66	23.20	1.68	24.90	24.92	

TABLE III

Experiment number	Per cent water in product = c	Calories evolved per gram	Heat of dilution	J	J from straight line equation	Powder photograph
12	23.42	38.92	1.30	40.22	32.57	
13	16.28	45.11	1.99	47.10	47.10	
14	31.09	16.04	1.05	17.09	16.98	
15	11.30	55.81	1.41	57.22	57.22	Monohydrate lines
16	40.14	−2.05	1.98	−0.07	−1.38	Hexahydrate lines

dehydration. In no case was more than four moles lost even on prolonged dehydration in the Abderhalden apparatus at 100°C.

The data of Table III are for zinc sulphate hexahydrate.

When the values of J reported in Tables I and II are plotted against the corresponding values of c, two straight lines are obtained which intersect at a small angle at a value of c corresponding to the empirical formula $CuSO_4$, 3.3 H_2O. It is clear therefore that under the experimental conditions the pentahydrate dehydrates first to the trihydrate, and, when the pentahydrate is used up, the trihydrate formed decomposes to monohydrate.

The straight lines fitted to the values of Tables I and II by the method of least squares are respectively,

$$J = 75.24 - 2.276\ c\ (25.29 < c < 36.07)$$
$$J = 82.74 - 2.552\ c\ (10.14 < c < 25.29)$$

The values of J in Table III lie on one straight line, with the exception of Expt. 12, which has been discarded. There is therefore again no evidence for intermediate hydrate formation in these experiments. The equation of the best straight line fitted to these points is

$$J = 80.22 - 2.032\ c\ (10.04 < c < 40.10)$$

By substituting the proper values of c in these equations, the heats of solution for the crystalline hydrates given in Table IV are obtained.

TABLE IV

Hydrate	c	J, cal. per gram	J, Kcal. per formula weight	Temp. of solution, °C.
$CuSO_4 \cdot 5H_2O$	36.07	− 6.85	−1.71	20.1
$CuSO_4 \cdot 3H_2O$	25.29	17.69	3.78	20.1
$CuSO_4 \cdot H_2O$	10.14	56.87	10.10	20.1
$ZnSO_4 \cdot 6H_2O$	40.10	− 1.27	−0.34	20.0
$ZnSO_4 \cdot H_2O$	10.04	59.82	10.74	20.0

Part III

Effect of Dehydration Pressure on Formation of Amorphous Product

As mentioned in the introduction, the main purpose of this work was to dehydrate copper sulphate pentahydrate and zinc sulphate hexahydrate at a series of water vapor pressures, and, from measurements of the heats of solution of the products obtained, to determine the effect of dehydration pressure on the fractional amount of amorphous product formed. The choice of the heat of solution method was made in view of the relatively high energy difference between amorphous and crystalline salts to which reference has been made.

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Experimental Method

The apparatus used for dehydration is shown in Fig. 6.

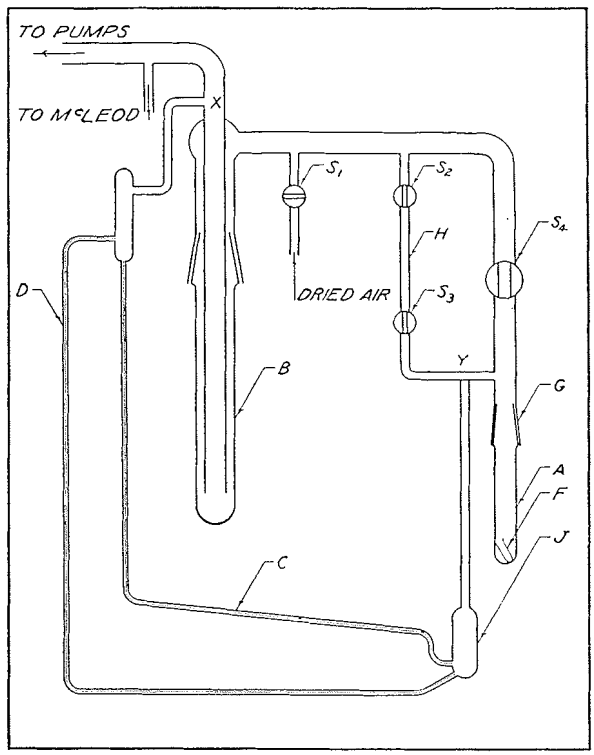

FIG. 6. *Apparatus for the control and measurement of water vapor pressure in the reaction zone during dehydration.*

About 0.5 gm. of the hydrate, between 60 and 100 mesh, was weighed into the tared glass thimble, F, and placed in the tube A, which was surrounded by a constant temperature bath (not shown).

The manometer JCD, which was calibrated before each experiment, contained Amoil-S. One millimeter on the vertical gauge D corresponded to approximately 0.07 mm. mercury, while one millimeter on the slant gauge C corresponded to 0.006 mm. mercury. Control experiments indicated no solubility of water vapor in the Amoil-S at the low pressures, and over the times employed.

The control of pressure in A was effected by adjusting the stopcocks S_2, S_3, and S_4, a manostat being impractical for the low pressures required. For very low pressures, the 12 mm. stopcock S_4 was left open. For higher pressures, the stopcock S_4 was closed and the pressure was controlled by means of the 3 mm. stopcocks S_2 and S_3. Greater ease of adjustment was made possible by having the stopcock S_2 of a 'throttling' type, that is, the core had tapering

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grooves cut in its circumference to permit small adjustments of the size of the leak. It will be observed that the manometer measured the pressure gradient between the points X and Y in Fig. 6.

In carrying out a dehydration, all the air was first evacuated from the system by leaving the stopcocks open for a few minutes. This was possible because of the induction period preceding nucleation of the sample; that is, active dehydration would not begin during a two or three minute degassing period. The stopcocks were then adjusted to give the desired pressure gradient, and the dehydration carried out for a definite time with the vacuum pumps in operation. It was found that the pressure, as read by the vertical and slant gauges could be accurately maintained under these conditions.

At the conclusion of the dehydration period, the pumps were shut off, the sample was cooled to about 15°C., and the water vapor pressure allowed to drop gradually by opening the stopcocks. Then, after about five minutes, dry air was admitted to the system by way of stopcock S_1, and the thimble removed, capped, and weighed. Most of the sample was then transferred to the heat of solution cylinder, and the thimble reweighed. It was found by control experiments that these weighing and transfer operations could be carried out without the occurrence of crystallization. In most of the experiments, small samples were taken for X-ray powder determinations. Determinations of the heat of solution were made exactly as has been described in Part II.

Experimental Data for Copper and Zinc Sulphates

In Table V are reported the experimental results, and other pertinent data, for a series of experiments in which samples of copper sulphate pentahydrate were dehydrated at pressures ranging from 0.02 to 2.21 mm. of mercury. As before, J, is the heat of solution in calories per gram calculated to infinite dilution, and c is the per cent of water in the product.

Several experiments were also carried out in which the pentahydrate was dehydrated at as low a pressure as possible (< 0.01 mm.) and for long periods of time, as long as several days in some cases in contrast with less than six hours for the experiments of Table V. The data for these experiments are given in Table VI. It will be observed that these prolonged dehydrations gave products containing less than one mole of water per formula weight of copper sulphate. It is interesting to note, however, that these products were X-ray amorphous.

Data for zinc sulphate hexahydrate are given in Table VII.

Treatment of Data for Copper Sulphate Pentahydrate

It will be observed from Tables V and VI that dehydrations were carried out at approximately 45°C. and at pressures ranging from a few hundredths of a millimeter to a little over 2 mm. At 45°C., the equilibrium pressures

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TABLE V

Expt. No.	Sample wt. (gm.)	P_{H_2O} (mm.)	Dehydration temperature, (°C.)	Dehydration time (min.)	Loss in wt. (gm.)	c	J	Solution temperature, (°C.)	Powder photographs
19	0.52536	0.02	45.2	170	0.06404	27.18	28.10	20.08	No lines
20	0.94927	0.07	45.0	203	0.10776	27.87	25.30	20.14	
21	0.61436	0.13	44.8	259	0.10794	22.43	45.80	20.18	
22	0.22873	0.21	45.1	154	0.03836	23.12	41.04	20.08	No lines
23	0.38447	0.44	45.0	215	0.06209	23.75	39.07	20.19	Doubtful
24	0.43994	0.84	45.3	176	0.02709	31.86	8.12	20.11	Doubtful
25	0.34727	1.05	45.0	225	0.01657	32.86	3.77	20.06	Doubtful
26	0.25096	1.11	45.0	350	0.01984	30.57	9.62	20.06	
27	0.36186	1.27	45.0	327	0.01428	33.43	0.47	20.06	
28	0.63175	1.38	45.0	180	0.02651	33.26	0.11	20.07	
29	0.60501	1.46	45.0	353	0.08146	26.11	19.93	20.13	
30	0.21145	1.51	45.0	339	0.02580	27.17	16.83	20.10	Monohydrate lines
31	0.40276	1.81	45.0	241	0.04898	27.21	17.91	20.06	
32	0.50922	2.21	45.0	320	0.12601	15.05	50.42	20.10	Monohydrate lines

TABLE VI

Expt. No.	Sample wt. (gm.)	P_{H_2O} (mm.)	Dehydration temperature, (°C.)	Dehydration time (hr.)	Loss in wt. (gm.)	c	J	Solution temperature, (°C.)	Powder photograph
33	0.40113	0.01	25 to 40	66	0.12690	6.24	116.5	20.11	No lines
34	0.22180	0.01	30	41	0.06861	7.42	110.76	20.11	No lines
35	0.36622	0.01	31.5	23	0.10762	9.45	101.65	20.17	No lines
36	0.32927	0.01	31	137	0.10260	7.12	113.96	20.16	No lines
37	0.36689	0.01	30 to 45	86	0.11785	5.80	121.11	20.14	No lines
38	0.20531	0.01	30	41	0.06407	7.03	111.67	20.10	No lines
39	0.24712	0.01	35	30	0.07549	7.94	107.35	20.15	No lines

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TABLE VII

Expt. No.	Sample wt. (gm.)	P_{H_2O} (mm.)	Dehydration temperature, (°C.)	Dehydration time (min.)	Loss in wt. (gm.)	c	J	Solution temperature, (°C.)	Powder photograph
40	0.45452	0.02	25.0	710	0.14781	11.29	97.54	20.04	No lines
41	0.37507	0.12	45.0	160	0.11680	13.07	89.29	20.01	
42	0.31084	0.45	45.0	180	0.08323	18.24	66.90	19.96	Hexahydrate lines
43	0.25050	0.71	45.0	115	0.05328	23.97	40.08	19.98	Hexahydrate lines
44	0.33884	0.82	45.0	150	0.07081	24.33	33.30	20.01	
45	0.24230	0.95	45.0	120	0.05209	23.75	32.52	19.97	
46	0.39010	1.12	45.0	120	0.10442	18.25	45.48	20.01	
47	0.47002	1.14	45.0	150	0.13463	16.12	51.61	20.00	
48	0.57399	1.22	45.0	110	0.15517	18.10	45.24	20.01	
49	0.34243	1.55	45.0	93	0.09358	17.63	46.89	19.96	Monohydrate lines
50	0.35524	2.62	45.0	120	0.10672	14.43	53.68	19.96	Monohydrate lines

corresponding to the penta-trihydrate equilibrium, and the tri-monohydrate equilibrium are 31.8 and 21.8 mm. respectively. The equilibrium pressure of the mono-anhydrous equilibrium may be estimated to be between 4 and 5 mm. It follows that the anhydrous salt is the thermodynamically stable phase in the very low pressure range used. However, Garner and Tanner (3) found that, even at very low pressures, dehydration proceeds very slowly past the monohydrate stage. This observation has been confirmed in the present work. At 80°C., crystals of monohydrate lose much less than 1% per hour of their weight, in high vacuum. The weight loss per hour at 45°C. is negligible. We may therefore conclude that no anhydrous salt was produced in Expts. 19 to 32 in which dehydration was stopped before all of the pentahydrate was decomposed.

It has been pointed out, however, that products containing less than one mole of water per formula weight of copper sulphate are produced in the very long vacuum dehydrations, reported in Table VI.

The question now arises as to whether trihydrate may also be formed even though the pressures are far below the region in which trihydrate may exist as a thermodynamically stable phase. Obviously this could be so if the trihydrate, like the monohydrate, decomposes very slowly. All workers (3, 7, 18) are in agreement that in high vacuum at temperatures below 50°C. the trihydrate does not form except possibly as a short lived intermediate, and that the end product is monohydrate. Hume and Colvin (7) found that at 20°C. the presence of water vapor at low pressure retards the reaction velocity of the pentahydrate decomposition, while under greater pressures the decomposition gives first trihydrate, which decomposes only after all the pentahydrate has been used up. In some experiments which have been done in this laboratory on the kinetics of the pentahydrate decomposition, we have observed the formation of trihydrate at water vapor pressures of the order of 1 mm. These experiments, however, were done in a closed system in which a constant water vapor pressure was maintained. In high vacuum, or in the type of apparatus used in the present work where there was a continuous movement of water molecules away from the reaction interface, we have obtained no evidence of trihydrate formation in kinetic experiments.

Unfortunately, data obtained by X-ray powder examination have proved inconclusive. Expts. 30 and 32 of Table V gave a clear pattern of monohydrate lines with no evidence of trihydrate. Expts. 23, 24, and 25, however, gave patterns of lines which could not be accurately identified and are therefore indicated in Table V as doubtful. In these experiments the powder was held in small thin-walled glass (707 DG Pyrex) capillaries, sealed in a flame at one end and with paraffin wax at the other. Even under these conditions, it was difficult to avoid having the sample a little too thick, which gave the effect of having more than one center and consequently made the identification of some lines difficult. The clear monohydrate patterns obtained in Expts. 30 and 32, and the complete absence of trihydrate lines in these samples (when

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they would be most likely to occur), leads us to believe that the formation of trihydrate, if it occurs at all, is likely to be small. The possible effect of trihydrate formation in the mathematical treatment of the data of Tables V and VI will be referred to below.

Consideration must be also given to the occurrence of adsorbed water. Because of the electric charge of the copper and sulphate ions in the amorphous intermediate, and because of the polarity of the water molecules escaping from the underlying pentahydrate lattice, water molecules will be adsorbed at the reaction interface. These, however, will have a strong tendency to escape into the low pressure region outside of the reaction zone, since the adsorption forces are certainly not greater than the binding forces in the original lattice. Furthermore, it appears likely that only a comparatively small adsorption is required to induce nucleation and consequent crystallization of the amorphous material, which therefore could not exist at all if the adsorption were very great.

Since we have no means of determining quantitatively, the extent of this interfacial adsorption of water, we shall assume for the moment that it does not occur in such amounts as will seriously affect the quantitative approach now to be made. An estimation of the effect of this assumption will be made later.

Assuming then the absence of the anhydrous salt, and of such quantities of trihydrate or of adsorbed water as would seriously affect the quantitative deductions to be made, the end state of the dehydration process will result in a mixture of three or fewer of the following substances:

(*a*) Undecomposed pentahydrate; which will presumably be in the form of cores underlying the reaction zones.

(*b*) Crystalline monohydrate, probably in the form of very small crystals.

(*c*) Amorphous material, assumed, in the absence of adsorbed water, to have the composition, $CuSO_4 \cdot H_2O$, but to be in such a state that X-rays are not diffracted by it.

Now, what we wish to determine is a quantity, Q, which we shall define as the ratio of the weight of amorphous monohydrate in the product to the total weight of monohydrate, whether crystalline or amorphous.

Defining the following quantities:

x = the heat of solution of crystalline pentahydrate in calories per gram,
y = the heat of solution of crystalline monohydrate in calories per gram,
z = the heat of solution of amorphous monohydrate in calories per gram,
a = the per cent of water in pentahydrate,
b = the per cent of water in monohydrate,
c = the per cent of water in the product,
A = the number of grams of crystalline pentahydrate in 1 gm. of product,
B = the number of grams of crystalline monohydrate in 1 gm. of product,
D = the number of grams of amorphous monohydrate in 1 gm. of product,
J = the heat of solution at infinite dilution per gram of product,

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we have,

$$\begin{aligned} aA + bB + bD &= c \\ xA + yB + zD &= J \\ A + B + D &= 1. \end{aligned}$$

Hence,

$$Q = \frac{D}{B + D}$$

$$= \frac{\begin{vmatrix} a & b & c \\ x & y & J \\ 1 & 1 & 1 \end{vmatrix}}{\begin{vmatrix} a & b & c \\ x & y & J \\ 1 & 1 & 1 \end{vmatrix} + \begin{vmatrix} a & c & b \\ x & J & z \\ 1 & 1 & 1 \end{vmatrix}}$$

$$= \frac{J\,(b - a) + c\,(x - y) + ay - bx}{(c - a)\,(z - y)}$$

$$= \frac{(a - b)}{(z - y)} \cdot \frac{(J - x)}{(a - c)} + \frac{(x - y)}{(z - y)}$$

Substituting the proper values of x, y, a, and b from Table IV, we obtain:

$$Q = \frac{25.93}{(z - 56.87)} \cdot \frac{(J + 6.85)}{(36.07 - c)} - \frac{(63.72)}{(z - 56.87)}.$$

It is apparent that Q can be calculated if z (the heat of solution per gram of the amorphous product) is known.

There are now, two ways in which z may be evaluated.

(1) It will be observed from Table VI that the samples in Expts. 33 to 39 were dehydrated to water contents below the percentage of water in the monohydrate (10.14%). Since these samples were X-ray amorphous, if the values of J are plotted against the corresponding values of c, extrapolation to $c = 10.14$ should give the heat of solution of the amorphous monohydrate. These values lie fairly consistently on a straight line, but the extrapolation is best performed by the method of least squares. There is obtained;

$$J = 149.0 - 5.098\,c \quad (0.00 < c < 10.14).$$

Hence for $c = 10.14$, $J = z = 97.3$ cal. per gm. at 20.1°C.

(2) The data of Table V may also be used for evaluating z based on the assumption that Q approaches unity as the pressure maintained during dehydration is decreased to zero. The heat of solution of all the monohydrate in a given sample, regardless of state of aggregation, should then increase as the pressure is decreased, reaching its maximum value at zero pressure.

From defining equations used in the foregoing, and letting J' be the heat of solution of the monohydrate without regard to state of aggregation, it is easy to show that,

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$$J' = \frac{J - xA}{1 - A}$$

and that

$$A = \frac{(c - b)}{(a - b)}$$

therefore,

$$J' = \frac{J\,(a - b) - x(c - b)}{(a - c)}$$

$$= \frac{(J - x)\,(a - b)}{(a - c)} + x.$$

Substituting the proper numerical values for a, b, and x, we obtain,

$$J' = \frac{25.93\ (J + 6.85)}{(36.07 - c)} - 6.85.$$

Applying this formula to the lower pressure experiments of Table V we obtain the results given in Table VIII.

TABLE VIII

Expt.	P_{H_2O}(mm.)	c	J	$36.07 - c$	$J + 6.85$	J'
19	0.02	27.18	28.10	8.89	34.95	95.09
20	0.07	27.87	25.30	8.20	32.15	94.82
21	0.13	22.43	45.80	13.64	52.65	93.24
22	0.21	23.12	41.04	12.95	47.89	89.04
23	0.44	23.75	39.07	12.32	45.92	89.80
24	0.84	31.86	8.12	4.21	14.97	85.35
28	1.38	33.26	0.11	2.81	6.86	57.36

When the values of J' corresponding to the lower pressures, are plotted against the values of P_{H_2O}, the points are found to lie on a nearly straight line excepting the value for Expt. 22. The intercept on the zero pressure axis is 95.5 cal. per gm.

The difference between the values of z as determined by these two methods is not significant in the evaluation of Q. However, the discrepancy of 1.8 cal. per gm. cannot be ascribed to calorimetric error. It seems more likely that this difference is due to the presence of adsorbed water, and is possibly indicative of the error introduced by ignoring the presence of adsorbed water in the equations used to calculate Q. It will be recalled that the dehydrations reported in Table VI were very prolonged; evacuation was continued long after water vapor had ceased to be given off in appreciable quantities. On the other hand, the dehydrations reported in Table V were discontinued when only a fraction of the pentahydrate had decomposed, under which conditions water molecules would be passing through the pseudomorph from the reaction interface when the dehydration was stopped. In the interval between discontinuing dehydration and the admission of dry air to the dehydration system

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it is certain that some adsorption would occur. The heat of solution of the product obtained would therefore be expected to have a lower value than that obtained for evacuated amorphous products, which is seen to be the case.

Using the value of z of 95.5, the expression obtained for Q reduces to:

$$Q = 0.6712 \frac{(J + 6.85)}{(36.07 - c)} - 1.65.$$

In Table IX are given the results obtained when this formula is applied to the data of Table V. These results are plotted in Fig. 7.

TABLE IX

Expt. No.	P_{H_2O}(mm.)	J	c	Q
19	0.02	28.10	27.18	0.99
20	0.07	25.30	27.87	0.98
21	0.13	45.80	22.43	0.94
22	0.21	41.04	23.12	0.83
23	0.44	39.07	23.75	0.85
24	0.84	8.12	31.86	0.73
25	1.05	3.77	32.86	0.57
26	1.11	9.62	30.57	0.36
27	1.27	0.47	33.43	0.21
28	1.38	0.11	33.26	0.01
29	1.46	19.93	26.11	0.15
30	1.51	16.83	27.17	0.14
31	1.81	17.91	27.12	0.22
32	2.21	50.42	15.05	0.18

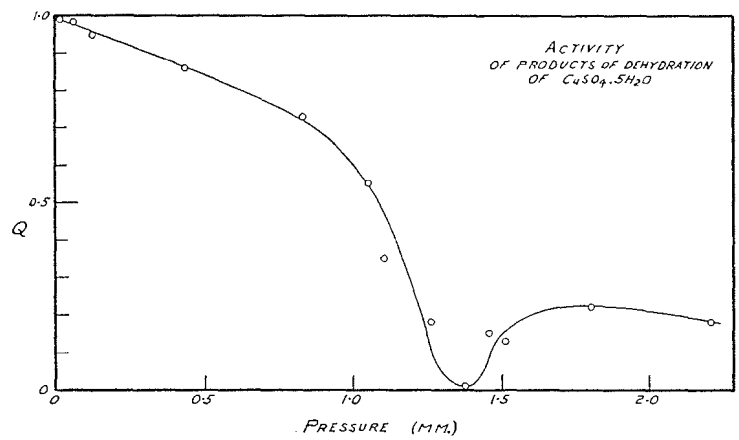

FIG. 7. *Dependence of formation of energy-rich amorphous product on water vapor pressure in reaction zone* ($CuSO_4 \cdot 5H_2O$).

The curious character of the Q-curve will be discussed after the results obtained for zinc sulphate hexahydrate have been given. It is desirable at this point however to refer again to the type of error that may have been introduced into our evaluation of Q by ignoring the possibility of trihydrate formation.

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Let us suppose that copper sulphate pentahydrate partly dissociates into crystalline monohydrate, and that the product contains c per cent of water and has a heat of solution of J_1 calories per gram. Alternatively, let us suppose that the pentahydrate dissociates into both trihydrate and monohydrate to such an extent that the percentage of water in the product is again equal to c, but that the heat of solution per gram is now J_3. It is not difficult to show that:

$$J_3 = J_1 - 2.00\,\beta$$

where β is the number of grams of trihydrate per gram of product. It will be seen, therefore, that J_3 can never be greater than J_1. The experimental heats of solution are actually very much higher than would be the case if the product consisted only of crystalline penta- and monohydrates, except at the minimum of the Q-curve where (as will be seen from Table VIII) the value of J' is equal to the heat of solution of pure crystalline monohydrate within the limit of error. This higher heat of solution cannot therefore be accounted for by the presence of trihydrate, and can only be due to the presence of the energy-rich amorphous aggregate. It will also be seen that J_3 does not differ greatly from J_1 for small quantities of trihydrate. This, of course, is because the heat of solution of trihydrate is not far from that of a mixture of monohydrate and pentahydrate of the same value of c.

Treatment of Data for Zinc Sulphate Hexahydrate

It has been shown in Part II that at 56°C. the dehydration of zinc sulphate hexahydrate at atmospheric pressure proceeds directly to the monohydrate, one straight line fitting all the points when the heat of solution is plotted against the water content of crystalline material. It is therefore very improbable that intermediate hydrates are formed as part of the final product in dehydrations at 45°C. in high vacuum or at low pressures of water vapor, provided there is a continual movement of water molecules away from the reaction interface. The X-ray evidence has been found to support this view. The diffraction pattern obtained for the hepta-, hexa-, and monohydrates are very distinctive and no evidence for lines other than those for the hexa- or monohydrate have been obtained in this work.

The data for 11 experiments with zinc sulphate hexahydrate have been given in Table VII. These data may be used to evaluate the heat of solution of amorphous zinc sulphate monohydrate by the same methods which have been developed in the foregoing. For this case, it may be shown that,

$$J' = \frac{30.06\ (J + 1.27)}{(40.10 - c)} - 1.27.$$

Applying this formula to the data of Table VII, and plotting J' against the pressure, the intercept on the zero pressure axis is found to be 102.2 cal. per gm., which will be taken as the heat of solution of amorphous zinc sulphate monohydrate. Using this value, the formula for Q becomes,

$$Q = \frac{0.709\ (J + 1.27)}{(40.10 - c)} - 1.44.$$

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The values of Q obtained for Expts. 40 to 50 are given in Table X and are plotted against water vapor pressure in Fig. 8.

TABLE X

Expt. No.	P_{H_2O}(mm.)	J	c	Q
40	0.02	97.45	11.29	0.99
41	0.12	89.29	13.07	0.94
42	0.45	66.90	18.24	0.77
43	0.71	40.08	23.97	0.38
44	0.82	33.30	24.33	0.12
45	0.95	32.52	23.75	0.03
46	1.12	45.48	18.25	0.08
47	1.14	51.61	16.12	0.12
48	1.22	45.24	18.10	0.06
49	1.55	46.89	17.63	0.08
50	2.62	53.68	14.43	0.08

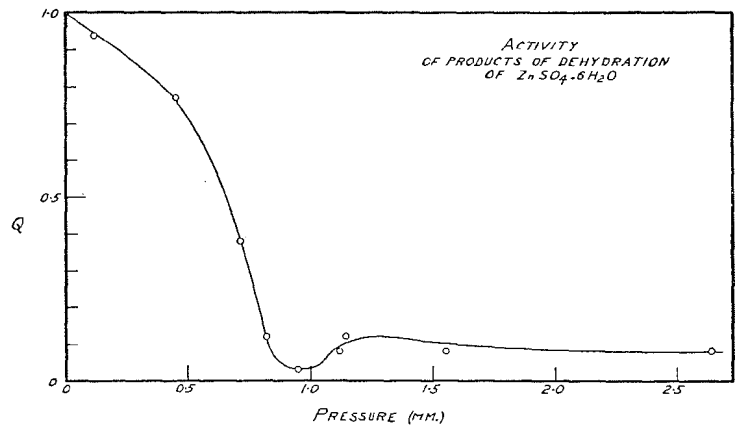

FIG. 8. *Dependence of formation of energy-rich amorphous product on water vapor pressure in reaction zone ($ZnSO_4 \cdot 6H_2O$).*

It will be observed that the Q curve has the same character as that obtained for copper sulphate pentahydrate.

Heats of Transition

From the values of the total heats of solution of the crystalline and amorphous monohydrates given in the foregoing, we may now calculate the following values for difference in heat content between the crystalline and amorphous monohydrates. We obtain:

$$CuSO_4 \cdot H_2O \text{ (amorphous)} \rightarrow CuSO_4 \cdot H_2O \text{ (crystalline)}$$

$$\underset{293}{\triangle H} = -7170 \text{ cal. mole}^{-1}$$

$$ZnSO_4 \cdot H_2O \text{ (amorphous)} \rightarrow ZnSO_4 \cdot H_2O \text{ (crystalline)}$$

$$\underset{293}{\triangle H} = -7600 \text{ cal. mole}^{-1}$$

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General Discussion

Inspection of the curves shown in Figs. 7 and 8 shows that the values of Q decrease with increasing water vapor pressure, pass through a minimum, and then rise to a small value before steadily decreasing. These minima lie at pressures of 1.4 mm. for copper sulphate and at 0.95 mm. for zinc sulphate. These curves would seem to indicate that the fractional amount of amorphous material decreases with increasing pressure of water vapor up to the limiting values given, but then increases with increasing pressure over the range indicated by the curves.

In order to interpret this surprising result we may first recall the experiments reported in Part I in which no evidence was obtained of any amorphous to crystalline transition above a pressure maximum in the vicinity of 1.8 mm. for copper sulphate. This coincides within the range of the experiments of Part I, to the minimum of the Q curve. The anomalous rise in values of Q at pressures above this value cannot therefore be due to the formation of an amorphous intermediate which may spontaneously crystallize. Cause for this increase must therefore be sought in other factors. It must be emphasized however that the increase in Q to the right of the minimum corresponds to the formation of a product of higher heat of solution than the crystalline monohydrate. It has been shown in the foregoing that the heat of solution of the amorphous material formed on vacuum dehydration of copper sulphate pentahydrate exceeds that of the crystalline monohydrate, by 38.6 cal. per gm. Simple calculation shows that the material formed at the maximum of the anomalous portion of the Q curve for copper sulphate exceeds the heat of solution of the crystalline monohydrate by nearly nine calories per gram.

It will be helpful at this stage to attempt to form some sort of working hypothesis as to the nature of the dehydration process. Copper sulphate pentahydrate crystallizes in the triclinic system, and the lattice parameters and crystal structure have been determined by Beevers and Lipson (1). They found that each copper ion is surrounded octahedrally by (*a*) four water molecules in the form of a slightly distorted square and (*b*) two oxygen atoms of adjacent sulphate ions. The fifth water molecule is joined to two sulphate oxygens and two of the coordinated water molecules by a tetrahedral arrangement of bonds. Copper sulphate monohydrate approaches an orthorhombic structure. Its lattice parameters differ markedly from those of the pentahydrate (6). The detailed structure has not been worked out. Taylor and Klug (16) have discussed several aspects of the mechanism of dehydration of the pentahydrate in terms of the lattice parameters, and Garner and Pike (4) have studied the shapes of the dehydration nuclei, which they have shown to form more readily along certain planes than on others.

Although many details are doubtful, we may tentatively visualize the processes of dehydration somewhat as follows. As the pentahydrate crystal loses water, a decomposition interface is set up on one side of which is the pentahydrate lattice, and on the other side a 'skeleton lattice' having the

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pentahydrate structure, but less the four co-ordinated water molecules. This skeleton lattice probably collapses after a very short life into the X-ray amorphous condition with which the foregoing experiments have been concerned.

This amorphous condition may be a disordered assembly of microcrystals of a size below the limit required for X-ray diffraction. Roginsky (12) has presented powerful arguments for this point of view. It is conceivable however that it may be regarded as disordered assembly of copper ions and sulphate ions to the latter of which presumably the 'fifth' water molecule remains attached. In such a state, the ions would be subject to interionic attractions such as exist in a highly concentrated solution, but orientation into a lattice structure would be prevented by lack of mobility. Such a state might also be pictured as a very highly strained or distorted lattice.

The experimental work reported in this paper does not contribute in any way toward deciding between these points of view. We have found however that the second one lends itself more readily to vizualization and we shall use it in a tentative way. As dehydration proceeds, water molecules continue to escape from the pentahydrate side of the decomposition interface. These will be attracted by the positive and negative ions of the pseudomorph layer, resulting in some interfacial adsorption, which will in turn reduce the interionic attractions and increase the ionic mobility. Nucleation will therefore result, followed by a growth of the crystalline phase of the end product. The evolution of heat following dehydration is undoubtedly due to this crystallization following a nucleation period.

This picture is therefore helpful in visualizing the probable mechanism of the processes occurring in the experiments reported in Part I of this paper. It leaves much unexplained in interpreting the effect of external water vapor pressure on the fractional amount of amorphous material formed. Qualitatively, it might be supposed that as the external water vapor pressure is increased, an increasing adsorption occurs, resulting in the increased ionic mobility, nucleation, and crystallization referred to. At a certain limiting pressure the amorphous state might be expected to have only a transitory existence and would crystallize as soon as formed. Above this limiting pressure, therefore, the dehydration would to all intents and purposes proceed directly to the end crystalline product.

However, it will be observed from the Q-curves of Figs. 7 and 8 that the decrease in amount of amorphous product is extremely sensitive to increasing water vapor pressure over a very narrow range. The minimum in the Q-curve for copper sulphate pentahydrate occurs at only 1.4 mm. We have no knowledge as to how the interfacial adsorption of water vapor varies with pressure over this very small range, nor can such knowledge be readily obtained. The change in adsorption is probably very small. It is of course possible and indeed probable that the extent of adsorption required to induce ionic mobility is also very small.

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It is clear, however, that whatever the role and extent of interfacial adsorption may be, we have to do with the following over-all reactions:

I. Initial lattice → amorphous state + water vapor
II. Initial lattice → crystalline end product + water vapor
III. Amorphous state → crystalline end product.

The experimental data reported in this paper indicate clearly that under high vacuum, or very low pressures of water vapor, the dehydration proceeds according to Reaction I. At higher pressures, it proceeds by Reaction II. Reaction III must proceed by volume nucleation of the amorphous product, followed by movement of a crystalline-amorphous interface through the mass.

At low pressures, Reaction III must occur so slowly relative to the rate of Reaction I that no crystalline end product is in contact with the decomposing primary lattice, in which case the over-all rate of dehydration will be the rate of Reaction I. At higher pressures, the experimental data indicate that Reaction III occurs so rapidly that the crystalline end product always keeps in contact with the surface of primary lattice, in which case the over-all rate of dehydration would be that of Reaction II. Both of these over-all rates should decrease with increasing water vapor pressures.

Intermediate between these extremes we might imagine the case when the reaction rate is governed by the rate of Reaction III. This rate may be expected to be very sensitive to the presence of water, in terms of the picture suggested in the foregoing. From a purely qualitative point of view it should increase with increasing external water vapor pressure, although no deduction can be made as to by what mechanism this process would influence the over-all rate as a function of water vapor pressure.

It follows from these considerations that the Q-curves obtained for the copper and zinc sulphate hydrates must be interpreted, in part, from the standpoint of the rates of these dehydration processes. It would at least be expected that the over-all rates would not have a simple relation to the water vapor pressures.

Smith and Topley (14) have studied the rate of decomposition of copper sulphate pentahydrate over a pressure range of zero to 0.04 mm. They found that the rate merely decreased with pressure over this range. However, Topley and Smith (17) and Volmer and Seydel (19) found that the rate of decomposition of manganous oxalate dihydrate had a curious dependence on external water vapor pressure, falling rapidly at first, then rising, passing through a maximum, and then slowly decreasing. These results have been thoroughly discussed in an excellent paper by Colvin and Hume (2).

The data of Tables V and VII may be used to estimate the form of the relationship between rate of dehydration and water vapor pressure. Let the following assumptions be made:

(*a*) The decomposing hydrates consist of a large number of identical spherical particles of radius r_0 cm.,

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(*b*) In all cases, all the particles are completely nucleated over their entire surface as soon as the system is evacuated,

(*c*) The impedance effects of the pseudomorph are negligible. These assumptions are, of course, only approximate, but, of the three, the second is most likely to cause error in the relative values of the calculated rates. This is because the induction period preceding nucleation is an unknown and highly variable quantity.

Now, let it be further assumed that the reaction interface in each particle is in the form of a contracting spherical envelope, and that the linear rate of advance of the interface is constant and equal to v centimeters per minute. At any time, t, the rate of loss in weight of each particle is given for copper sulphate pentahydrate by,

$$\frac{dw}{dt} = 4\pi \text{ (radius of envelope)}^2 \rho v \frac{72.24}{249.71}$$

where ρ is the density, and 72.24 gm. of water is liberated by 249.71 gm. of pentahydrate.

If, now, we let W be the total loss in weight per particle during the dehydration period, the loss in weight per gram is given by,

$$\frac{W}{\frac{4}{3}\pi r_0^3 \rho} = \frac{4\pi\rho v \ (0.289)}{\frac{4}{3}\pi r_0^3 \rho} \int_0^{t'} (r_0 - vt)^2 \, dt,$$

where t' is the time at the end of the dehydration.

The expression on the right reduces to 0.867 B, where

$$B = A - A^2 + \tfrac{1}{3} A^3$$

and

$$A = \frac{vt'}{r_0}.$$

Hence, $B = \frac{1}{0.867}$ (loss in weight per gram at the end of the dehydration period)

$$= \frac{1.153 \ (36.06 - c)}{(100 - c)},$$

where, as before, 36.06 is the per cent of water in copper sulphate pentahydrate, and c is the per cent of water in the product. The analogous formula for zinc sulphate hexahydrate is,

$$B = \frac{0.913 \ (40.14 - c)}{(100 - c)}.$$

From the values of c given in Tables V and VII we may calculate B for each dehydration time, and hence obtain $\frac{v}{r_0}$. The values obtained are given for copper sulphate pentahydrate in Table XI and for zinc sulphate hexahydrate in Table XII.

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The rate constants evaluated in Tables XI and XII are plotted against the dehydration water vapor pressure in Fig. 9.

TABLE XI

Expt. No.	P_{H_2O}(mm.)	c	t' (min.)	$\frac{v}{r_0}\cdot 10^4$
19	0.02	27.18	170	9.8
20	0.07	27.87	203	7.5
21	0.13	22.43	259	10.3
22	0.21	23.12	154	16.4
23	0.44	23.75	215	11.1
24	0.84	31.86	176	4.4
25	1.05	32.86	225	2.6
26	1.11	30.57	350	2.9
27	1.27	33.43	327	1.5
28	1.38	33.26	180	2.8
29	1.46	26.11	353	5.4
30	1.51	27.17	339	4.9
31	1.81	27.21	241	6.9
32	2.21	15.05	320	14.9

TABLE XII

Expt. No.	P_{H_2O}(mm.)	c	t' (min.)	$\frac{v}{r_0}\cdot 10^4$
41	0.12	13.07	160	30
42	0.45	18.24	180	20
43	0.71	23.97	115	22
44	0.82	24.33	150	16
45	0.95	23.75	120	21
46	1.12	18.25	120	30
47	1.14	16.12	150	27
48	1.22	18.10	110	33
49	1.55	17.63	93	40
50	2.62	14.43	120	36

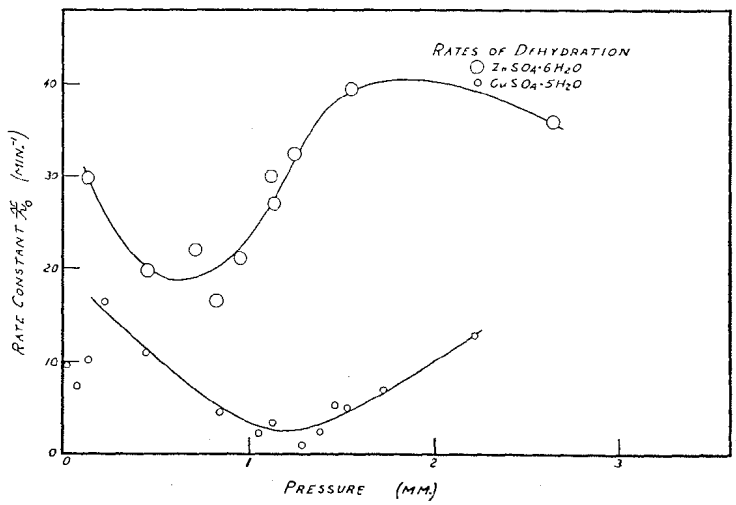

FIG. 9. *Calculated dependence of over-all rates of dehydration on water vapor pressure.*

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These curves strongly suggest that the type of relationship found by Topley and Smith, and by Volmer for manganous oxalate, and hitherto regarded as a unique case, should also be found for copper sulphate pentahydrate and zinc sulphate hexahydrate and possibly for other salts in which an amorphous intermediate plays a role in the dehydration mechanism. The desirability of extending the experiments of Smith and Topley into a higher pressure range is indicated.

Returning once more to a consideration of Figs. 7 and 8, it is clear then that the decreasing values of Q to the left of the minima may be explained by the decreasing rate of formation of amorphous material in the pressure ranges involved. In other words, as the amorphous material is formed, there is an increasing rate of crystallization as the water vapor pressure is increased. At the minimum of the Q-curve, the rates of formation and crystallization of amorphous material are equal. To the right of the minimum, the tendency to crystallization will exceed the tendency to form amorphous material. It is probable that this will result in the formation of very small crystals having high surface energies relative to those formed more slowly at higher pressure, or also relative to those formed at the minimum of the Q-curve where the amorphous forming and crystalline forming rates are equal. Powder photographs made of the product obtained in the anomalous region show in the main a broadening in the lines suggesting smaller size or possibly the presence of imperfections in the crystallites. However, much more experimental work on this aspect is necessary before valid conclusions can be drawn.

While this explanation of the increase in energy content of the product formed at dehydration pressures above those corresponding to the minima must be regarded as tentative, the experiments reported seem to indicate a definite difference in character in the energy-rich products formed at pressures to the right and left of these minima, in that the latter show a tendency to spontaneous crystallization, whereas the former do not.

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THE DISTILLATION, EXTRACTION, AND CHROMATOGRAPHIC SEPARATION OF THE C_2–C_8 FATTY ACIDS[1]

BY D. FAIRBAIRN AND R. P. HARPUR

Abstract

Thirty-five milliliters of an aqueous solution containing 5 to 70 micromoles of volatile C_2 to C_8 acids was distilled to constant volume without refluxing. The distillate was titrated, made alkaline, and evaporated to dryness at 110°C. The free acids were regenerated by the addition of 0.03 ml. of 10 *N* sulphuric acid, absorbed on filter paper, and extracted quantitatively with 3 ml. of chloroform–butanol (99:1). Acids present in the extract were separated by chromatography on a composite silica-gel column employing two internal indicators, and after elution were determined by titration, the details for which are given. The preparation of a reproducible silica is described.

Introduction

The use of silica gel for the quantitative separation of small amounts of fatty acids, ranging from acetic to butyric (2, 12, 17), valeric to decanoic (18), and undecanoic to stearic (19), has been reported from several laboratories. In general, different solvents (both developing and stationary), separate columns, and separate samples of acids have been required for the analysis of each group of acids. The only method reported which attempts to bridge the gap between two groups of acids is not presented in sufficient detail (15). Difficulties have been encountered in the preparation of reproducible silicas (6), and there is no method available for the quantitative transfer of milligram quantities of the lower fatty acids from the aqueous solutions in which they usually occur to the small volumes of organic solvents required for the chromatographic analysis (3).

Our investigation of the fatty acids excreted by nematode parasites made the use of a single small sample imperative, despite the fact that these acids varied in constitution from acetic to hexanoic and higher. Moyle, Baldwin, and Scarisbrick (11) successfully separated the acids in the acetic to octanoic range by the use of three separate buffered-silica columns, together with a fractional titration of the eluate. Unfortunately, their method is laborious and unsuitable for numerous analyses.

As already reported (4) it has been possible to modify the original methods of Ramsey and Patterson (17) and of Elsden (2) in such a way that acetic, propionic, butyric, valeric, hexanoic, and octanoic acids may be quantitatively

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separated and estimated when presented in a single small sample. We now wish to present further details of the chromatographic analysis, together with a description of a simplified distillation procedure and a micromethod for the extraction of the fatty acids from water to chloroform–butanol. Application of the latter procedures to aqueous solutions containing 5 to 70 micromoles of individual or mixed C_2 to C_8 saturated fatty acids makes the entire sample available for chromatographic analysis.

Experimental

Reagents

Silica was prepared from commercial sodium silicate solution (40°–42° Bé.) by a modification of the method described by Gordon, Martin, and Synge (6). Seven batches of silicate obtained from two manufacturers (Mallinckrodt Chemical Works; General Chemical Company) have yielded gels which are virtually identical with one another.

The sodium silicate solution (500 ml.) was diluted with two volumes of water and the gel precipitated by the careful addition of concentrated hydrochloric acid in the presence of a trace of methyl orange. Acid was added until thymol blue, used externally, indicated pH 8.5, and at such a rate that the temperature of the suspension did not rise above 28°C. The hydrogen ion concentration of the suspension was maintained constant for four hours, after which the gel was washed with water, resuspended in water, and hydrochloric acid added so as to give a final concentration of 0.2 *N*. After 48 hr. ageing at 20°–24°C., washing by filtration was repeated until the filtrate washing reached pH 2. The washed gel was dried in a hot-air oven for 48 hr. at 110°C., sized through a No. 30 U.S. standard sieve (nominal aperture 0.589 mm.), and returned to the oven for a further period of 48 hr. It was then placed in a tightly stoppered bottle and stored at room temperature for periods of several months without any apparent change.

Chloroform (U.S.P.) was washed with dilute alkali, then with water, dried over calcium chloride and distilled through a short Vigreux column. This solvent was recovered after use by application of the same procedure. Reagent grade *n*-butanol was used without further purification.

All solvent mixtures were made by volume; the mixtures routinely used were chloroform–butanol 199: 1, 99: 1, and 9: 1 ($CB_{\frac{1}{2}}$, CB_1, and CB_{10}), respectively. Unless stated to be "dry" all mixtures of chloroform–butanol were equilibrated with 1/10th volume of water and filtered through a coarse paper before use.

Sodium ethoxide (0.01 *N*) was prepared by the addition of 0.55 ml. of an aqueous saturated sodium hydroxide solution to 1 liter of pure, carbon dioxide-free absolute ethanol.

Titration

Separate acids and mixtures of acids dissolved in 30 to 35 ml. of water, chloroform, or chloroform–butanol were titrated with 0.01 *N* sodium ethoxide,

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using one drop of 3% phenolphthalein (in aldehyde-free absolute ethanol) as indicator. In all titrations the appropriate blank value was subtracted.

Chloroform and aqueous solutions received a preliminary gassing (two and five minutes, respectively) with carbon dioxide-free air at the rate of 350 ml. per minute, and gassing was continued during the titration. The titration vessel was a 100 ml. beaker covered with a glass plate. The tips of the burette and the gassing tube passed into the solution through two holes in this plate.

Although cresol red has been recommended for use in this type of titration (11), this indicator could not be used in the present investigation because of the formation of a highly acid residue when the solution was evaporated to dryness by the procedure to be described later.

Distillation of Acids

Volatile acids may be separated from other components in the medium by steam distillation. A more convenient method, in which excessively large volumes of distillate were avoided, was to distill the medium without reflux.

Thirty-five milliliters of the solution containing the fatty acids was acidified to Congo red paper by addition of 1 *N* sulphuric acid, and transferred to the modified McClendon flask (9) (Fig. 1). The flask was jacketed with a 40 oz. tin can which rested upon an asbestos board base. The nipple at the bottom of the flask passed through a hole in the center of the asbestos base and a smooth distillation was obtained by applying heat from a microburner to the nipple. The heat input was adjusted so that the temperature of the air jacket, at the level of the side arm, ranged from 95°–100°C. Foaming was prevented by the addition of a small amount of silicone (Antifoam A, Dow Corning Corp.) to the contents of the flask. Distillation was continued until the residual volume in the flask was 1.7 ml. The distillate was titrated and transferred to a 50 ml. Erlenmeyer flask. A 2 ml. excess of 0.01 *N* alkali was added, and the solution was evaporated to dryness by allowing it to stand overnight in a hot-air oven at 110°C.

Acids in the C_4 to C_8 range distilled quantitatively. Acids higher than C_8 were not examined. The distillation of acetic and propionic acids was not quantitative, but by arbitrarily fixing the initial and final volumes of the solution in the flask at 35 and 1.7 ml., respectively, it was found that 80 to 81% of the acetic, and 97% of the propionic, distilled with such constancy that an appropriate correction could be made at the completion of the analysis. The recovery of formic acid was about 70% but since specific methods for the estimation of this acid and its destruction prior to distillation are well known (5) it should be possible to alter the scheme of analysis when the need arises.

Acids such as pyruvic and lactic, if present, are distilled to a small extent. Such acids do not interfere with subsequent analysis, since they are not eluted from the chromatographic column.

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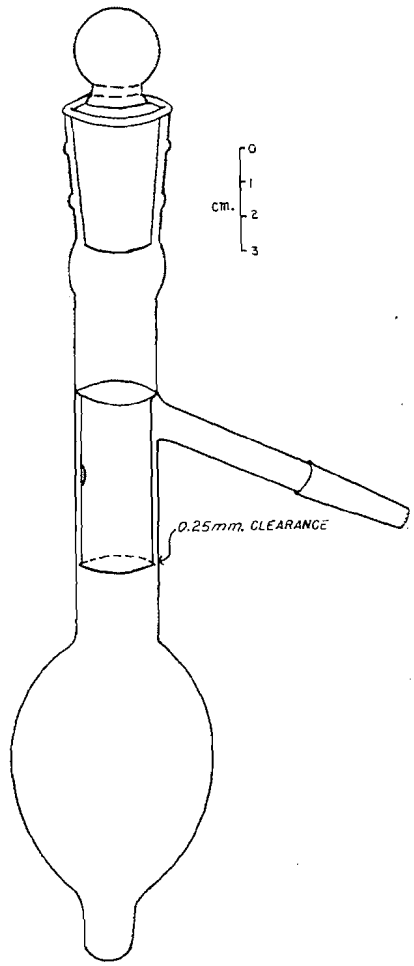

FIG. 1. *Distillation flask.*

Extraction of Acids

The analysis of small quantities of acids requires that the whole of, or at least a large proportion of, the acids be transferred to the chromatographic column. Previously existing methods (2, 17) are unsatisfactory for micro-quantities of acids.* The following method was found to be satisfactory.

The 50 ml. Erlenmeyer flask containing a dry film of the C_2 to C_8 sodium salts was removed from the oven, corked, allowed to cool, and extracted within 12 hr. One drop (0.03 ml.) of 10 *N* sulphuric acid was added and spread quickly and completely over the bottom of the flask with a glass rod. Two circles of coarse filter paper (12 mm. diameter, Reeve Angel, No. 202) were added and moved rapidly but firmly round the bottom of the flask. This latter operation

* *Neish (13, 14) has described recently a method for transferring acids in aqueous solution to a silica (Celite) column.*

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was greatly facilitated when the end of the glass rod was not fire-polished. One milliliter of dry CB_1 was then run into the flask and swirled gently once or twice. The circles were removed from the flask with stainless steel forceps and placed in a small funnel (Fig. 2), which contained already a single circle of filter paper wetted down with dry CB_1. A small dropper was used for washing the forceps and stirring rod. The solution in the flask was then poured at a moderate rate into the funnel, through which it passed into a 3 ml. volumetric flask. The Erlenmeyer flask contents and the filter paper were further extracted with 1.0 and 0.5 ml. portions of dry CB_1. After it was made to volume, the extract was ready for analysis. As a rule 2 ml. was placed on the column and 1 ml. was titrated in order to check the efficiency of the extraction.

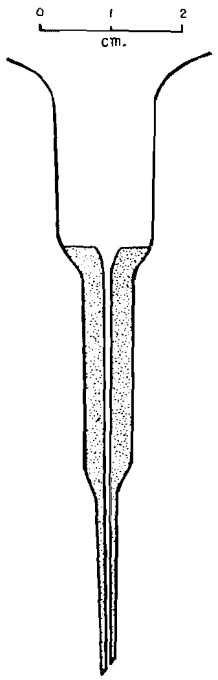

FIG. 2. *Microextraction funnel.*

When judged by titration values alone, C_3 to C_8 acids were extracted completely from aqueous solution by this method. Acetic acid extraction was 95 to 96%, and quite constant. Subsequent chromatography of the extracts showed that some changes had occurred when the sodium salts were dried at 110°C. Mention of this point will be made later. The recovery of formic acid was so low (75%) that in this case the method is unreliable.

Preparation of Silica Columns

Although an external indicator (12) and fractional titration (11, 16) have been used for the detection of fatty acids as they are eluted from a chroma-

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tographic column, their detection by means of an internal indicator is simpler and more convenient. In addition, it is desirable that a column may be used more than once, and that it should be easy to prepare. It was with these points in mind that the following method was developed.

Water, alkali, and indicator were mixed with sufficient silica for 10 or more columns. The different solutions added are shown in Table I.

TABLE I

PREPARATION OF SILICA FOR STORAGE AT −20°C.

Column	Silica (gm.)	Indicator (0.2%) (ml.)	NaOH (0.1 *N*) (ml.)	Water (ml.)	Additions before slurrying*
Alphamine red *R***	20	10	8	3	0.7 ml. water
Bromocresol green	20	5	16	–	0.7 ml. NaOH

* *The* total *volume of water required for different preparations of silica may vary slightly.*
** *R–NH₄ indicator (8) (Alphamine red R (Herstein), Amend Drug and Chemical Corp., New York).*

The silica was mixed carefully with the ingredients shown and portions of the mixture corresponding to 2 gm. silica were weighed into small dry bottles which were stoppered tightly and stored at −20°C.* For the preparation of a column, the silica was poured from the small bottle into an evaporating dish or mortar. The last column in Table I shows the amount of water, or alkali solution, which it was necessary to add at this point to reach the full water capacity of the silica. After thorough mixing of the extra water or alkali, CB_1 was added in 5 ml. portions and the gel slurried. The slurry was poured into a glass tube (14 mm. internal diameter) and packed with gentle pressure. An alphamine red *R* and a bromocresol green column were prepared in this manner and joined in series. It may be mentioned that the techniques described by Neish (12) are helpful in obtaining evenly packed columns.

Two or three milliliters of CB_1 containing the acids to be analyzed was added to the upper (alphamine red *R*) column and pressure was applied by the simple arrangement described previously (4), until the solution had passed into the upper column. This was followed by two washings with 1 ml. portions of CB_1 and development of the chromatogram with the same solvent. Valeric and higher acids passed quickly into the second (bromocresol green) column, which was considerably more alkaline than the first. When the butyric acid band reached the bottom of the alphamine red *R* column, the columns were separated and the two groups of acids were developed independently with CB_1. CB_{10} was used for the elution of propionic and acetic acids. Each column may be used three or four times, although the visual sensitivity of the alphamine red *R* column decreases gradually.

* *Storage at temperatures above 0°C. resulted in undesirable changes in the silica with respect to its water-holding capacity, together with increased threshold volumes and degree of "tailing" of the individual acids.*

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Separation and Determination of Acids

A typical example of the type of analysis for which the method may be used has already been given (4). However, in the elaboration of the method it was necessary to carry out a more detailed investigation of the behavior of the fatty acids on the columns under consideration.

From a study of the R_F values, Elsden (2) demonstrated that the rate of passage of a given acid through a silica column decreased with decreasing concentration of the acid. This observation was confirmed using threshold volumes instead of R_F (Fig. 3). In addition, we observed that the threshold volume of a given acid decreased in the presence of the next lower, or following acid (Fig. 3). It is apparent that these effects, if sufficiently strong, will lead to confusion in the identification of an acid by threshold volume or R_F value alone. Fortunately, neither effect is large enough to limit the usefulness of the method. It should be noted that the data shown in Fig. 3 were obtained by using $CB_{\frac{1}{2}}$ as the eluting solvent throughout. In an actual analysis this solvent is used only until the threshold volume of butyric acid is reached.

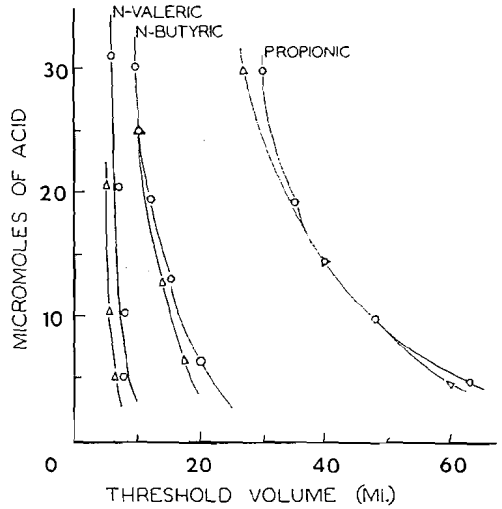

FIG. 3. *Relationship of threshold volume* to concentration: effect of one acid upon another.*
O *single acid.*
Δ *30 micromoles of the next lower acid also present.*
* *$CB_{\frac{1}{2}}$ was used as developing and eluting solvent.*

The efficiency of the chromatographic column in the separation of varying concentrations of the C_2 to C_8 acids in synthetic mixtures is shown by the results in Table II. In Expts. 1 to 8 the acid mixtures were prepared directly in CB_1; in Expt. 9 the mixture was prepared in water, distilled, dried, and extracted before application to the column.

It is apparent from the table that considerable variation in the relative proportions of acids is permissible except in the separation of small amounts of valeric from much larger amounts of butyric acid. Another point of interest

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TABLE II

DETERMINATION OF VOLATILE ACIDS IN SYNTHETIC MIXTURES

Experiment No.*	Micromoles of acid added and (in parenthesis) recovered						Total acid recovered (%)
	Octanoic	Hexanoic	Valeric	Butyric	Propionic	Acetic	
1	15.3 (*15.0*)	7.4 (*7.7*)	15.5 (*15.3*)	—	—	—	100
2	4.3 (*4.1*)	16.4 (*16.6*)	4.3 (*4.3*)	—	—	—	100
3	—	16.4 (*16.4*)	17.2 (*17.4*)	0.0 (*0.1*)	4.6 (*4.6*)	—	101
4	—	—	17.2 (*16.9*)	4.2 (*4.2*)	4.6 (*4.6*)	—	99
5	—	—	4.3 (*3.8*)	16.9 (*17.5*)	—	—	100
6	—	14.8 (*14.5*)	15.5 (*15.7*)	2.5 (*2.6*)	2.7 (*2.7*)	2.9 (*2.9*)	100
7	—	—	—	16.9 (*16.9*)	4.6 (*4.6*)	19.4 (*19.2*)	99
8	9.2 (*8.8*)	12.6 (*12.9*)	11.9 (*11.8*)	10.4 (*10.3*)	15.0 (*14.8*)	16.7 (*16.7*)	99
9	7.1 (*6.0*)	6.4 (*6.8*)	6.5 (*6.2*)	6.7 (*6.5*)	6.5 (*6.4*)	6.4 (*6.7*)	98

* *Acid mixtures in Expts. 1–8 were prepared in CB_1 and chromatographed directly. The mixture in Expt. 9 was prepared in 35 ml. of water, distilled, neutralized, dried, extracted into CB_1 and then chromatographed. In this experiment propionic and acetic acid recoveries were corrected for known losses during distillation and extraction (see text).*

in this table is the separation of subvisible amounts of butyric, propionic, and acetic acids. In general, 4 to 7 micromoles of hexanoic and valeric acids, and 3 to 5 micromoles of butyric, propionic, and acetic acids must be present if the appropriate band is to remain visible when the threshold volume of the acid is reached. Usually the sharper bands present at the top of the column during the initial separation permit the visual detection of somewhat smaller quantities. If the presence of an acid is suspected, even though the acid itself is not visible, it is usually possible to make the determination from a knowledge of the threshold volumes, and the volume of eluate necessary for the complete collection of the preceding acid. In Expt. 3, for example, butyric acid was absent. In analyzing this sample the hexanoic and valeric acids passed quickly from the alphamine red *R* column on to the bromocresol green column. The columns were divided after 21 ml. of solvent had passed through, that is, at the threshold volume for a subvisible amount of butyric acid (see Fig. 3) had this acid been present. Titration of the eluate preceding propionic acid then showed that butyric acid was absent. In Expt. 6, with a subvisible amount of butyric acid present, the same procedure was applied and a quantitative recovery of this acid was obtained. The same mixture contained amounts of propionic and acetic acids which were clearly visible when still near the top of the column but which were barely visible when their threshold volume was reached. These acids were also recovered quantitatively.

Expts. 1 to 8 demonstrate the efficiency of separation of pure acids which have not been subjected to the distillation, drying, and extraction required for unknown aqueous mixtures. As already reported (4) octanoic and heptanoic acids are not separated by this method and the separation of heptanoic from hexanoic acid is incomplete (80%). Expt. 9 shows the results obtained when the six acids were prepared in aqueous solution and submitted to the complete analytical procedure. Propionic and acetic acid recoveries were corrected for known losses in the distillation and extraction. The total recovery fell to 98%, with most of the loss accounted for in the octanoic acid fraction. This loss of

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octanoic acid occurs for the most part when it is dried (as the sodium salt) at 110°C. under the conditions described. No method for overcoming this difficulty has been found as yet.

Discussion

The choice of indicators for the columns was dictated by the following considerations. With bromocresol green, only limited concentrations of butanol may be used without excessive leaching of the dye. This renders the elution of the lower acids difficult. On the other hand, alphamine red *R* is not leached by comparatively high concentrations of butanol but unfortunately this indicator is not as sensitive as bromocresol green and may only be used over a limited alkali concentration range. Hence it was necessary to construct a composite column which made use of the chief attributes of each indicator.

Although paper chromatography has been used for the qualitative analysis of the volatile fatty acids (1, 7), it may be mentioned that the bromocresol green column alone is also suitable for this purpose. The silicas prepared in this laboratory, in addition to being reproducible, have been used successfully in other methods for C_2 to C_4 acids (12) and for C_5 to C_{10} acids (18).

In view of the disagreement which exists concerning the use of the term "partition chromatography" in describing phenomena of the type which have been presented (discussed in Reference 10), we have adhered for the present to the unmodified "chromatography." Nevertheless, it is clearly recognized that partition between solvents plays an important part in the separation of the C_2 to C_8 acids, despite the strong suggestion of absorptive effects shown by the curves in Fig. 3.

Finally, it may be emphasized that with a suitable silica and some experience in the preparation of columns, the chromatographic method is comparatively simple. The limits of analytical precision reside, not in the chromatographic separation, but in the associated techniques.

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STUDIES ON RDX AND RELATED COMPOUNDS

IV. THE BACHMANN OR COMBINATION PROCESS[1]

By H. L. Williams and C. A. Winkler

Abstract

The effect of varying the concentrations of nitric acid and ammonium nitrate on the yield of RDX has been determined at 35°C., using hexamine, hexamine mononitrate, and hexamine dinitrate. The activation energies for the formation of RDX from hexamine, hexamine mononitrate, and hexamine dinitrate were found to be approximately 11 kcal., 12.5 kcal., and 16.5 kcal., respectively.

Introduction

A study of the production of RDX from ammonium nitrate, paraformaldehyde, and acetic anhydride, reported in a previous paper (2), indicated that hexamine dinitrate and nitric acid were intermediates in the reaction. Conversion of these intermediates to RDX presumably corresponds to the reactions involved in the Bachmann process (1), in which the starting materials are hexamine, nitric acid, ammonium nitrate, and acetic anhydride in a glacial acetic acid medium and the reaction temperature is about 70°C.

Studies were therefore continued using the Bachmann type of reaction system, since this permitted appropriate solutions of known concentrations of hexamine, nitric acid, and ammonium nitrate to be used. The present study was made to determine the effect of varying the concentrations of ammonium nitrate and nitric acid at 35°C., where kinetic studies are possible, and to determine the activation energies associated with certain simple steps possible in the conversion of hexamine to RDX.

Results and Discussion

The apparatus and techniques used were similar in all essential respects to those described previously (2).

Experiments to determine the effect of nitric acid concentration on yield, and of ammonium nitrate concentration on rate and yield of RDX were made in different types of reaction media. One of these consisted of absolute nitric acid in acetic anhydride, and two others contained absolute nitric acid in acetic anhydride – acetic acid mixtures of which the acetic anhydride contents were 50% and 87%. In three other analogous reaction systems the acetic anhydride was replaced by propionic anhydride, and the acetic acid by propionic acid. A few experiments were also made with nitrogen pentoxide in acetic anhydride.

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While the different systems differed in details of behavior with variation of reactant concentrations, the general type of behavior observed is indicated by the results shown in Fig. 1. The rate and yield values were reproducible within about ±5%.

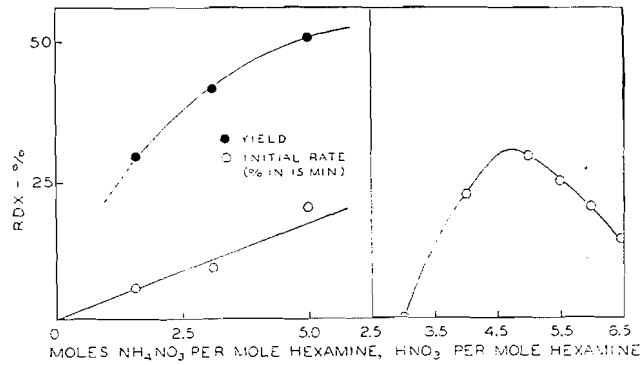

FIG. 1

The optimal nitric acid concentration at 35°C. for various systems studied are given in Table I. These values remained essentially unaltered when the ammonium nitrate concentration was changed from 1.5 to 5 moles per mole hexamine. No marked difference in rate of formation or yield of RDX was observed when nitrogen pentoxide rather than absolute nitric acid was used. Some experiments with copper nitrate trihydrate showed that it too could serve efficiently as the source of nitric acid.

TABLE I

OPTIMAL NITRIC ACID CONCENTRATIONS AT 35°C.

	Optimal nitric acid concentration, moles/mole hexamine			
	50% anhydride	87% anhydride	100% anhydride	N_2O_5 in anhydride
Acetic anhydride				
Hexamine	4.5	3.5	3.5	3.5
Hexamine mononitrate	–	–	2.5	–
Hexamine dinitrate	1.5	2.0	2.0	3.0
Propionic anhydride				
Hexamine	7.0	5.5	7.5	–
Hexamine dinitrate	4.0	4.5	5.5	–

The minimal concentration of ammonium nitrate for maximal yield of RDX was found to be between 5 and 6 moles per mole hexamine or its mono- or dinitrate, in the various media used.

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Throughout the study, a marked superiority of acetic over propionic anhydride was readily recognized in respect of both rate of production and yield of RDX (Table II), although in the general trends of rate and yield with variation of nitric acid and ammonium nitrate there was little to distinguish the behavior of the two anhydrides.

TABLE II

RATES OF PRODUCTION AND YIELDS OF RDX AT 35°C. IN ACETIC AND PROPIONIC ANHYDRIDE – ACID SYSTEMS

	50% anhydride		87% anhydride		100% anhydride		N_2O_5 in anhydride	
	Rate*	% Yield	Rate*	% Yield	Rate*	% Yield	Rate*	% Yield
Acetic anhydride								
Hexamine	6.2	34	5.6	34	6.8	25	5.6	28
Hexamine dinitrate	6.8	28	18	65	14.6	56	12.8	51
Propionic anhydride								
Hexamine	2.2	7.9	2.8	14	4.5	16	–	–
Hexamine dinitrate	1.1	18	3.4	31	5.6	29	–	–

* *Rates were determined from smoothed reaction-time curves and are expressed as per cent RDX formed after 15 min. reaction. Both rates and yields are calculated on the assumption that one mole of hexamine can theoretically produce two moles of RDX. Optimal concentration of nitric acid throughout.*

The superiority of acetic anhydride may be partly ascribed to a solvent effect (2), but is probably concerned to a large extent with the production of the active nitrolyzing agent. That anhydride is involved in this way is indicated by the observation that prolonged azeotropic distillation with benzene of reaction mixtures containing optimal hexamine, nitric acid, and ammonium nitrate concentrations in acetic acid, nitromethane, or nitrobenzene, failed to yield even traces of RDX. If, however, as little as 8% acetic anhydride was added to such dried mixtures, appreciable yields of RDX were obtained. It seems unlikely that the active nitrolyzing agent produced in the presence of anhydride is acetyl (or propyl) nitrate (3), but it might be nitrogen pentoxide or a cationic agent resulting from dehydration of nitric acid (cf. 4).

Activation Energies for the Conversion of Hexamine, Hexamine Mononitrate, and Hexamine Dinitrate to RDX

Rates of RDX formation were determined at different temperatures using hexamine, or one of its nitrates, in the presence of the corresponding optimal amounts of nitric acid and ammonium nitrate. Initial rates of RDX formation were used for calculating the activation energies with an error estimated to be of the order $\pm$ 1.0 kcal.

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The activation energies obtained in the temperature range 20° to 40°C., from rates determined at 5° intervals, were:

Hexamine 11 kcal.
Hexamine mononitrate 12.5 kcal.
Hexamine dinitrate 16.5 kcal.

While there is probably no significant difference between the first two values, the value for hexamine dinitrate was significantly higher. These activation energies would seem to indicate that hexamine dinitrate is not an intermediate in the conversion of hexamine to RDX by the Bachmann reaction at 35°C. There remain the possibilities that neither nitrate, or alternatively that the mononitrate, is involved in this reaction. It is the intention to present evidence in favor of the second possibility in a subsequent paper dealing with the thermochemistry of the system.

Acknowledgment

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A DILUTION EFFECT IN REACTIONS BETWEEN DIPOLAR MOLECULES IN SOLUTION[1]

By Osias Bain[2] and Cyrias Ouellet

Abstract

A study has been made of the variation of the reaction rate constant with increasing dilution in the case of three reactions between pairs of dipolar substances in ethanol solution. The reactions examined were those between aniline and 2,4-dinitrochlorobenzene, *p*-toluidine and 2,4-dinitrochlorobenzene, and *p*-toluidine and 2,4-dinitrobromobenzene. As the concentrations of the reactants in the first two cases are increased 50-fold, the bimolecular velocity coefficient decreases by approximately 12% in the case of the first reaction, and by 7% in the case of the second one. The rates decrease sharply as the solubility limits of the products in ethanol are approached, while they become relatively constant as high dilutions are attained.

Introduction

In kinetics, the name given to the variation in the constants of the Arrhenius equation, viz. k, A, and E as a function of a change in initial concentration of the reactants, is the 'dilution effect'. The dilution effect has been experimentally studied and theories have been developed for ion–ion, ion–dipole, enzyme, and chain reactions, as well as for unimolecular decompositions (8). Apart from their possible significance in the interpretation of reaction mechanism and solvent effects, these dilution effects are of interest because they may have to be taken into account in the comparison of the rates of a reaction in different solvents. We are here concerned with the dilution effect in the case of reactions between two dipolar substances.

The bimolecular velocity coefficient of reactions between alkyl halides and ions in hydroxylic solvents increases as the dilution is increased, often tending to a limiting value at high dilutions which is from two to four times as great as the value found at a concentration of one gram mole per liter. Thus Hecht and Conrad (6) found that the rate of the reaction between methyl iodide and sodium ethoxide in ethanol solution at 36°C. was doubled when the dilution was increased from 2 to 100 liters per mole. Acree and Robertson (1) interpreted these phenomena in terms of the dual hypothesis and derived a relation of the type

$$k = k_m + \alpha(k_i - k_m)$$

where k_i and k_m are the reactivities of the ion and of the undissociated molecule, and α is the degree of ionization. Later workers, e.g. Mitchell (7) found that k_m was negligible in many reactions of this type, and thus concluded that the bimolecular velocity coefficient calculated on the basis of the concentration of the reactive ion rather than on the total concentration of base was independent of dilution.

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[2] *Holder of a Bursary and a Studentship under the National Research Council of Canada.*

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The observation of a dilution effect in a dipole–dipole reaction where a is assumed to be negligible appears to have been first made by Rheinlander (11) in 1923. Rheinlander in measuring the rates of reactions between several aromatic compounds of the type $C_6H_3(NO_2)_2X$ with aniline and methylaniline in ethanol, observed in the case of 2,4-dinitrobromobenzene that when the concentration of the halide was kept constant and that of the base increased, the value of k diminished. When that of the halide was increased the value of k also diminished, although more slowly. This same observation was later confirmed for analogous reactions by van Opstall (13) and by Peacock and Singh (10). The latter authors investigating the reaction between several aromatic amines and 2,4-dinitrochlorobenzene in ethanol solution found that a decrease in velocity of 20% and an increase in the energy of activation of about 500 cal. per mole was in certain cases found to attend a doubling of the concentration. The dilution effect thus measured by these authors was examined over a small range of variation of concentration and was incidental to a study of the effect of various functional groups on the reaction rate.

The present work was initiated with the view of accurately determining the dilution effect in reactions of the type examined by Peacock, and over a wide range of concentrations. Although the investigation could not be further extended, the results, in spite of their limited scope, are presented as a contribution to the experimental data on the subject.

Experimental

Examining the rate of reaction between aniline and 2,4-dinitrochlorobenzene (I), *p*-toluidine and (I), and *p*-toluidine and 2,4-dinitrobromobenzene (II) in ethanol solution over a concentration range varying from 1 to 50 on a relative scale necessitated the use of large volumes of ethanol at the low concentrations, in order to secure a significant accuracy in the determination of k. Commercial ethanol was refluxed for several hours with silver nitrate and potassium hydroxide to remove aldehydes. In order to remove the small amount of water present an azeotropic distillation with about 15% benzene by volume was carried out. After distilling off the initial ternary azeotrope through a 30-plate bubble-cap column, the binary azeotrope benzene–ethanol was distilled off until the index of refraction of a distillate sample equalled 1.3595 for the sodium D-line at 25°C. The remaining solvent, approximately 50% by volume of the original mixture, had an index of refraction $n_D = 1.3595$ at 25°C., which is that of absolute ethanol at 25°C. The binary azeotrope was then utilized in removing water from a fresh sample of commercial absolute alcohol.

According to the data of Barbaudy (2), the purity of the solvent is estimated to be in excess of 99.6% ethanol, the principal impurity considered to be benzene. It is notable that both benzene and water, together and separately, raise the index of refraction of ethanol, the former linearly throughout the entire range of concentration, and the latter attaining a maximum $n_D = 1.3629$ at close to 80% ethanol at 25°C.

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Merck's acetanilide was saponified with sodium hydroxide, and the resulting aniline was steam-distilled, extracted with ether, and fractionally distilled, setting aside the first and last quarters. It was kept at all times in the dark, and coloration was very slight.

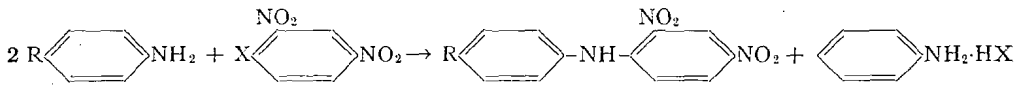
Merck's *p*-toluidine was crystallized from petroleum ether. The product melted sharply at 43.6°C., and was kept also in the dark. Eastman Kodak's 2,4-dinitrochlorobenzene was decolorized with charcoal and subsequently crystallized from a methanol–ethanol solution. The product had a melting point of 50.8°C. Brickman's 2,4-dinitrobromobenzene was crystallized from a methanol–ethanol solution, the product melting at 71.8°C.

The reactions were carried out in Kimble volumetric flasks of 100, 250, and 500 ml. capacity, suspended in a 110 liter constant-level water bath whose temperature was constant to 0.01°C. The temperature of the bath was read on a certified thermometer of the Bureau of Standards. The dilution effects were measured at 35.07°C.

Solutions of I, II, and of *p*-toluidine were prepared by weighing the reactants and dissolving in ethanol to the required strength in a volumetric flask. Aniline solutions were approximately prepared, and these were then volumetrically estimated by means of a titration with a standard solution of potassium bromate, by the method of Riedel (12).

A reaction was initiated by adding a determined volume of one reactant solution to a determined volume of the other, both already at the temperature of the water bath, and, as quickly as possible, followed by the adjustment of the volume to the mark with ethanol. The flask was then well agitated. The timing was started after one half of the aniline or *p*-toluidine solution had been added to the solution of the halide. Only one analysis was performed per experiment, since at high dilutions, there was relatively little product formed. Reactions were performed in duplicate and halted at from 10% (high concentration region) to 40% (low concentration region) completion.

The three reactions occurring are



R = H	X = Cl	(1)
R = CH_3	X = Cl	(2)
R = CH_3	X = Br	(3)

The above reactions are of the second order (10, 11), following the law

$$\frac{dx}{dt} = k(a - 2x)\,(b - x).$$

where x is the concentration in gm–ion per liter of the halide ions produced, a and b are the initial concentrations in mole per liter of the amine and the

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dinitrohalobenzene respectively. According to Rheinlander (11) and Peacock and Singh (10), these reactions proceed in two steps. First one molecule of the amine attacks a molecule of the 2,4-dinitrohalobenzene forming 2,4-dinitrodiphenylamine or 2,4-dinitro (4′-methyl) diphenylamine plus the hydrogen halide. An additional molecule of the amine now reacts with the hydrogen halide molecule formed at a rate far greater than in the first step. The rate-determining step is the first one.

Analyses of the halide ions produced by the reaction were performed by precipitating with silver nitrate and weighing as silver chloride or bromide. A reaction was terminated by inverting the flask containing the reaction mixture into a beaker containing dilute silver nitrate solution and a dilute solution of nitric acid, both in slight excess. The flask was then rinsed thoroughly by washing with water and benzene. It was verified that no detectable halide ions were produced from the 2,4-dinitrohalobenzene in acid aqueous medium.

In the case of the reaction between aniline and I, the molarities of the aniline solutions were approximately twice those of the solutions of I. In view of the precision sought an expanded version of the following classical equation was used:

$$k = \frac{1}{t(a - 2b)} \cdot \ln \left[\frac{b(a - 2x)}{a(b - x)}\right], \tag{2}$$

where a, b, and x are defined as above, and t is the time measured in minutes.

Expanding the logarithm term,

$$k = \frac{A - B}{t(a - 2b)} \cdot \left[1 + \frac{1}{2}(A + B) + \frac{1}{3}(A^2 + AB + B^2) + \ldots\ldots\right] \tag{3}$$

where $$A = \frac{a - 2b}{a - 2x} \quad \text{and} \quad B = \frac{a - 2b}{a}. \tag{4), (5}$$

If $\frac{a}{2} = b \pm (5\%$ of $b)$, then accuracy in k to five significant figures is obtained with the first two terms of the above expansion. There results

$$k = \frac{2x}{ta(a - 2x)} \cdot \left[1 + \frac{(a - x)(a - 2b)}{a(a - 2x)}\right]. \tag{6}$$

In the case where $\frac{a}{2} = b$, the above equation reduces to

$$k = \frac{2x}{ta(a - 2x)}. \tag{7}$$

Results

The analytical data and the calculated values of the constant k for various initial concentrations of the reactants are given in Tables I, II, and III. In Fig. 1, kt is plotted vs. t in the case of the reaction between aniline and I, where the concentration of the former is initially 0.3218 M and that of the latter

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TABLE I

DILUTION EFFECT

REACTION BETWEEN ANILINE AND 2,4-DINITROCHLOROBENZENE (I)

Aniline conc., mole/l.	I conc., mole/l.	Time, min.	AgCl weight, gm.	Flask volume, ml.	Cl ions conc., gm-ion/l.	k (mean) $\times 10^3$ l.mole^{-1} min.$^{-1}$
0.006418	0.003200	12760.	0.0845	500	0.001178	7.13
0.006418	0.003200	12760.	0.0847	500	0.001182	
0.07945	0.04000	852.6	0.4609	250	0.01286	7.039
0.07945	0.04000	852.6	0.4635	250	0.01294	
0.1511	0.07700	222.5	0.2115	100	0.01476	7.025
0.1511	0.07700	222.5	0.2097	100	0.01463	
0.2424	0.1230	95.50	0.2380	100	0.01661	6.732
0.2424	0.1230	93.40	0.2323	100	0.01621	
0.3278	0.1600	79.45	0.3258	100	0.02274	6.336
0.3278	0.1600	79.45	0.3251	100	0.02269	

TABLE II

DILUTION EFFECT

REACTION BETWEEN *p*-TOLUIDINE AND 2,4-DINITROCHLOROBENZENE (I)

p-Toluidine conc., mole/l.	I conc., mole/l.	Time, min.	AgCl weight, gm.	Flask volume, ml.	Cl ions conc., gm-ion/l.	k (mean) $\times 10^2$ l.mole^{-1} min.$^{-1}$
0.006400	0.003200	13256.	0.0751	250	0.002096	2.24
0.07000	0.03500	696.5	0.2628	100	0.01834	2.249
0.07000	0.03500	696.4	0.2619	100	0.01824	
0.1280	0.06400	350.6	0.4549	100	0.03174	2.192
0.1280	0.06400	350.7	0.4547	100	0.03173	
0.2360	0.1180	145.7	0.7209	100	0.05029	2.152
0.2360	0.1180	133.3	0.6812	100	0.04752	
0.2800	0.1400	132.5	0.8912	100	0.06219	2.155
0.3200	0.1600	135.2	1.1004	100	0.07676	
0.3200	0.1600	86.7	0.8428	100	0.05880	2.109
0.3200	0.1600	77.8	0.7884	100	0.05500	

TABLE III

DILUTION EFFECT

REACTION BETWEEN *p*-TOLUIDINE AND 2,4-DINITROBROMOBENZENE (II)

p-Toluidine conc., mole/l.	II conc., mole/l.	Time, min.	AgBr weight, gm.	Flask volume, ml.	Br ions conc., gm-ion/l.	k (mean) $\times 10^2$ l.mole^{-1} min.$^{-1}$
0.07000	0.03500	551.2	0.3766	100	0.02006	3.467
0.07000	0.03500	551.2	0.3757	100	0.02001	
0.1280	0.06400	215.8	0.5840	100	0.03110	3.422
0.2360	0.1180	114.0	1.0501	100	0.05591	3.351
0.2360	0.1180	105.6	1.0094	100	0.05374	

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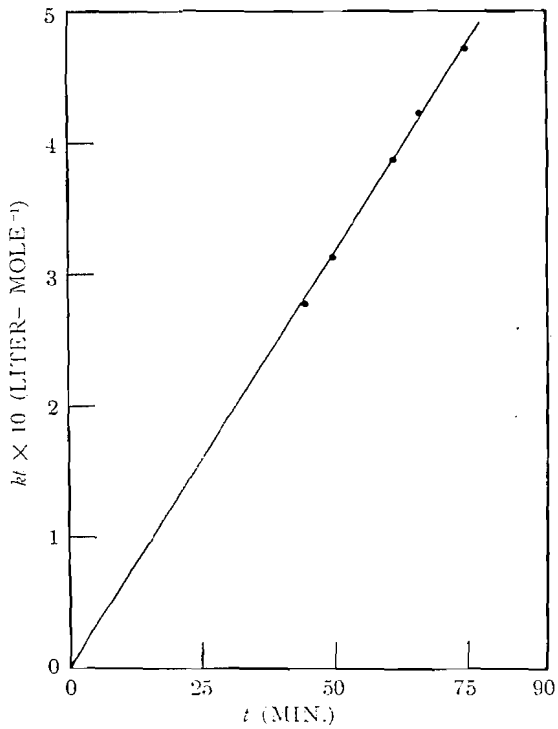

FIG. 1. *Reaction between 0.16 M 2,4-dinitrochlorobenzene and 0.3218 M aniline in ethanol solution at 35.07°C.*

0.1600 *M*. The linear curve up to 13% completion of the reaction indicates that the reaction follows the second order law up to that region. The slope of the curve, k, is equal to 6.34×10^{-3} l. mole^{-1} min.$^{-1}$ for this reaction.

Discussion

The dilution effects in the three reactions investigated are illustrated in Figs. 2, 3, and 4, where the values of k are plotted against the concentrations of the dinitrohalobenzene. It is seen that k decreases with increasing concentration. The decrease is 3.3% for a 3.4-fold increase in concentration in the case of the reaction *p*-toluidine–II; 6.6% for a 50-fold increase in concentration in the case of the reaction *p*-toluidine–I, and 11% for a 50-fold increase in concentration in the case of the reaction aniline–I.

The values of k in the reactions with I level off at low concentrations where the solution tends toward ideality; they decrease sharply at the higher concentrations, where the saturation point of the 2,4-dinitrohalobenzene in ethanol is approached. However, the effects are so small that the exact forms of the curves cannot be obtained.

In principle, it is difficult to apply the second-order law in the presence of a dilution effect, since the rate constant or the activity coefficients of the reactants may be expected to vary during the course of the reaction as the con-

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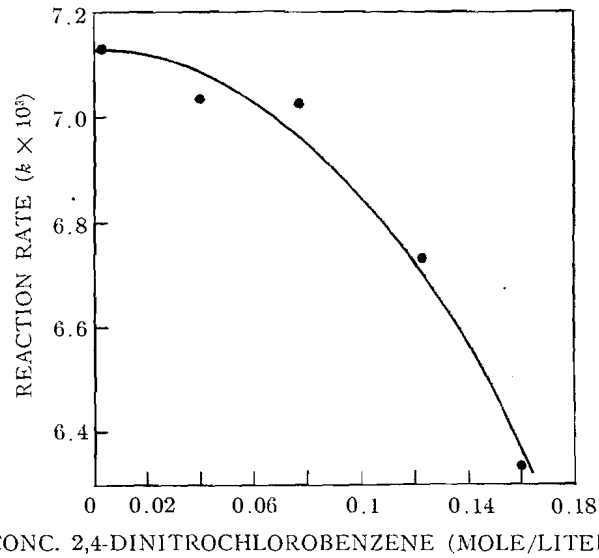

FIG. 2. *Dilution effect in the reaction between 2,4-dinitrochlorobenzene and aniline in ethanol solution at 35.07°C.*

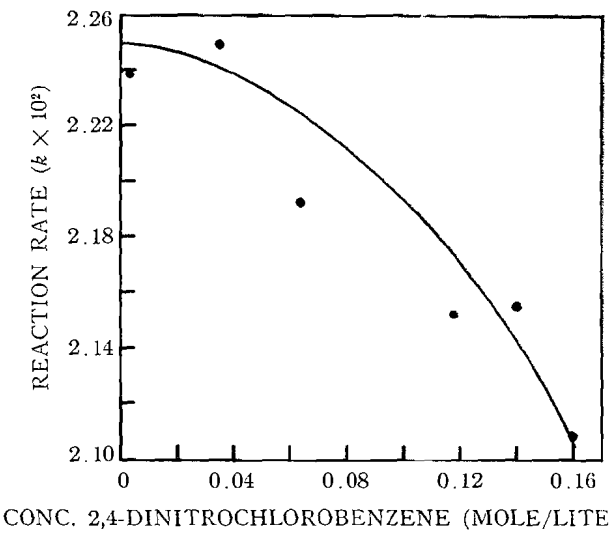

FIG. 3. *Dilution effect in the reaction between 2,4-dinitrochlorobenzene and p-toluidine in ethanol solution at 35.07°C.*

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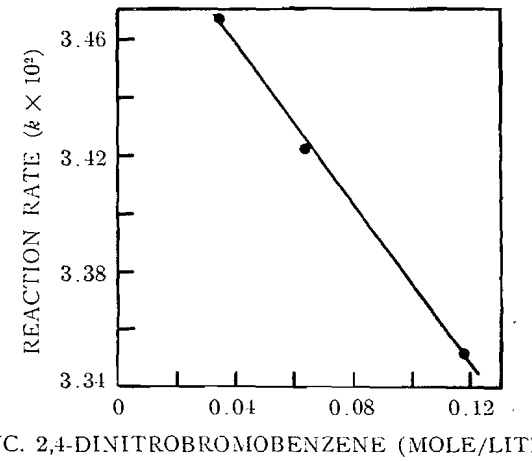

FIG. 4. *Dilution effect in the reaction between 2,4-dinitrobromobenzene and p-toluidine in ethanol solution at 35.07°C.*

centrations of the reactants decrease. However, if the dilution effects were caused by certain groups in the reacting molecules whose concentration in the medium remains constant because these groups are not destroyed in the reaction, then k would be affected by the initial concentrations only and the second-order law would hold. In our reactions, the nitro groups could play such a role. In fact, the works of Rheinlander (11) and Peacock and Singh (10) and some of our results (Fig. 1) suggest that k remains essentially constant during a reaction of the type with which we are concerned. Owing to the poor solubility of the products, our experiments at the higher concentrations, where a drift in the value of k would be detectable, had to be stopped at about 12% conversion, and the second-order law was taken as a sufficient approximation.

A dilution effect of opposite sign to the one reported here has been found by Peacock and Singh (9) for the reaction between benzyl chloride and aniline at 35° and 40°C. in ethanol. They observed a rise in the reaction rate of 29% at 35°C. and 18% at 40°C. for a doubling of the concentration. It thus appears that the roles of the solvent ethanol in this type of reaction between an aryl amine and an aryl halide are dissimilar, being dependent upon whether the halogen atom is attached directly to the benzene nucleus, although activated by two nitro groups in *o*-, *p*-positions, or whether it is attached to the benzene nucleus through a methylene group.

A theory of the dilution effects should take into account such constitutional factors together with the physical influence of dipole–dipole association, and the degrees of solvation of both the reactants and the activated complex. That dipole-swarming can lead to either a positive or a negative dilution effect is shown by Hartmann's theory (3, 4, 5) which has been applied to the reaction between pyridine and methyl iodide. For the reactions studied in this work, it seems that Hartmann's theory would predict a curvature opposite to that

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shown in Figs. 2 and 3. However, the very small variations of k in our case preclude a fruitful application of Hartmann's equations since even the sign of the effect they predict depends rather critically on certain constants such as molecular radii which are not known with enough precision.

Acknowledgments

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Résumé

On a étudié l'effet de la dilution sur la vitesse de réaction entre trois paires de substances dipolaires en solution dans l'éthanol, soient: entre l'aniline et le 2,4-dinitrochlorobenzène, la para-toluidine et le 2,4-dinitrochlorobenzène, la paratoluidine et le 2,4-dinitrobromobenzène. Dans les deux premiers cas une augmentation de concentration d'un facteur de 50 produit une diminution de la constante d'environ 12% et 7% respectivement. Pour la troisième réaction, la concentration n'a pu être augmentée que d'un facteur 3.4 à cause de la faible solubilité du 2,4-dinitrobromobenzène dans l'éthanol: il en est résulté une diminution de 3% dans la constante de vitesse. En général les constantes décroissent rapidement lorsqu'on approche la limite de solubilité des réactifs: par contre elles varient peu aux grandes dilutions.

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ISOTOPIC EXCHANGE REACTIONS IN THE SYSTEM BROMINE - BROMATE - HYPOBROMOUS ACID[1]

By R. H. Betts and Agnes N. MacKenzie

Abstract

Radiotracer studies with Br^{82} show that bromine and bromate ion in perchloric acid solution undergo isotopic exchange at a measurable rate. The kinetics of the process suggest that secondary chemical reactions occur, leading to the formation of significant concentrations of hypobromous acid in the system. The isotopic exchange between hypobromous acid and bromine is complete within the time required to separate these species.

Introduction

At chemical equilibrium in any system, the rates of forward and reverse reactions are by definition equal. If the kinetics of these reactions are known separately, it is possible, by application of the Law of Mass Action, to predict both the position of equilibrium and the rates of the forward and reverse reactions at equilibrium. By the use of radioactive tracers, one may in many cases measure the rates of such compensating reactions. A comparison of these rates with those predicted from the Mass Action Principle may furnish valuable checks on proposed reaction mechanisms. In addition, these comparisons may uncover anomalies inaccessible to, or undisclosed by, more conventional experimental techniques.

The present study deals with the isotopic exchange reaction between bromine and bromate ion in acid solutions, using Br^{82} as a radiotracer. Isolated qualitative references to this exchange reaction occur in the chemical literature, e.g., Libby (8) reported that this couple undergoes exchange at a measurable rate. However, no systematic investigation has been hitherto reported. It is convenient to summarize here the existing nonequilibrium studies as an essential background for much of the subsequent discussion.

In moderately acid solution, bromate ion is believed to react quantitatively and rapidly with bromide ion to form bromine. The stoichiometry of the reaction is:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (1)$$

This reaction as written involves 12 reacting entities, and obviously must proceed in a stepwise fashion. Hinshelwood (7) has suggested recently the following sets of consecutive bimolecular reactions:

$$HBr + HBrO_3 \rightarrow HBrO_2 + HOBr \qquad (2)$$

$$HBr + HBrO_2 \rightarrow 2HOBr \qquad (3)$$

$$3(HOBr + HBr) \rightarrow 3(Br_2 + H_2O) \qquad (4)$$

(The reverse reactions lead to exchange between bromine and bromate ion.)

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Partial substantiation of some of these postulated reactions has been obtained by other investigators. In 1936, Sclar and Reisch (11) found that in the presence of allyl alcohol (which rapidly removes bromine and hypobromous acid formed in the reaction) the rate law for the process was given by:

$$-\frac{d[BrO_3^-]}{dt} = k[H^+]^2\,[BrO_3^-]\,[Br^-] \qquad (5)$$

The stoichiometry of the reaction in the presence of allyl alcohol was:

$$BrO_3^- + 2Br^- + 3H^+ \rightarrow \text{Products} \qquad (6)$$

The kinetics of the rate-governing step thus correspond with Equation (2) postulated by Hinshelwood, while the stoichiometry of the process suggests that in the presence of allyl alcohol, the reaction stops at hypobromous acid (sum of Equations (2) and (3) above).

More recently, Young (14) in his studies of the hydrogen peroxide – bromate reaction, found that his data could be interpreted best by assuming that Reaction (3) above is rapid. Reaction (4), involving formation of bromine and water from hypobromous and hydrobromic acids, has been generally assumed to be rapid, and indeed has been shown to be so in the present studies. The reverse of Reaction (4), i.e., hydrolysis of bromine, is also rapid, as is demonstrated by the practically instantaneous conversion of bromine into hypobromous acid on the addition of silver phosphate to remove hydrogen ions and bromide ions (12, 13). No pertinent data exist in the literature on the properties of either bromous or hypobromous acid, especially in the presence of a strong acid. However, the very fact that bromite compounds have never been surely identified in acid solutions argues for their extreme reactivity under these conditions.

Accordingly, it appears from this summary that whatever may be the intermediate products, the rate-controlling step in the over-all process is probably the reaction between bromide and bromate (Equation (2) above).

At chemical equilibrium, as we have stated, the rates of forward and reverse reactions are equal. Consequently, in the system containing bromine and bromate ion in dynamic equilibrium, whenever bromate is converted to bromine, an equivalent amount of bromine is converted to bromate. By incorporation of a radiotracer originally as bromine, it is possible to measure these rates. For a given set of conditions, the rate R in moles per liter per unit time for this exchange reaction is given by (5,10):

$$R = -\frac{2.303}{t}\,\frac{2[Br_2]\,[BrO_3^-]}{2[Br_2] + [BrO_3^-]}\,\log\,(1 - F) \qquad (7)$$

The square brackets refer to molar concentrations of the enclosed species, and F is the fraction of isotopic exchange at time t. The fraction of isotopic exchange F is given by the ratio of the specific activity of bromate to the mean specific activity of all forms of bromine. The term specific activity is defined conveniently in terms of experimental quantities by the ratio of the observed activity

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associated with a given species per unit volume of solution, to the concentration of that species in solution. Therefore F is given by:

$$\frac{\text{activity per ml. associated with bromate}}{\text{total activity per ml. of solution}} \times \frac{2[Br_2] + [BrO_3^-]}{[BrO_3^-]}$$

The factor *2* allows for the diatomic constitution of bromine. Further, if a single exchange path is operative, the rate is given also in more general terms by:

$$R = kf[Br_2]^n [BrO_3^-]^m [H^+]^p \quad (8)$$

where k is the rate constant and f involves the appropriate activity coefficient terms. By measurement of R as a function of these variables taken one at a time, it is possible to deduce the values of n, m, and p by straightforward methods (6). A more complete discussion of Equations (7) and (8) may be found elsewhere (6, p. 285; 9; 10).

Equation (8), together with the equilibrium expression for Reaction (1):

$$K = \frac{[Br^-]^5 [H^+]^6 [BrO_3^-]}{[Br_2]^3} \quad (9)$$

provides the quantitative link between the kinetics of the exchange reaction and the nonequilibrium measurements described earlier (7, 11). The work of Myers and Kennedy (9) on the iodine–iodate exchange reaction is an excellent example of how such correlations may be made. It will, of course, be understood that in order to make such comparisons, all intermediate species, e.g., bromous and hypobromous acid, must reach their equilibrium concentrations rapidly. Further, it is necessary that these entities be present in low concentrations relative to either bromine or bromate.

We describe in this paper some aspects of the kinetics of the bromine–bromate exchange reaction. In a succeeding paper (2), further chemical investigations are described dealing mainly with the role of hypobromous acid in this system.

Experimental

Materials

The original materials, potassium bromide, sodium bromide, and sodium bromate, were c.p. salts, further purified by two recrystallizations from doubly distilled water. Standard solutions of the last two compounds were prepared by accurate dilution of weighed portions with doubly distilled water. Reagent grade perchloric acid was used without further purification.

The radioactive tracer was prepared by neutron irradiation of 1 mgm. samples of potassium bromide in the NRX pile. After the 4.4 hr. Br^{80} had decayed, the sample was dissolved in dilute acid, and bromide precipitated as silver bromide. The precipitate was washed free of K^{42} activity, after which it was equilibrated for one hour at 80°–90°C. with added inactive sodium bromide solution. The sample was then cooled to room temperature, centrifuged, and the supernatant NaBr* solution removed. Portions of this tracer were used to

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"label" standard sodium bromide solutions. Measurements of the radioactive decay of this material indicated a half-life of 35.6 ± 0.5 hr., in good agreement with a recent value of 36.0 ± 0.1 hr. for Br^{82}(1).

Procedure

A measured volume (generally 1.00 ml.) of standard inactive sodium bromate in perchloric acid solution of the appropriate concentration was placed in a 1.5 ml. glass-stoppered tube. A solution of standard NaBr* (generally 0.20 ml.) was then added carefully so that virtually no mixing of the two solutions occurred during this operation. The tube was quickly stoppered, the top sealed with hot paraffin wax, and the contents thoroughly mixed. This method of closure was adequate to prevent loss of bromine. For each rate study, a set of up to ten such identical samples was prepared. The concentrations of bromine, bromate, and perchloric acid in each flask were calculated from a knowledge of the initial concentrations and volumes of reagents added. For this purpose, the stoichiometry of the reaction to form bromine was assumed to be given by Equation (1).

In later experiments, the required amount of *inactive* sodium bromide was added at zero time. After 96 to 100 hr., each tube was opened momentarily, 0.010 ml. of tracer solution added, and the tube then immediately re-stoppered. The time of exchange was, of course, measured from the time of addition of tracer.

In early experiments, four to six extractions with carbon tetrachloride were used to extract bromine from bromate after the desired exchange period. This procedure did not induce exchange in the system. Furthermore, separations made within one minute from zero time showed that not more than 0.1% of the total activity remained in the extracted aqueous phase, which indicated that at least 99.9% of the bromine was removed. Other tests showed that carbon tetrachloride did not react with bromate ion. On this basis, the separation procedure was believed to be satisfactory. In later experiments, benzene was substituted for carbon tetrachloride.

Analytical Methods

The total oxidizing power, i.e., bromine plus bromate ion, of representative solutions in each experiment was determined by reaction with excess potassium iodide, followed by titration of the liberated iodine with standard sodium thiosulphate. Similar titrations were made on the residual aqueous phase after extraction with carbon tetrachloride, as a measure of the concentration of bromate ion. For each series, these values were constant within experimental error (± 0.5%) and agreed within these limits with the concentrations calculated using Equation (1).

Measurement of Radioactivity

The total relative radioactive content of each sealed tube was determined by measurement of its associated γ-ray activity with a windowless Geiger–

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Mueller counter and associated scaling circuit. All tubes used were carefully selected to ensure geometrical uniformity of the samples. Each sample was placed in a fixed position relative to the counter in a lead "castle", and sufficient counts taken to reduce the probable statistical error to ± 0.8%. After extraction of the bromine, an aliquot of the residual aqueous phase was transferred to a clean tube, diluted to the same volume as the original solution, and the relative radioactive content associated with bromate measured as before. Corrections for coincidence losses, radioactive decay of the samples, and background were made in the usual way. From these data, the rate of the exchange reaction was calculated, using Equation (7). The over-all precision in the measurements of the rate was ± 2–3%.

Experimental Results and Discussion

Preliminary experiments showed that the rate of exchange was markedly accelerated by light. All experiments described in the present paper were made, therefore, in the absence of light at 25.0°C. unless otherwise stated.

When carbon tetrachloride was used to separate bromine from the solution, the apparent rate of the exchange reaction decreased continuously with time. The radiotracer was added at zero time. Fig. 1 is a typical plot of log $(1 - F)$

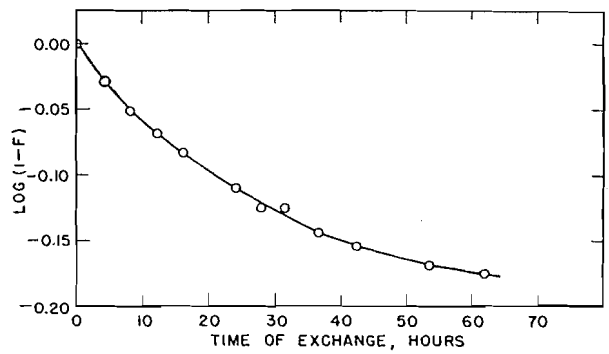

FIG. 1. *Rate function for isotopic exchange for a solution 1.66 M perchloric acid, 0.00235 M bromine, 0.0408 M sodium bromate. Carbon tetrachloride used as solvent for bromine.*

vs. t, for a solution 1.66 M perchloric acid, 0.00235 M bromine, and 0.0408 M sodium bromate. For an ideal isotopic exchange reaction, such a plot should yield a straight line, indicative of the fact that the reaction proceeds at a constant rate (10). From the slope of the plot in Fig. 1, it was calculated that the apparent rate of the exchange decreased from 6.6×10^{-5} to 9.8×10^{-6} moles per liter per hour, a sevenfold variation, for the time intervals 0–5 and 50–60 hr. respectively. Similar results, with, of course, different absolute values of the rates, were observed in the ranges 0.4–1.67 M perchloric acid, 0.0005–0.004 M bromine, and 0.003–0.082 M sodium bromate.

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Fig. 2 shows a typical plot of log $(1 - F)$ vs. t, when benzene was used to separate bromine from solution. Here again Br^{82} was introduced at zero time. This result was for a solution 1.67 M perchloric acid, 0.0825 M sodium bromate, and 0.00228 M bromine. The apparent rate of exchange still decreases with time as shown by the slight curvature of this plot, but the effect is much less pronounced than when carbon tetrachloride was used to remove bromine. The ratio between the rates for the periods 0–5 and 50–60 hr. was in this case 1.7, as compared with seven for the previous result. This behavior was observed over approximately the same range in concentration of reactants as recorded in the preceding paragraph.

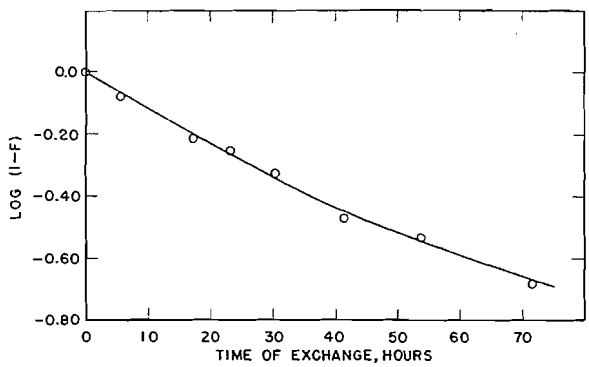

FIG. 2. *Rate function for isotopic exchange for a solution 1.67 M perchloric acid, 0.00228 M bromine, 0.0825 M sodium bromate. Benzene used as solvent for bromine.*

When the radioactive tracer was introduced 96–100 hr. after zero time, results of the type shown in Fig. 3 were observed. Benzene was used as the solvent for removal of bromine in these experiments. Since this plot is of the form prescribed for a reversible isotopic exchange reaction (10), this result suggests that the rate of exchange is constant for these conditions.

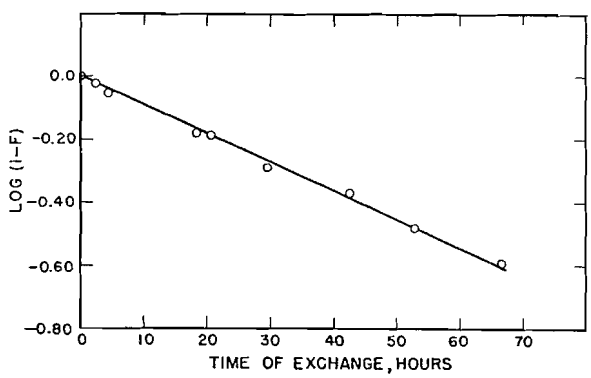

FIG. 3. *Rate function for isotopic exchange for a solution 1.67 M perchloric acid, 0.00237 M bromine, 0.0818 M sodium bromate. Tracer introduced after 100 hr.*

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Recently Norris (10) has discussed the interpretation of the kinetics of isotopic exchange reactions, and has given several possible reasons to account for a nonlinear relation between log $(1 - F)$ and t. Among these are: (1) nonequivalence of the atoms undergoing exchange, and (2) heterogeneous reaction in the system. In addition to these, at least four more possibilities suggest themselves. (3) The exchange reaction may be induced by the β- or γ-radiation of the tracer. (4) Two or more independent mechanisms of exchange may be operative, each proceeding at a different rate (6, p. 288). (5) Transient catalytic effects caused by labile impurities may be interfering. (6) Chemical equilibrium may not be established rapidly in the system, with consequent secular changes in the concentration of certain species.

Item (1) would require that the two bromine atoms in the bromine molecule be nonequivalent. This has been disproved by studies of the isotopic exchange reaction between bromine and bromide ion (4). Separate experiments in the present study showed that the results were unaffected either by changes in the surface area available to the system, or by changes in the absolute amount of radioactive material used as a tracer. Points (2) and (3) above may be thus excluded from further consideration. Effects related to transient catalysis by trace impurities would be expected to be nonreproducible, whereas no undue scatter of results was observed in duplicate experiments. In addition, careful repurification of the initial materials did not remove these effects. Accordingly, it is believed that subtle catalytic effects do not account for the observed results.

The possibility that two or more independent paths for exchange are operative cannot be excluded, but such an explanation is unlikely. The rationale of the following experiments, undertaken to clarify this point, is that the temperature coefficients of two such independent processes may reasonably be expected to differ significantly. The apparent rate of exchange was measured, for samples of the same solution, at three temperatures. From the slopes of the curves relating log $(1 - F)$ and t (Fig. 4), the rates of exchange and corresponding temperature coefficients were calculated as a function of time. The

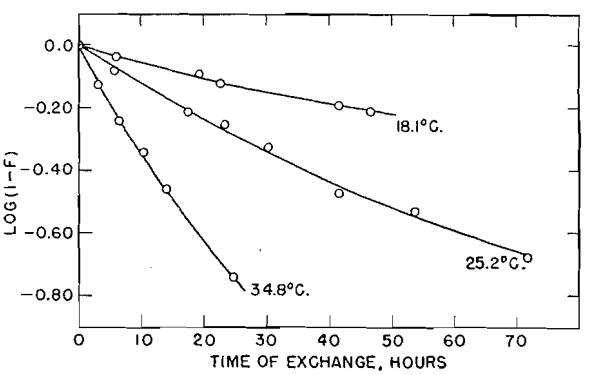

FIG. 4. *Effect of temperature on rate of exchange for a solution 0.0825 M sodium bromate, 0.00228 M bromine, 1.67 M perchloric acid. Tracer introduced at zero time.*

latter values were then compared with results calculated from similar experiments in which the tracer was added after 100 hr. (Fig. 5). For these latter conditions, the exchange proceeds at a constant rate, and by our hypothesis, only one reaction mechanism would be operative. We found in fact, no trend in the temperature coefficient with time, nor any significant differences in the mean temperature coefficient during the early stages compared with the average determined in the 100 hr. experiments. The average value of the energy of activation was 19.0 ± 1.5 kcal. per mole per degree. The mean value as a function of time differed by not more than 2.5 kcal. from this figure.

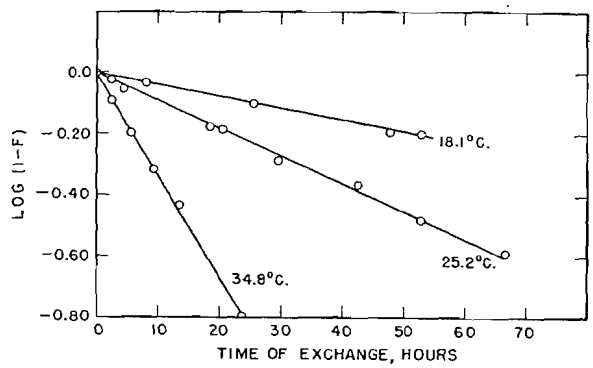

FIG. 5. *Effect of temperature on rate of exchange for a solution 0.0818 M sodium bromate, 0.00237 M bromine, 1.65 M perchloric acid. Tracer introduced after 100 hr.*

New experimental evidence presented in detail in a succeeding paper (2) indicates that Item (6) above is, in all likelihood, responsible for the anomalous behavior of this exchange reaction. Briefly, these experiments show that bromine and bromate are thermodynamically unstable with respect to formation of hypobromous acid, and moreover that the rate of attainment of this new equilibrium is finite and measurable. The kinetic expression for formation of hypobromous acid is (2):

$$\frac{d\,[\mathrm{HOBr}]}{dt} = \frac{k}{[\mathrm{HOBr}]} \tag{10}$$

An integrated form of this expression, $[\mathrm{HOBr}]^2 + k't + c$, indicates that the concentration of this species increases most rapidly in the early stages of the reaction, and more slowly thereafter. The stoichiometry of the process is:

$$(2H_2O) + 2Br_2 + HBrO_3 \longrightarrow 5HOBr \tag{11}$$

The chemical methods described earlier for the study of the chemical stability of this system did not disclose these reactions, since no net change occurs in the *average* oxidation number of all the bromine compounds during this process. Also, the conversion of a small fraction of bromate to hypobromous acid according to the stoichiometry of Equation (11) does not change the oxidizing power of the residual aqueous solution, after extraction by carbon tetrachloride, by an amount greater than the small experimental errors in the titrations themselves.

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We now show how these observations account satisfactorily for the anomalous behavior of the bromine–bromate exchange reaction.

The formation of macroconcentrations of hypobromous acid has at least two effects on the apparent rate of isotopic exchange between bromine and bromate ion. The first of these relates to the incomplete removal of HOBr* from the aqueous phase with carbon tetrachloride, and the second to the decrease in the concentration of bromide ion with increasing concentrations of hypobromous acid.

(*i*) Hypobromous acid is relatively inert toward carbon tetrachloride, as we have shown in separate experiments. Hence, extraction of the aqueous phase with this solvent does not remove all of this species formed by Reaction (11). Moreover, HOBr* will have at all times the same specific activity as Br_2*, as a result of the rapid interchange via the hydrolysis equilibrium[2]:

$$H_2O + Br_2^* \rightleftharpoons HOBr^* + H^+ + Br^- \qquad (12)$$

Thus the fractional exchange between bromine and bromate ion was not as great as indicated by measurement of the radioactive content of the aqueous phase after extraction with carbon tetrachloride. Since the rate of formation of hypobromous acid decreases continuously with time, the apparent rate of the exchange reaction will then appear to decrease also (Fig. 1).

(*ii*) Benzene has been shown recently to react rapidly and completely with hypobromous acid to form bromobenzenes (3). When this solvent is used to extract bromine, the residual activity in the aqueous phase is then associated only with bromate ion. This has been verified experimentally in the present study. The slow decrease in the rate of exchange still observed (Fig. 2) is believed to be caused by changes in concentration of one of the probable rate-determining species, i.e., bromide ion, concomitant with the formation of hypobromous acid. This can be shown by expressing the equilibrium relation for Equation (12) in the form:

$$[Br^-] = \frac{K_h[Br_2]}{[HOBr]\,[H^+]} \qquad (13)$$

K_h is the hydrolysis constant for bromine. Equation (13) indicates that provided the relative change in the concentration of hypobromous acid is much greater than for either bromine or hydrogen ion (a condition fulfilled in these studies) the concentration of bromide ion varies approximately inversely with the concentration of hypobromous acid.

Data which lend support to this interpretation are given in Table I.

The average rate of the exchange reaction (in arbitrary units) is given for the experiment shown in Fig. 2, for the indicated time intervals, together with the corresponding concentrations of hypobromous acid. The value enclosed in

[2]*Experimental evidence that equilibrium given by Equation (12) is reached and maintained soon after the start of the exchange reaction is provided by the following results. Radiotracer exchange experiments with either Br_2*–HOBr or Br_2–HOBr* showed complete exchange between these valence states within the time taken (minutes) for their separation.*

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TABLE I

RELATION BETWEEN RATE OF EXCHANGE AND CONCENTRATION OF HYPOBROMOUS ACID (DATA OF FIG. 2)

Time interval hr.	Rate of exchange (arbitrary units)	HOBr, $M \times 10^4$	$R \times$ [HOBr]
0- 5	12.2	(6.)	(77)
5-10	11.8	6.7	79
10-20	11.5	7.8	90
20-30	10.5	8.9	93
30-40	9.5	9.8	94
40-50	8.5	10.7	91
50-60	7.1	11.5	82
60-70	6.9	12.0	83

brackets is uncertain by about 20%, while the other values in column three are precise to $\pm$ 5%. A description of the method used to measure the concentration of hypobromous acid in the system is deferred to the next paper (2). In view of the approximations involved in the application of Equation (13), and of the uncertainties in the experimental quantities listed, the approximately constant values of the product $R \times$ [HOBr] shown in Table I may be taken as a satisfactory demonstration of the inverse relation between the rate of the exchange reaction and the concentration of hypobromous acid.

In the next paper (2), we show that after 100 hr., the concentration of hypobromous acid changes relatively slowly with time; for similar conditions, the rate of the exchange reaction (Figs. 3 and 5) is essentially constant. All of these observations may be taken as indirect confirmation of the rate-determining properties of bromide ion in the kinetics of the exchange reaction.

In conclusion, experiments were made in which the tracer was added after 100 hr., in order to obtain values of m, n, and p (Equation 8). The following rate law was found:

$$R = k[Br_2]^{0.3}\,[BrO_3^-]^{1.7}\,[H^+]^{1.1} \qquad (14)$$

The constant k has the value 0.023 moles$^{-2.1}$ l.$^{2.1}$ hr.$^{-1}$ at 25°C., and includes activity coefficient terms appropriate to an ionic strength of 1.75. An experimental error of $\pm$ 0.05 is assigned to the value of each exponent.

Equation (14) should be considered mainly as a convenient summary of the data, and no theoretical correlations between it and the Law of Mass Action are warranted. In fact, such correlations would be theoretically unjustifiable, since all intermediate species do not reach their equilibrium values rapidly and their concentrations are not negligible in comparison with either bromine or bromate ion. Even in the experiments in which tracer was added after 100 hr., chemical equilibrium is not reached (2). Nevertheless, the preceding discussion has shown that the results as a whole give semiquantitative information regarding the rate-determining stage in the exchange reaction. Further, the unexpected results have directed attention to certain aspects of the chemistry of bromine compounds previously unobserved.

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Acknowledgment

It is a pleasure for us to acknowledge the assistance of Rita K. Leigh during the preliminary experiments on this subject.

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FORMATION AND STABILITY OF HYPOBROMOUS ACID IN PERCHLORIC ACID SOLUTIONS OF BROMINE AND BROMATE IONS[1]

By R. H. Betts and Agnes N. MacKenzie

Abstract

Spectral and chemical data are presented which show that bromine and bromate ion in acid solution are unstable with respect to formation of hypobromous acid. At higher concentrations of hypobromous acid, the reaction is reversed, and this species decomposes relatively rapidly to bromine and bromate. Some aspects of the kinetics of these reactions are described, from which deductions are made regarding possible mechanisms of the two processes.

Introduction

In a preceding paper (2), the rate of isotopic exchange between bromine and bromate ion was shown to proceed in a manner consistent with the production of hypobromous acid in solution. In this paper are presented experimental results relating to the formation and stability of hypobromous acid in this system.

Experimental

Materials

The preparation of solutions of sodium bromide and sodium bromate has been described previously (2). Bromine solutions were prepared by dissolving c.p. bromine in doubly distilled water. Aqueous solutions of hypobromous acid were made from this latter solution by reaction with excess solid silver phosphate (5, 6):

$$3Br_2 + 3H_2O + Ag_3PO_4(s) \longrightarrow 3HOBr + 3AgBr + H_3PO_4$$

This was followed by vacuum distillation of the product in an all-glass still. Undue exposure of the product to light was avoided during the distillation. The distillate was stored in the dark at 5°C. Since aqueous solutions of this compound decompose slowly even under these conditions, new solutions were prepared as required. When freshly made, an 0.05 M hypobromous acid solution contained less than 4×10^{-4} M bromine or bromate ion.

Analytical Methods

Both chemical and physical methods were used for the analysis of solutions.

(*i*) Estimation of total oxidizing power (hypobromous acid + bromine + bromate ion) was made by titration with standard sodium thiosulphate after addition of excess potassium iodide. The sum of hypobromous acid + bromate ion was measured in the same way after extraction of bromine with a minimum amount of carbon tetrachloride. This solvent was purified by repeated treat-

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ments with aqueous potassium permanganate, followed by fractional distillation. Small corrections were applied to this titration to take account of the slight reaction which occurred between hypobromous acid and the organic solvent during the extraction of bromine. The concentration of bromate ion was estimated by addition of excess allyl alcohol, which removes both bromine and hypobromous acid by rapid addition at the double bond of the alcohol, followed by titration with sodium thiosulphate as before. From these data the concentrations of hypobromous acid and bromine were calculated by difference.

(*ii*) These chemical methods obviously suffer in accuracy when bromate ion is the major reducible species in solution. Therefore, many of the analyses for bromine and hypobromous acid were made by spectral methods, using a Beckman spectrophotometer. The extinction coefficients* for each species were measured separately over a range of wave lengths. The concentration of bromine and hypobromous acid in an unknown solution could then, in many cases, be calculated from a knowledge of the optical densities at wave lengths where bromate ion does not interfere (above 280 mμ, See Fig. 1). The method of calculation is in principle straightforward, involving the solution of simultaneous equations of the type:

$$\begin{aligned} D_a &= E_a(\text{HOBr})\ [\text{HOBr}] + E_a(\text{Br}_2)[\text{Br}_2] \\ D_b &= E_b(\text{HOBr})\ [\text{HOBr}] + E_b(\text{Br}_2)[\text{Br}_2] \end{aligned} \qquad (1)$$

The subscripts a and b denote any two suitable wave lengths above 280 mμ; the square brackets refer to molar concentrations. For 1 cm. cells, the factor l disappears (See footnote). In practice, it was convenient to solve several sets of such equations, and the final values were the average of several calculations for wave lengths from 310 to 395 mμ.

In the studies of the rate of formation of hypobromous acid, where the concentration of this species was low compared to that of bromine, calculations of the foregoing type were not always satisfactory, since uncertainities of the order of 1% in extinction coefficient of bromine introduced disproportionately large errors into the calculation of the concentration of hypobromous acid. *For these conditions*, a useful approximation was developed which gave changes (Δ[HOBr]) in the concentration of hypobromous acid from zero time, but did not give the absolute concentration of this species. This approximation is:

$$\Delta[\text{HOBr}]_t = \frac{1}{E_{310}(\text{HOBr})}\left[D_{310,\,t} - D_{310,\,0} \times \frac{D_{395,\,t}}{D_{395,\,0}}\right] \qquad (2)$$

The subscripts t and 0 refer to time, while subscripts 310 and 395 refer to wave lengths for which the absorption for hypobromous acid and bromine, respectively, are large relative to each other. (See Fig. 1.) The derivation of this

* *The extinction coefficient $E_\lambda(A)$ for species A at a wave length λ is defined by the relation:*

$$\textit{Optical density} = D_\lambda = l.E_\lambda(A).c = \log \frac{I_0}{I},$$

where l is the length of the absorption cell in cm., c is the molar concentration of species A, I_0 is the intensity of light transmitted by the appropriate blank cell, and I is the intensity of light transmitted by the solution containing species A.

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equation follows. The change in optical density at 310 mμ due to the formation of hypobromous acid, $\Delta D_{310,\ HOBr}$, is equal to the observed change *plus* the change for that wave length caused by the disappearance of bromine. This is given by:

$$\Delta D_{310,\ HOBr} = D_{310,\ t} - D_{310,\ 0} + D_{310,\ 0}\left[\frac{D_{395,\ 0} - D_{395,\ t}}{D_{395,\ 0}}\right] \qquad (3)$$

The term in brackets in a quantitative measure of the relative change in the concentration of bromine between zero time and time t; since the absorption at all wave lengths at zero time is due almost entirely to bromine, this term multiplied by $D_{310,\ 0}$ represents the change in optical density at 310 mμ due to the disappearance of bromine. Equation (3) simplifies to Equation (2) except for the factor $\frac{1}{E_{310}(HOBr)}$ which is, of course, required to express molar concentration in terms of optical density. The superiority of Equation (2) over Equation (1) lies in the fact that Equation (2) eliminates the large errors referred to earlier arising from slight uncertainties in the value of the extinction coefficients for bromine. It is emphasized, however, that Equation (2) does not permit the calculation of the absolute concentration of hypobromous acid, but only changes in the concentration of this species with time.

Procedure

Solutions of bromine and sodium bromate were prepared by addition of sodium bromide to excess sodium bromate dissolved in perchloric acid. Other solutions were prepared from the appropriate stock solutions by dilution. The samples for spectral analysis were prepared in 1 cm. Corex or silica optical cells, and stored in the cell compartment of the spectrophotometer at 25.0°C. in the absence of light. These cells were fitted with ground-glass stoppers, and sealed with wax to prevent loss of bromine. Optical measurements were made at intervals by comparison of the intensity of light transmitted by the test solution with that transmitted by an appropriately prepared blank matched cell. When chemical analyses were to be made, a series of samples was prepared and stored in the dark at 25.0°C. These were opened separately as required, aliquot portions analyzed, and the remainder of the solution discarded after analysis.

Experimental Results and Discussion

Fig. 1 gives the extinction coefficients of bromine, hypobromous acid, and bromate ion in 1.6–1.7 *M* perchloric acid. The general features of this spectrum of bromine agree with those in the literature (1), although the quantitative agreement is not exact for all wave lengths. The spectra of hypobromous acid and bromate ion agree, so far as they are recorded, with earlier measurements (3). It is evident from Fig. 1 that bromate ion does not interfere with the optical analyses for either of the other two species at wave lengths above 280 mμ. These spectra were rather insensitive to the concentration of perchloric acid, at least between 0.4–1.7 *M*.

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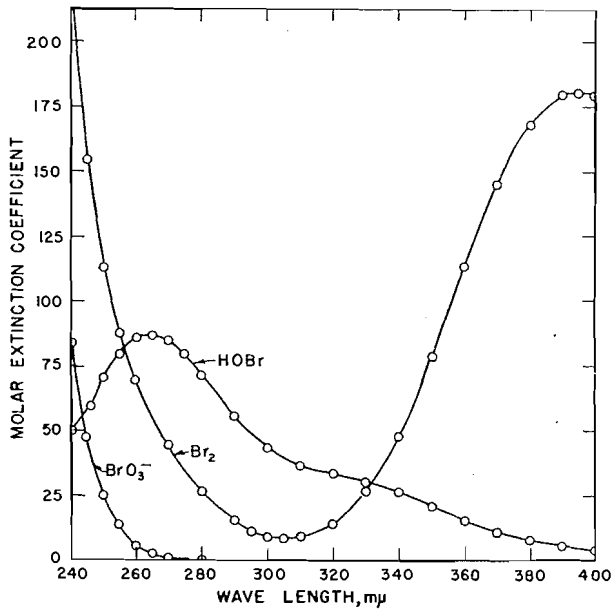

FIG. 1. *Extinction coefficients of bromine, hypobromous acid, and bromate ion in 1.66 M perchloric acid.*

(*i*) *Reaction between Bromine and Bromate Ion*

Fig. 2 shows a typical initial spectrum, and that after 217 hr., of a solution initially 0.0025 *M* bromine, 0.0825 *M* sodium bromate, and 1.66 *N* perchloric acid. This solution was prepared by addition of standard sodium bromide to excess sodium bromate dissolved in perchloric acid. The optical density increased with time at wave lengths less than 345 mμ, and decreased at longer wave lengths, pointing to the disappearance of bromine, and the appearance of a new species in solution. Fig. 3 gives for this same experiment a plot of the difference between the final optical density and that measured soon after the

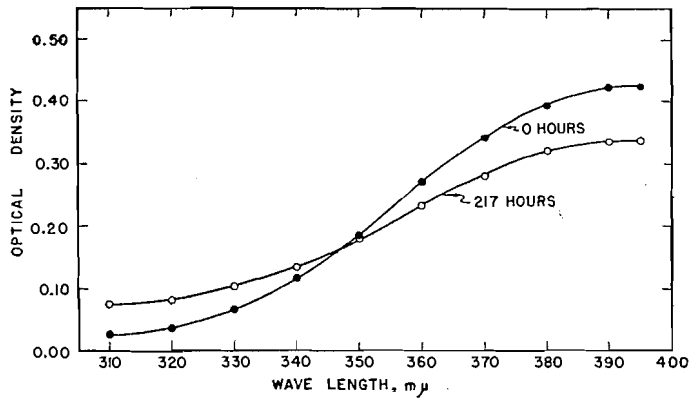

FIG. 2. *Initial and final spectra for a solution originally 0.0825 M bromate, 1.66 M perchloric acid, 0.0025 M bromine.*

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solution was prepared. Superimposed on this plot is a graph of the function $\frac{E(\text{HOBr})}{E(\text{Br}_2)}$ vs. wave length. At the wave length corresponding to zero change in optical density, the value of this ratio is 0.4. The area inscribed on the lower curve in Fig. 3 represents the probable error in this correlation. It is evident that this change in optical density with time of a bromine–bromate solution may be associated with a reaction in which bromine disappears and hypobromous acid is formed, according to:

$$2\text{Br}_2 \longrightarrow 5\text{HOBr} \qquad (5)$$

This stoichiometry accounts within experimental error for the observed changes in optical density at all wave lengths examined. In particular, in the region of 345 mμ, since $E_{(\text{HOBr})} = 0.4\ E_{(\text{Br}_2)}$, no change in optical density will occur as Reaction (5) proceeds. No precise measure of the corresponding small *change* in the concentration of bromate ion could be made in this system.

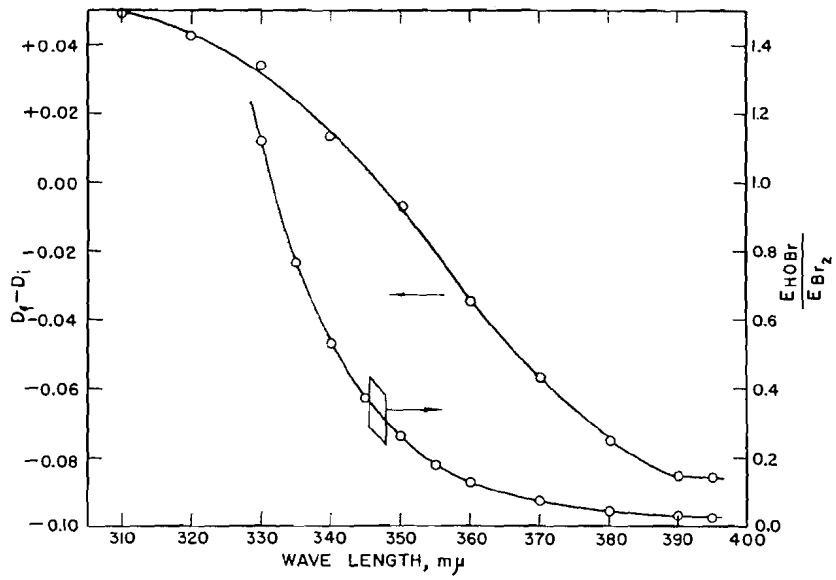

FIG. 3. *Difference between initial and final spectra shown in Fig. 2 (left scale); plot of ratio* $E_{\text{HOBr}}/E_{\text{Br}_2}$ *(right scale).*

In Fig. 4 are shown the changes in concentration of hypobromous acid as a function of time for a solution initially 0.0025 *M* bromine, 1.66 *M* perchloric acid, and 0.0825 *M* bromate ion. The calculations leading to this result were made by application of Equation (2) above to the optical data. It will be recalled that such a curve must pass through the origin because of the nature of the calculation. Since in Fig. 4 the square of the concentration of hypobromous acid is plotted vs. time, the essential linearity of this plot during the first 100 hr. leads to the rate law:

$$+\frac{d[\text{HOBr}]}{dt} = \frac{k}{[\text{HOBr}]} \qquad (6)$$

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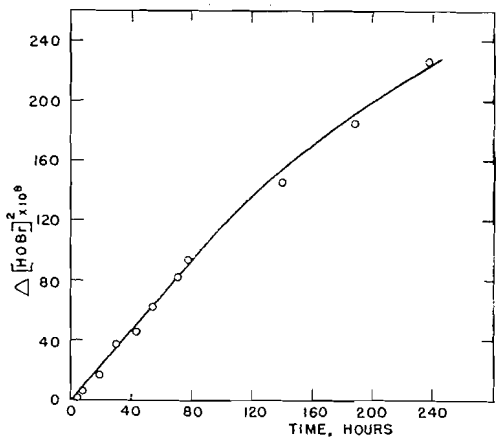

FIG. 4. *Kinetics of formation of hypobromous acid for a solution originally 0.0825 M bromate, 1.66 M perchloric acid, 0.0025 M bromine. Changes in the concentration of hypobromous acid from zero time are plotted.*

An integrated form of this expression is:

$$\frac{1}{2}[\mathrm{HOBr}]^2 = kt + D, \tag{7}$$

corresponding to the plot in Fig. 4, except that the integration constant D is zero. The apparent rate constant k, evaluated from the slope of the initial linear portion of Fig. 4, has the value 5.9×10^{-9} moles $^{+2}$ l.$^{-2}$ hr.$^{-1}$. This value of k includes essentially constant terms involving the concentrations of hydrogen ion, bromate ion, and bromine. The value of the rate constant does not, of course, depend on a knowledge of D. We shall consider later the problem of the experimental evaluation of this constant, i.e., the concentration of hypobromous acid at zero time.

The gradual change in slope of the plot in Fig. 4 after 100 hr. may be ascribed mainly to the approach of true chemical equilibrium. In support of this statement, data are now presented relating to the reverse reaction involving disproportionation of hypobromous acid.

(ii) Decomposition of Hypobromous Acid

Fig. 5 shows the initial optical density of 0.01 M hypobromous acid in 1.67 M perchloric acid, together with the optical density after 193 hr. The original optical density corresponds with that for pure hypobromous acid (See Fig. 1), while the subsequent changes in the spectrum reveal clearly the disappearance of this entity, and the appearance of a species which absorbs light most strongly in the region of 390 mμ. Again it was found that the optical density did not change with time at 345 mμ. Quantitative calculations of this result for all wave lengths examined lead to the following stoichiometry:

$$5\mathrm{HOBr} \longrightarrow 2\mathrm{Br}_2, \tag{8}$$

clearly the exact reverse of the reaction described earlier leading to the formation of hypobromous acid from bromine.

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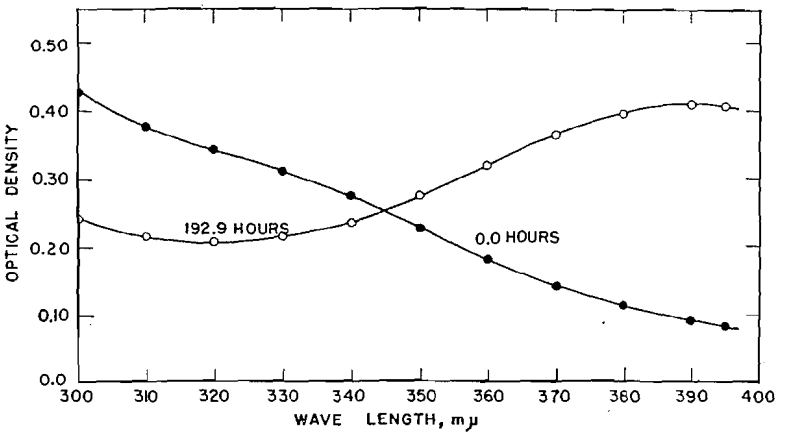

FIG. 5. *Initial and final spectra for a solution initially 0.01 M hypobromous acid in 1.67 M perchloric acid.*

Fig. 6 gives a plot of $\frac{1}{[HOBr]}$ vs. time for the same experiment. The concentration of hypobromous acid was calculated from the optical data, using appropriate forms of Equation (1). The filled circles in Fig. 6 are the results of parallel chemical analyses of identical solutions. For reasons noted earlier, they are not of high accuracy, and have been included mainly to give independent confirmation of the interpretation of the optical data. In addition, chemical analyses were made for the concentrations of bromate ion in the system; it was found that 0.17 ± 0.03 mole of bromate were formed for each mole of hypobromous acid that disappeared.

In Fig. 7 are shown further data relating to the disproportionation of hypobromous acid. Plots are given of $\frac{1}{[HOBr]}$ vs. time for two solutions originally

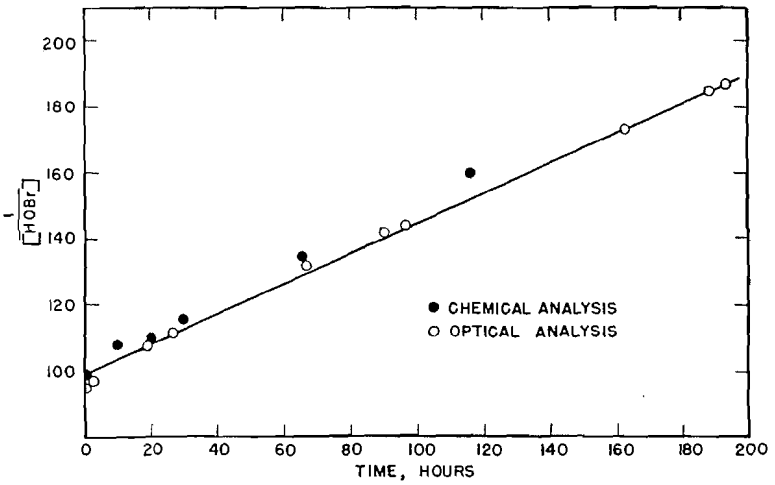

FIG. 6. *Kinetics of disproportionation of hypobromous acid in 1.67 M perchloric acid.*

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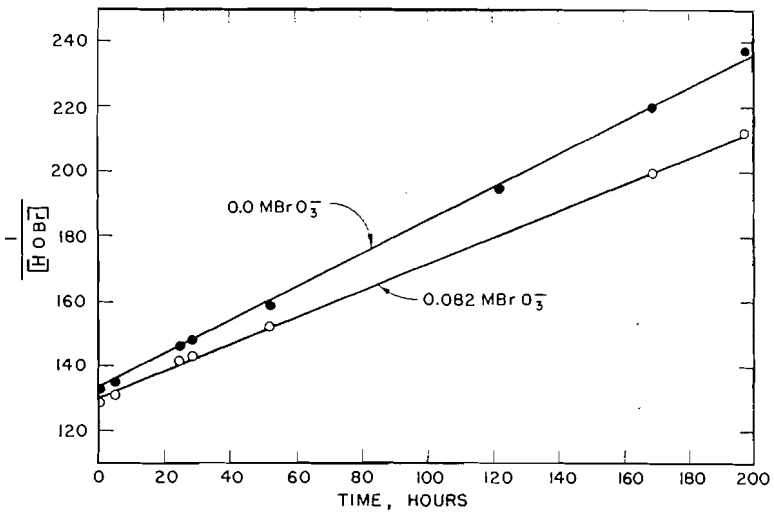

FIG. 7. *Kinetics of disproportionation of hypobromous acid in 1.67 M perchloric acid and indicated concentration of bromate ion.*

0.0077 *M* hypobromous acid in 1.67 *M* perchloric acid, and containing initially 0.0 *M* and 0.082 *M* sodium bromate. The upper result is essentially a duplicate of that given in Fig. 6. The lower result in Fig. 7 shows that the rate of disproportionation of hypobromous acid is relatively insensitive to the concentration of bromate ion up to at least 0.082 *M*. Further, since both these lines are straight, the reverse reaction involving formation of hypobromous acid from bromine is still unimportant after 200 hr.

This evidence shows therefore that hypobromous acid in higher concentrations is unstable with respect to decomposition into bromine and bromate, the rate law being:

$$-\frac{d[\mathrm{HOBr}]}{dt} = k_1[\mathrm{HOBr}]^2 \qquad (9)$$

Equation (9) gives on integration the experimentally derived relation:

$$\frac{1}{[\mathrm{HOBr}]} = k_1 t + D_1 \qquad (10)$$

The rate constant k_1 has the value 0.42 mole^{-1} l.^{1} hr.$^{-1}$ for disproportionation of hypobromous acid in 0.082 *M* sodium bromate, 1.67 *M* perchloric acid. The value of the integration constant D_1 has in this case no particular significance; it is related to the (arbitrary) concentration of hypobromous acid at zero time.

(iii) Discussion

It is permissible to equate the kinetic expressions for the formation (Equation (6)) and disappearance (Equation (9)) of hypobromous acid, and solve for the

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steady state concentration of this species for the particular solution for which the rate constants are known. Thus:

$$0.42[\mathrm{HOBr}]^2 = \frac{5.9 \times 10^{-9}}{[\mathrm{HOBr}]} \tag{11}$$

Solution of Equation (11) leads to a value of 2.4×10^{-3} M for this quantity. This represents a conversion, at equilibrium, of about forty per cent of the original amount of bromine in the system (since 0.4 mole bromine form 1.0 mole of hypobromous acid).

Other calculations showed that the rate of the disproportionation of hypobromous acid given by Equation (9) was sufficient to account for the observed departure from linearity after 100 hr. of the function giving the rate of formation of hypobromous acid (Fig. 4). This substantiates the tentative explanation already put forward to account for this effect.

An instructive approximate calculation of the steady state concentration of hypobromous acid can be made by combining the hydrolysis equilibrium:

$$K_h = \frac{[\mathrm{HOBr}]\,[\mathrm{Br}^-]\,[\mathrm{H}^+]}{[\mathrm{Br}_2]} \tag{12}$$

with the equilibrium constant for the over-all reaction between bromide ion and bromate ion:

$$K = \frac{[\mathrm{Br}_2]^3}{[\mathrm{Br}^-]^5\,[\mathrm{H}^+]^6\,[\mathrm{BrO}_3^-]} \tag{13}$$

The thermodynamic equilibrium concentration of hypobromous acid $[\mathrm{HOBr}]_{eq}$ is given by eliminating $[\mathrm{Br}^-]$ between Equations (12) and (13), leading to:

$$[\mathrm{HOBr}]_{eq} = K^{0.2} K_h\,[\mathrm{Br}_2]^{0.4}\,[\mathrm{BrO}_3^-]^{0.2}\,[\mathrm{H}^+]^{0.2} \tag{14}$$

Values for the constants K and K_h are given in the literature (4, p. 54) together with activity coefficient data for perchloric acid and sodium bromate (4, p. 323). A value of one was assumed for the activity coefficients of the uncharged species bromine and hypobromous acid. Equation (14) can therefore be solved, leading to a value of $[\mathrm{HOBr}]_{eq}$ of $\sim 5 \times 10^{-3}$ M for a solution initially 0.0025 M bromine, 0.082 M sodium bromate, and 1.67 M perchloric acid. Due allowance was made in the calculation for the fact that the equilibrium concentrations of bromine and bromate differ from their initial concentrations because of the formation of hypobromous acid. The agreement of this quantity with the value of 2.4×10^{-3} M determined from the kinetic data may be taken as reasonable for this type of calculation.

Qualitatively, the implication of the foregoing calculation is clear: the equilibrium concentration of bromide given by the hydrolysis of bromine (Equation (12)) is greater than that for the equilibrium involving bromide, bromine, and bromate (Equation (13)). This conclusion is strengthened by solution of Equations (12) and (13) for their respective equilibrium concentrations of bromide ion, using the appropriate values of the equilibrium constants (4, p. 54). The concentration of bromide ion in equilibrium with 0.0025 M bromine in 1.67 M perchloric acid is found to be $3 \times 10^{-6} M$, while for the

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same system containing 0.082 M sodium bromate, the corresponding value is approximately $5 \times 10^{-10} M$. Consequently it is possible for the equilibria to shift in such a way as to reduce the concentration of bromide, i.e., by oxidation of bromide and bromine, and reduction of bromate, to hypobromous acid.

In an earlier paper (2), it was pointed out that the rate of oxidation of bromide by bromate was given by:

$$-\frac{d[BrO_3^-]}{dt} = k[Br^-][BrO_3^-][H^+]^2 \quad (15)$$

It is reasonable to expect that the same rate-controlling process will be operative in the formation of hypobromous acid by reaction between bromide and bromate, i.e.,

$$+\frac{d[HOBr]}{dt} = k'[Br^-][BrO_3^-][H^+]^2 \quad (16)$$

Substitution for $[Br^-]$ from Equation (12) into Equation (16) leads to:

$$+\frac{d[HOBr]}{dt} = k''\frac{[BrO_3^-][H^+][Br_2]}{[HOBr]} \quad (17)$$

for the kinetic expression governing the rate of formation of hypobromous acid. If the concentrations of bromate, hydrogen ion, and bromine are essentially constant (i.e., in the early stages of the reaction) Equation (17) reduces to:

$$+\frac{d[HOBr]}{dt} = \frac{k'''}{[HOBr]} \quad (18)$$

This is identical with the experimentally observed relation (Equation (6)) for the rate of formation of hypobromous acid in this system.

We are led, therefore, to the following as a reasonable, if somewhat idealized, explanation of the processes involved. Bromide ion, at concentrations provided by the hydrolysis of bromine, is unstable with respect to reaction with bromate. This reaction probably leads to the formation of hypobromous acid and consequent destruction of bromine according to:

$$HBrO_3 + HBr \longrightarrow HBrO_2 + HOBr \text{ (rate controlling)} \quad (19)$$

$$HBr + HBrO_2 \longrightarrow 2HOBr, \quad (20)$$

with an accompanying shift in the hydrolysis equilibrium:

$$2Br_2 + 2H_2O \longrightarrow 2HBr + 2HOBr \quad (21)$$

leading as a net result of Equations (19), (20), and (21) to:

$$HBrO_3 + 2Br_2 + 2H_2O \longrightarrow 5HOBr \quad (22)$$

The stoichiometry of the formation of hypobromous acid from bromine suggested by Equation (22) is in accord with that found experimentally.

The disproportionation of hypobromous acid could be considered as the same series in reverse:

$$2HOBr \longrightarrow HBrO_2 + HBr \quad (23)$$

$$HBrO_2 + HOBr \longrightarrow HBrO_3 + HBr \quad (24)$$

$$2HBr + 2HOBr \longrightarrow 2Br_2 + 2H_2O \quad (25)$$

$$5HOBr \longrightarrow HBrO_3 + 2Br_2 + 2H_2O \quad (26)$$

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Equation (26) accounts for all aspects of the experimentally observed stoichiometry. The observed rate law for this latter process:

$$-\frac{d[\mathrm{HOBr}]}{dt} = k_1[\mathrm{HOBr}]^2, \tag{9}$$

suggests, but of course does not confirm, that Reaction (23) is rate-controlling in the over-all disproportionation of hypobromous acid.

In conclusion we return briefly to the problem of the concentration of hypobromous acid near zero time, i.e., the evaluation of the integration constant D in Equation (7). Careful examination at zero time of the spectra of several solutions nominally 0.0025 M bromine, 0.082 M sodium bromate in 1.67 M perchloric acid led to a value of approximately $3 - 4 \times 10^{-4}$ M for the concentration of hypobromous acid. These solutions were prepared in the usual way by addition of sodium bromide to an excess of sodium bromate. These results imply that in the probable sequence of reactions leading to the formation of bromine from bromide and bromate:

$$\mathrm{HBr} + \mathrm{HBrO_3} \longrightarrow \mathrm{HBrO_2} + \mathrm{HOBr} \tag{27}$$

$$\mathrm{HBrO_2} + \mathrm{HBr} \longrightarrow 2\mathrm{HOBr} \tag{28}$$

$$3(\mathrm{HOBr} + \mathrm{HBr}) \longrightarrow 3\mathrm{Br_2} + 3\mathrm{H_2O}, \tag{29}$$

bromate competes favorably with hypobromous acid for the available bromide ions. Thus, hypobromous acid formed in Reactions (27) and (28) is not completely converted to bromine before the concentration of bromide ion is (rapidly) reduced to its equilibrium value with respect to Reaction (29). This effect may be considered as a protective action of high concentrations of bromate ion on hypobromous acid, with respect to reaction with bromide ion.

A more direct proof of this protective action was obtained in the following way. A solution of sodium bromide (0.70 ml. of 0.0240 M, 0.0168 millimole) was added to 29.7 ml. of a solution 0.10 M sodium bromate, 6.18×10^{-4} M hypobromous acid (0.0184 millimole), and 1.67 M perchloric acid, contained in a 10 cm. optical cell. Spectral analysis of the resulting solution soon after the addition of the sodium bromide showed its concentration to be 5.5×10^{-4} M hypobromous acid (0.0167 millimole) and 3.44×10^{-4} M bromine (0.0105 millimole). If all the added sodium bromide had reacted with hypobromous acid, and none with sodium bromate, then the final concentrations would be:

$$\frac{0.0168}{29.7 + 0.7} = 5.52 \times 10^{-4}\ M \text{ bromine}$$

$$\text{and } \frac{0.0184 - 0.0168}{29.7 + 0.7} = 5.3 \times 10^{-5}\ M \text{ hypobromous acid.}$$

Clearly part of the added sodium bromide reacted with bromate ion to produce hypobromous acid; by straightforward calculation from these data it can be shown that 38% of the added bromide reacted with bromate ion to produce hypobromous acid, and 62% reacted with hypobromous acid to form bromine. It should be emphasized that this protective action will be appreciable only

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when bromate ion is present in large excess. Similar experiments made with hypobromous acid and bromate ion in equal concentration showed no such effects, all the added bromide reacting exclusively with hypobromous acid to form bromine.

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BIOCHEMISTRY OF THE USTILAGINALES

IV. THE CONFIGURATIONS OF SOME β-HYDROXYACIDS AND THE BIOREDUCTION OF β-KETOACIDS[1]

By R. U. Lemieux and Jacques Giguere[2]

Abstract

The phytochemical reduction of the β-keto-*n*-caproic and β-keto-*n*-caprylic acids yielded the corresponding D-β-hydroxyacids. This observation is contrasted to bioreduction of β-ketobutyric acid to L-β-hydroxybutyric acid. The basis for the assignment of the above configurations is discussed. L-α-Hydroxy-*n*-valeramide was reduced with lithium aluminium hydride and the product was acetylated to yield L-1-acetamido-2-acetoxypentane. The enantiomorphic form of the latter compound was obtained through the Curtius degradation of D-β-hydroxy-*n*-caprohydrazide. The configurations assigned to the β-hydroxy-*n*-caprylic acids are based on the Levene–Marker Rule for the optical rotations of homologous compounds. The β-hydroxy-*n*-caproic and β-hydroxy-*n*-caprylic acids derived from ustilagic acid were thus shown to belong to the L-series. The use of infrared spectroscopy in configurational correlations is discussed and the infrared spectra of L-β-hydroxybutyrhydrazide, L-β-hydroxy-*n*-caprohydrazide, L- and DL-β-hydroxy-*n*-caprylhydrazides and D-, L-, and DL-1-acetamido-2-acetoxypentane are given.

Friedmann (6) found that the phytochemical reduction of β-ketobutyric acid yielded a large preponderance of the dextrorotatory form of β-hydroxybutyric acid (rotation measured in water). We have confirmed the work of Friedmann and have extended the bioreduction of β-ketoacids, by rapidly fermenting baker's yeast (22, pp. 75-117), to the β-keto-*n*-caproic and β-keto-*n*-caprylic acids. The β-hydroxy-*n*-caproic and β-hydroxy-*n*-caprylic acids thus obtained possessed levorotatory methyl ester and hydrazide derivatives, the rotations measured in chloroform and water, respectively. On the other hand, the methyl ester and hydrazide derivatives of the phytochemically produced β-hydroxybutyric acid were dextrorotatory under the same conditions of measurement. The magnitudes of the rotations of the methyl esters were such that it appeared, on the basis of the Levene–Marker Rule (20) for the establishment of the configurational relationship of homologous compounds, that the bioreduction yielded configurationally related β-hydroxy-*n*-caproic and β-hydroxy-*n*-caprylic acids but gave a β-hydroxybutyric acid of opposite relative configuration. This apparent inconsistency in the stereochemical course of the phytoreduction of these homologous compounds was definitely established by the correlation of the configurations of the β-hydroxybutyric acids and the β-hydroxy-*n*-caproic acids on the following basis. Karrer and Klarer (10) and Levene and Haller (15) independently correlated the configurations of the β-hydroxybutyric acids with those of the lactic acids. The configurational relationships between the lactic acids and the α-hydroxy-*n*-valeric acids were estab-

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[2] *National Research Council of Canada Postdoctorate Fellow.*

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lished by Levene and Haller (17). We have correlated the configurations of the β-hydroxy-*n*-caproic acids with those of the α-hydroxy-*n*-valeric acids and thus with those of the β-hydroxybutyric acids.

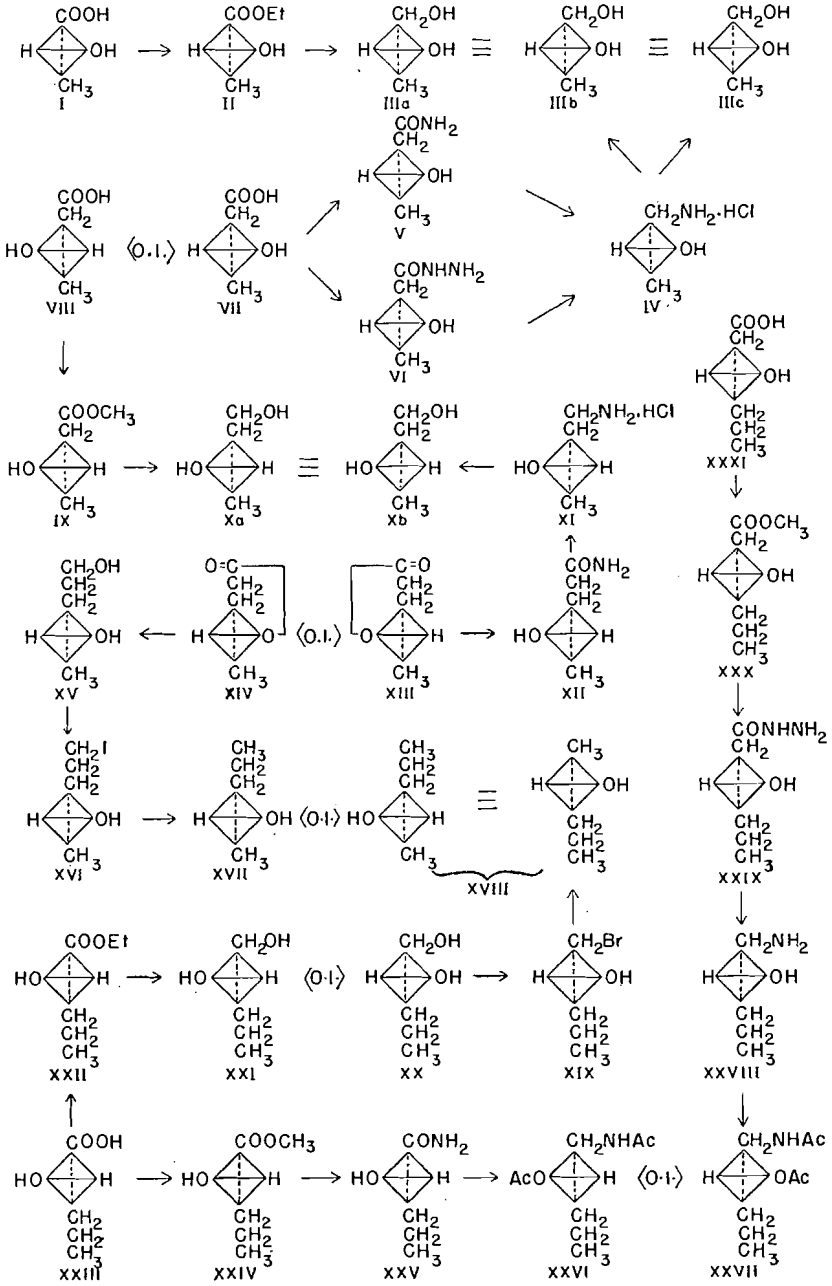

FIG. 1. *The correlation of the configurations of* D-β-*hydroxy-n-caproic acid* (*XXXI*) *and* D-*lactic acid* (*I*). *The names, rotations, and references to the literature for the compounds are given in Table I. O.I. = Optical isomers.*

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Fig. 1 and Table I review briefly the important work by Levene and co-workers (14-18) on the correlation of the configurations of the α-hydroxy-*n*-valeric acids, through the β-hydroxybutyric acids, to those of the lactic acids. Further, the substances prepared by us for the correlation of the configurations of the β-hydroxy-*n*-caproic acids to those of the α-hydroxy-*n*-valeric acids are included. Table I lists the optical rotations which were measured in the characterization of the compounds shown in Fig. 1. These values are not necessarily those to be expected for optically pure preparations.

It is our purpose to assign D- and L-configurations to the compounds encountered in this work and, in doing so, it seemed desirable to extend the allocation of configurations to all the compounds shown in Fig. 1. Such assignments are based on conventions which have been stated explicitly only for the sugar

TABLE I

THE ASSIGNMENT OF CONFIGURATIONS AND THE OPTICAL ROTATORY POWER OF THE SUBSTANCES IN FIG. 1

No.*	Compound	Optical rotatory power				Reference
		$[\alpha]_D$	°C.	Solvent	*c*	
I	D-Lactic acid	*levo*	–	–	–	15
II	Ethyl D-lactate	+10.7	22	Undiluted	–	15
III(*a*)	D-1,2-Propanediol	− 1.85	21	Ethanol	35	15
III(*b*)	D-1,2-Propanediol	*levo*	–	Water	–	14
III(*c*)	D-1,2-Propanediol	− 1.548	–	Water	8.17	10
IV	D-1-Amino-2-propanol hydrochloride	−31.2	26	Water	1.6	14
V	D-β-Hydroxybutyramide	−22.49	20	Water	2.55	10
VI	D-β-Hydroxybutyrhydrazide	−29.3	31	Ethanol	2.05	14
VII	D-β-Hydroxybutyric acid	−24.5	25	Water	5.06	14
VIII	L-β-Hydroxybutyric acid	+10.3	22	Water	6.1	16
IX	Methyl L-β-hydroxybutyrate	+ 8.6	22	Undiluted	–	16
X(*a*)	L-1,3-Butanediol	+ 7.5	22	Ethanol	10.0	16
X(*b*)	L-1,3-Butanediol	+18.5	22	Ethanol	10.0	16
XI	L-1-Amino-3-butanol hydrochloride	+11.8	22	Water	13.3	16
XII	L-γ-Hydroxyvaleramide	+ 9.4	22	Ethanol	2.02	16
XIII	L-γ-Valerolactone	−23.2	22	Undiluted	–	16
XIV	D-γ-Valerolactone	+13.5**	20	Undiluted	–	18
XV	D-1,4-Pentanediol	− 4.90	22	Ethanol	31.6	18
XVI	D-1-Iodo-4-pentanol	–	–	—	–	18
XVII	L-2-Pentanol	− 1.20**	–	Undiluted	–	18
XVIII	D-2-Pentanol	+14.3	20	Ethanol	7.00	17
XIX	D-1-Bromo-2-pentanol	+10.5**	20	Undiluted	–	17
XX	D-1,2-Pentanediol	+16.2	20	Ethanol	8.00	17
XXI	L-1,2-Pentanediol	− 9.8	20	Ethanol	7.80	17
XXII	Ethyl L-α-hydroxy-*n*-valerate	− 5.05**	20	Undiluted	–	17
XXIII	L-α-Hydroxy-*n*-valeric acid	+ 1.5	20	Aq. $BaCl_2$	12.7	17
XXIV	Methyl L-α-hydroxy-*n*-valerate	+16.6	23	Chloroform	1.2	
XXV	L-α-Hydroxy-*n*-valeramide	−60	24	Ethanol	1.5	
XXVI	L-1-Acetamido-2-acetoxypentane	−25	23	Chloroform	1.1	
XXVII	D-1-Acetamido-2-acetoxypentane	+21	23	Chloroform	0.33	
XXVIII	D-1-Amino-2-pentanol	–	–	–	–	
XXIX	D-β-Hydroxy-*n*-caprohydrazide	−15.9	23	Water	1	
XXX	Methyl D-β-hydroxy-*n*-caproate	−27.1	24	Chloroform	1	
XXXI	D-β-Hydroxy-*n*-caproic acid	*levo*	–	Chloroform	–	

* *These numbers refer to the stereo-formulas of Fig. 1.*
** *Observed rotation.*

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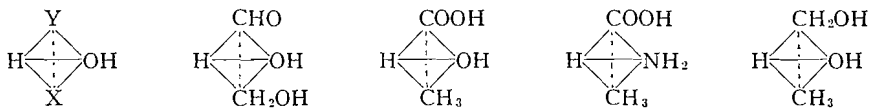
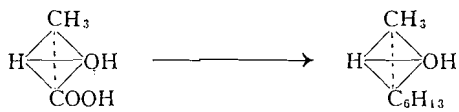
(2; 7, pp. 1-22; 26) and amino-acid (31, 33) groups of substances. Consequently, it is necessary to state the basis for the assignments made in Table I. Since all the compounds involved in this discussion possess normal carbon skeletons, Fischer's first convention (7, p. 7) for writing stereo-formulas can be applied without ambiguity. Hudson has emphasized that Fischer's stereo-formulas are quite independent of any plan of nomenclature and to quote (7, p. 1) "these stereo-formulas that are written in a plane, and independently also the assigned systematic names, define the mechanical models of the two substances in three-dimensional space". This viewpoint amounts to a provisional assignment of absolute configurations and should be contrasted to that described by Wheland (32, p. 181). Although the interpretation of plane configurations in the manner outlined by Wheland does not infer unknown points of structure, the use of Fischer stereo-formulas and Hudson's suggestion (7, p. 7; 8) for their more definitive representation have gained, for good reasons, wide acceptance in stereochemistry (2). The assignment of D- and L-configurations to enantiomorphic pairs of compounds on the basis of Fischer's stereo-formulas depends on conventions for the orientation of the reference centers. No agreed upon set of conventions exists which can be applied generally and, for example, Wolfrom, Lemieux, and Olin (33) have recently pointed out that it is not clear whether malic acid should be treated as 2-hydroxy- or 3-hydroxy-succinic acid. According to recently published rules (2) for carbohydrate nomenclature, the following *glycero*-compound is assigned the D-configuration if *Y* is the principal function. However, a basis for the classification of functional groups was not provided. A survey of the literature where D- and L-configurations were allocated reveals that in practice the functional group with



the higher degree of oxidation was considered the principal function. Thus, the stereo-formulas assigned to D-glyceraldehyde (7, p. 9), D-lactic acid (34), D-alanine (33), and D-1, 2-propanediol (21) are as shown. The names assigned to the stereo-formulas shown in Fig. 1 and listed in Table I were formulated on this basis except for compounds XVII and XVIII, the enantiomorphic 2-pentanols. The assignment of D- and L-configurations to these substances, on the basis of the above scheme, is not straightforward. However, O'Gorman and Lucas (25) have assigned the D-configuration to *dextro*-2-octanol. Since Levene and Harris (19) have provided evidence that *dextro*-2-octanol can be



considered as derived from L-lactic acid as shown, the methyl group was considered the principal function. Furthermore, Leroux and Lucas (13) have since assigned the following formula to L-2-butanol.

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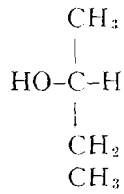

It is on this basis that compounds XVII and XVIII were termed L- and D-2-pentanol, respectively.

L-α-Hydroxy-*n*-valeric acid (XXIII), which is dextrorotatory in aqueous barium chloride solution, was converted through the methyl ester (XXIV) to L-α-hydroxy-*n*-valeramide (XXV). The reduction of simple amides with lithium aluminum hydride usually yields amines (24, 30). The product of the reduction of L-α-hydroxy-*n*-valeramide, m.p. 78°–79°C., $[\alpha]_D$ −60° (ethanol), by this reagent was acetylated. Fractional distillation of the product yielded L-1-acetamido-2-acetoxypentane (XXVI), which after recrystallization melted at 57°–58°C. with $[\alpha]_D$ −25° (chloroform) and +15° (ethanol). The crystalline substance possessed, except for some small shifts, the same infrared absorption spectrum (see Fig. 2) as that found for crystalline DL-1-acetamido-2-acetoxy-

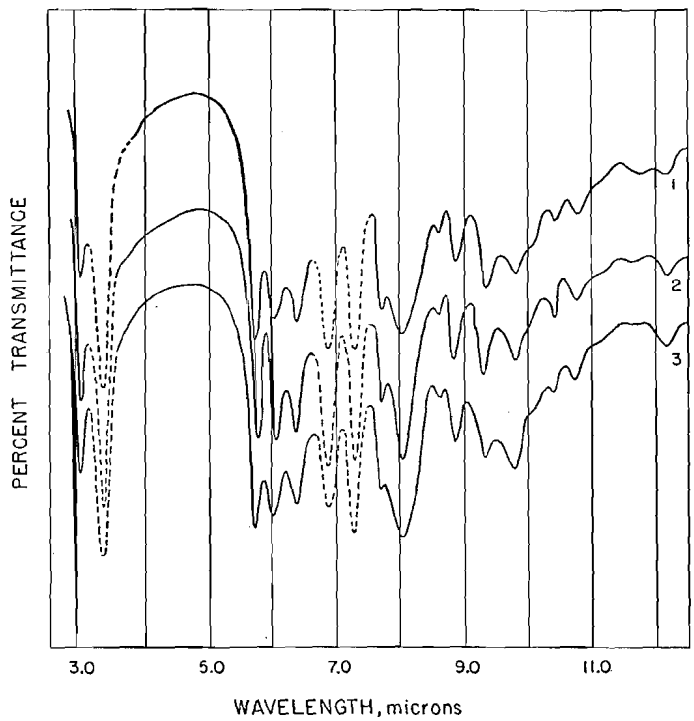

FIG. 2. Infrared spectra. *Curve 1.* D-*1-acetamido-2-acetoxypentane.*
Curve 2. DL-*1-acetamido-2-acetoxypentane.*
Curve 3. L-*1-acetamido-2-acetoxypentane.*
- - - - *Nujol absorption bands.*

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pentane, m.p. 73.5°–74°C., prepared in the same manner from DL-α-hydroxy-*n*-valeramide, m.p. 133°–134°C. The structure of the DL-1-acetamido-2-acetoxypentane was substantiated by the fact that the material possessed the expected elementary composition, showed infrared absorption bands characteristic of both esters and amides, and possessed three terminal methyl groups.

The *levo*-β-hydroxy-*n*-caprohydrazide (XXIX) (aqueous solution), prepared from the β-hydroxyacid (XXXI) obtained by phytochemical reduction of β-keto-*n*-caproic acid, was subjected to Curtius degradation (14). The *sym*-urea produced was hydrolyzed to 1-amino-2-pentanol (XXVIII) which was not isolated but acetylated to yield a product which on fractional distillation afforded a component which, after two recrystallizations from ether–Skellysolve C, melted at 55°–59°C. with $[\alpha]_D$ +21° (chloroform) and $[\alpha]_D$ −10° (ethanol). The substance (XXVII) possessed an infrared absorption spectrum (Fig. 2) identical to that found for the above described L-1-acetamido-2-acetoxypentane (XXVI). However, the compound possessed optical rotatory properties which were opposite in sign to these found for the L-isomer. That the substances were optical antipodes was further established by admixture of the two materials and recrystallization to yield a substance identical to DL-1-acetamido-2-acetoxypentane. It was thus clear that the *levo*-β-hydroxy-*n*-caproic acid (XXXI) obtained by bioreduction possessed the D-configuration. Since the *dextro*-β-hydroxybutyric acid (VIII) obtained by the phytochemical reduction of β-ketobutyric acid (6) was shown (10, 15) to have the L-configuration, it is clear that the phytochemical reduction of the C_4- and C_6-β-ketoacids yielded configurationally unrelated hydroxyacids.

Table II lists the specific rotations of the hydrazide and methyl ester derivatives of both the D- and L-forms of the β-hydroxybutyric, β-hydroxy-*n*-caproic, and β-hydroxy-*n*-caprylic acids. Since Friedmann (6) showed that the phytochemical reduction of β-ketobutyric acid did not yield optically pure L-β-hydroxybutyric acid, it is possible that the rotation shown for the methyl *levo*-β-hydroxy-*n*-caprylate is somewhat low. On the other hand, the rotation shown for the methyl *dextro*-β-hydroxy-*n*-caprylate may be somewhat high because of incomplete separation from the methyl *dextro*-β-hydroxy-*n*-caproate with which it occurred in ustilagic acid (11). Since the numerical value for the specific rotations of the enantiomorphic methyl esters must be intermediate between these two values, the Levene–Marker Rule (20) can be applied without reservation to assign the configurations shown. A decision based on the rotations of the hydrazides yields the same result but is considered somewhat more hazardous.

Thus the phytochemical reduction of the β-keto-*n*-caproic and β-keto-*n*-caprylic acids followed the same stereochemical routes to yield D-hydroxyacids while L-β-hydroxybutyric acid was obtained on the bioreduction of β-ketobutyric acid. Table II lists the rotations found for the L-β-hydroxy-*n*-caproic and D-β-hydroxy-*n*-caprylic acids in chloroform solution. On the basis of these values, the β-hydroxydecanoic acid derived by Jarvis and Johnson (9) from the

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TABLE II

THE OPTICAL ROTATORY PROPERTIES OF SOME β-HYDROXYACIDS AND THEIR DERIVATIVES

	Free acid			Methyl ester			Hydrazide				Source
	$[\alpha]_D$	Solvent	c	$[\alpha]_D$	Solvent	c	$[\alpha]_D$	Solvent	c	M.p., °C.	
D-β-Hydroxybutyric acid	−24.5°	H_2O	5.06	–	–	–	−29.3°	C_2H_5OH	2.05	129–30	Resolution (14)
D-β-Hydroxy-*n*-caproic acid	–	–	–	−27.1°	$CHCl_3$	1	−15.6	H_2O	0.9	130–1	Phytochemical reduction
D-β-Hydroxy-*n*-caprylic acid	−21	$CHCl_3$	1.9	−18.4	$CHCl_3$	1	−11.4	H_2O	1	127.5–8	Phytochemical reduction
D-β-Hydroxy-decanoic acid	−21	$CHCl_3$	2.5	–	—	–	–	–	–	–	*Pseudomonas aeruginosa* (9)
L-β-Hydroxy-butyric acid	–	–	–	+33.3	$CHCl_3$	1.2	+32.7 +26.8	H_2O C_2H_5OH	0.85 0.9	129	Phytochemical reduction
L-β-Hydroxy-*n*-caproic acid	+30	$CHCl_3$	2	+28	$CHCl_3$	0.8	+15.9	H_2O	0.75	131–2	*Ustilago zeae* (11)
L-β-Hydroxy-*n*-caprylic acid	–	–	–	+24	$CHCl_3$	0.85	+12	H_2O	1.1	127–8	*Ustilago zeae* (11)

glycolipid formed in *Pseudomonas aeruginosa* cultures possessed the D-configuration. It is interesting to note that D-β-hydroxybutyric acid is widely distributed in nature (1; 3, p. 154; 12) and L-β-hydroxy-*n*-caproic and L-β-hydroxy-*n*-caprylic acids were isolated from ustilagic acid (11) but the phytochemical reduction of the corresponding ketoacids led in each case to the enantiomorphic form.

The infrared spectra found for Nujol mulls of the hydrazide derivatives of the L-β-hydroxybutyric, D-β-hydroxy-*n*-caproic, D-β-hydroxy-*n*-caprylic, and DL-β-hydroxy-*n*-caprylic acids are shown in Fig. 3. Since hydrazides form convenient derivatives for the identification of organic acids (27), these spectra may be of value for the future identification of the above substances. The infrared spectra of enantiomorphic forms are identical. Solutions of an optically active substance and the racemic modification should therefore display identical spectra unless strong differences in association exist, which is unlikely. The spectra of a substance in solution and in the crystalline state are well known to differ, often the difference is great. Since the optically active and racemic forms of an organic compound nearly always differ in melting point, the associations of the molecules in the crystal lattices must differ. Nevertheless, the possible use of the infrared spectra of crystalline substances in Nujol mulls for the identification of naturally occurring optically active substances which can be synthesized most readily in the racemic form is emphasized by the near identity of the spectra found for the D- and DL-forms of β-hydroxy-*n*-caprylhydrazide (Fig. 3) and for the D-, L-, and DL-forms of 1-acetamido-2-acetoxypentane (Fig. 2). Since organic structures can be determined quantitatively by this technique, the method should be of value to characterize materials prepared for the establishment of configurational correlations when the conditions used in the preparation unavoidably lead to partial racemization. This application should be especially useful when the materials in question cannot be obtained in the crystalline state.

Experimental

Instrumentation

The infrared spectra, specific rotations, and melting points were determined as previously described (11). All rotations were measured at room temperature, 23°–25°C. The melting points are uncorrected.

Saponification of the β-Ketoacid Ethyl Esters

Ethyl β-keto-*n*-caproate was prepared in the manner described by Fischer, Goldschmidt, and Nüssler (5). The same procedure was used for the preparation of ethyl β-keto-*n*-caprylate (28). The yield of twice distilled ester, b.p. 112°–113°C. (12 mm.) was 60% of theory.

A commercial preparation of ethyl acetoacetate was saponified in the manner described by Friedmann (6) to yield an aqueous solution of potassium β-ketobutyrate in 87% yield based on the decomposition of a sample in dilute sul-

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phuric acid and the estimation of the acetone formed and isolated by distillation using the alkaline hypoiodite method (23, p. 274). The higher esters, 100 m.e., were dissolved in 60 ml. of ethanol and to the mechanically stirred solutions, cooled in ice water, 108 m.e. of aqueous potassium hydroxide, 0.5 *N*, was added dropwise. After they were stirred for an additional hour, the solutions were allowed to stand at room temperature overnight. The solutions were concentrated *in vacuo* to about 100 ml. and made neutral to phenolphthalein. Although the analysis of methyl propyl and methyl pentyl ketones by the above method for the estimation of acetone was probably not quantitative, the yields of potassium β-keto-*n*-caproate and potassium β-keto-*n*-caprylate, thus measured, corresponded to 85 and 89% of theory, respectively.

Phytochemical Reductions

The potassium salt of the β-ketoacid, about 80 m.e. in aqueous solution, was combined with D-glucose, 400 gm., and water to yield one liter of solution. Fleischmann baker's yeast, 900 gm., was dispersed by gentle agitation in a Waring blendor into one liter of water which contained 1 gm. of potassium dihydrogen phosphate and 0.5 gm. of magnesium sulphate. The yeast suspension and the glucose solution were combined in a nine liter glass bottle and efficiently stirred at room temperature for one to two days. The fermentation mixture was then diluted with two liters of water, 40 ml. of 25% sodium hydroxide, and 10 ml. of toluene. The yeast cells were removed in a Sharples supercentrifuge and the centrifugate was freed of protein by the precipitation of zinc hydroxide according to Somogyi (29). The fermentation broth was adjusted to pH 7 and 200 ml. of a solution which contained 50 gm. of zinc sulphate heptahydrate was added. The amount of 25% sodium hydroxide required to completely precipitate the zinc ions was added and the voluminous precipitate was removed by filtration with the aid of Celite and washed with about one liter of water. The filtrate was concentrated *in vacuo* to about 700 ml. and after the addition of 25 ml. of concentrated hydrochloric acid, the solution was extracted continuously with ether. The ether extract was dried over sodium sulphate and the acid content was converted to methyl ester by diazomethane. After removal of the ether, the methyl esters were purified by fractional distillation. Some dimethyl succinate was always present and in some experiments succinic acid precipitated from the ether extract.

The yield of methyl L-β-hydroxybutyrate, n_D^{23} 1.4195, $[\alpha]_D$ +33.3° (*c*, 1.2 in chloroform), was 3.11 gm., that of methyl D-β-hydroxy-*n*-caproate, n_D^{23} 1.422, $[\alpha]_D$ −27.1° (*c*, 1 in chloroform), was 1.90 gm. and that of methyl D-β-hydroxy-*n*-caprylate, n_D^{24} 1.432, $[\alpha]_D$ −18.4° (*c*, 1 in chloroform), was 3.30 gm.

Hydrazides of the β-Hydroxyacids

These derivatives were prepared and characterized as previously described (11). Purification was by recrystallization from ethanol to constant rotation and melting point. The melting points and specific rotations found are listed in Table II and the infrared spectra are shown in Fig. 3.

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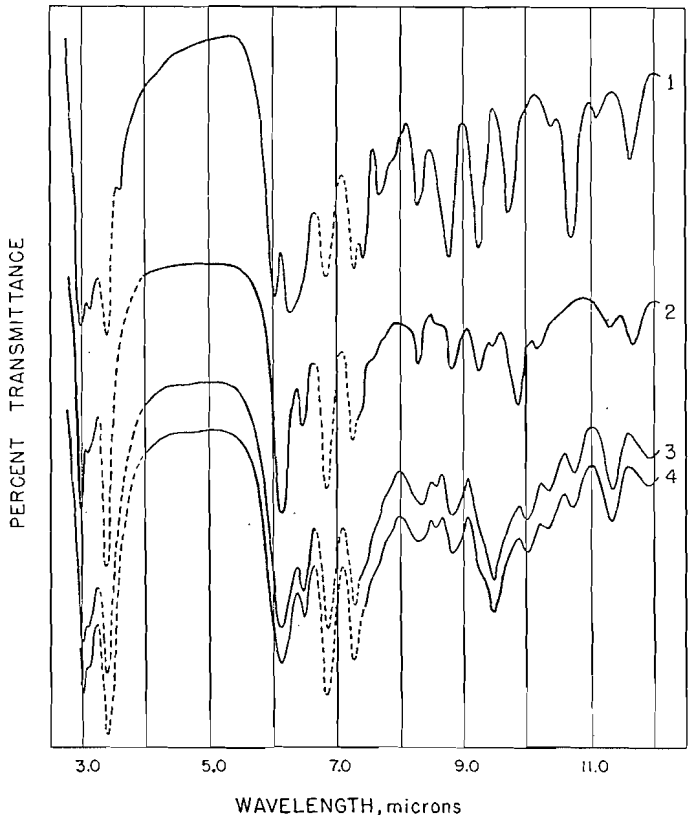

FIG. 3. Infrared spectra. *Curve 1.* L-β-*hydroxybutyrhydrazide.*
Curve 2. L-β-*hydroxy-n-caprohydrazide.*
Curve 3. L-β-*hydroxy-n-caprylhydrazide.*
Curve 4. DL-β-*hydroxy-n-caprylhydrazide.*
- - - - *Nujol absorption bands.*

Methyl L-α-*Hydroxy-n-valerate*

DL-α-Hydroxyvaleric acid was prepared by the acid hydrolysis of DL-α-hydroxyvaleronitrile. The nitrile was best prepared by the interaction of the butyraldehyde–sodium bisulphite addition compound with potassium cyanide. The acid was isolated by continuous ether extraction and converted to the ethyl ester which was purified by distillation. The pure ester was saponified and the acidified mixture was extracted continuously with ether to yield the DL-α-hydroxyvaleric acid which was resolved in the manner prescribed by Levene and Haller (17). The acid, 65 gm., was dissolved in 600 ml. of boiling acetone with 220 gm. of brucine. The salts which crystallized on cooling were recrystallized 13 times from acetone to yield 74 gm. of material. This salt was decomposed with hydrochloric acid and the hydroxyacid was obtained in ether solution by continuous extraction. The ether solution was treated with an excess of diazomethane and the methyl L-α-hydroxy-*n*-valerate, b.p. 69°–70°C. (25 mm.), n_D^{23} 1.4212, $[\alpha]_D$ +16.6° (*c*, 1.2 in chloroform) was isolated by frac-

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tional distillation at reduced pressure. Levene and Haller (17) reported the following optical properties for L-α-hydroxy-*n*-valeric acid (Fig. 1, XXIII) and its barium salt, $[\alpha]_D^{20}$ +1.5° (*c*, 12.7 in aqueous barium chloride) and $[\alpha]_D^{20}$ −4.9° (*c*, 3.16 in water), respectively. The rotations of the corresponding substances, derived from the above methyl ester, were found to be: free acid, $[\alpha]_D$ +1.3° (*c*, 12.7 in aqueous barium chloride by decomposition of the barium salt with hydrochloric acid), barium salt, recrystallized from aqueous acetone, $[\alpha]_D$ −9.6° (*c*, 3.2 in water).

L-α-*Hydroxyvaleramide*

Methyl L-α-hydroxyvalerate, 3.6 gm., $[\alpha]_D$ +16.6° in chloroform, was dissolved in 50 ml. of dry methanol saturated with ammonia and the solution was heated for six hours at 100°C. The solution was evaporated *in vacuo* to a sirup which soon crystallized. The crystals were treated with 150 ml. of warm ether and the insoluble portion was removed by filtration. The filtrate was diluted to turbidity with Skellysolve C. Large plates separated on cooling which were recrystallized from the same solvent mixture. The yield was 1.5 gm. of material, m.p. 78°–79°C., $[\alpha]_D$ −60° (*c*, 1.5 in ethanol). Calc. for $C_5H_{11}O_2N$: C, 51.26; H, 9.47%. Found: C, 51.20; H, 9.24%.

DL-α-*Hydroxyvaleramide*

This amide, m.p. 133°–134°C., was prepared as described above. However, owing to the sparing solubility in ether, it was purified by recrystallization from ethanol. Calc. for $C_5H_{11}O_2N$: C, 51.26; H, 9.47%. Found: C, 51.20; H, 9.62%.

L-1-*Acetamido-2-acetoxypentane*

L-α-hydroxyvaleramide, 1.5 gm., was dissolved in 250 ml. of dry ether. To the stirred solution, cooled in ice water, an excess of an ethereal solution of lithium aluminum hydride (4) was added over a period of one-half hour. The mixture was then refluxed for three hours. The excess lithium aluminum hydride was destroyed by the addition of ethanol and the solution was poured into 300 ml. of water. The ether was removed by heating on the steam bath and the insoluble salts were removed by filtration. The filtrate was made acid to Congo red indicator with hydrochloric acid and reduced *in vacuo* to a salt cake. The salts were heated with 50 ml. of acetic anhydride and 2 gm. of sodium acetate for three hours at 100°C. The resulting mixture was added to 100 ml. of ice water. After the acetic anhydride was hydrolyzed, the solution was extracted four times with ether and the combined ether extracts were neutralized with sodium bicarbonate. The ether layer was dried over sodium sulphate and removal of the ether by distillation gave a yellow oil which was fractionally distilled. The first fractions consisted of a colorless liquid, $[\alpha]_D$ +60° (*c*, 1.3 in chloroform), which appeared to be 1,2-diacetoxypentane. The highest boiling fraction, b.p. 102°C. (0.2 mm.) was a viscous liquid which soon crystallized. The yield was 0.70 gm. of substance which after recrystallization from ether–

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Skellysolve C melted at 57°–58°C. with $[\alpha]_D$ +15° (*c*, 1.1 in ethanol) and −25° (*c*, 1.1 in chloroform). The infrared spectrum of a Nujol mull is shown in Fig. 2. Calc. for $C_9H_{17}O_3N$: C, 57.75; H, 9.16%. Found: C, 57.40; H, 8.93%.

DL-*1-Acetamido-2-acetoxypentane*

Since DL-*α*-hydroxyvaleramide was only sparingly soluble in ether, the material was added to a light excess of lithium aluminum hydride by continous extraction. A sintered-glass funnel containing the amide, 1.5 gm., was suspended above the refluxing solution of the hydride in order that the condensate would percolate through and dissolve some of the amide before returning to the reaction flask. The extraction was complete after three days. DL-1-acetamido-2-acetoxypentane, m.p. 73.5°–74°C., was prepared from the reaction mixture in the manner described above for the preparation of the L-form. The material boiled at 100°C. at 0.17 mm. and was recrystallized from ether – Skellysolve C. The infrared spectrum of a Nujol mull is shown in Fig. 2. Calc. for $CH_3(C_4H_8ON)(COCH_3)_2$: N, 7.48%; terminal methyl groups as % acetyl, 68.9. Found: N, 7.44%; terminal methyl groups as % acetyl, 66.2.

D-*1-Acetamido-2-acetoxypentane*

D-*β*-Hydroxy-*n*-caprohydrazide, 1 gm., was dissolved in 20 ml. of 15% hydrochloric acid and 15 ml. of ether was added. To the mechanically stirred mixture, cooled to 0°C., a solution of 1 gm. of sodium nitrite in 2.5 ml. of water was added dropwise. The ether layer was isolated and the aqueous residue was extracted three times more with ether. The combined ether extracts were washed once with sodium bicarbonate solution and once with water and added to 35 ml. of 90% aqueous acetone. The ether was removed by distillation and the acetone solution was refluxed for 22 hr. The solvents were evaporated *in vacuo* to yield 0.78 gm. of the crystalline urea derivative which was not purified but was hydrolyzed directly by heating at 135°C. for six hours with 1 ml. of concentrated hydrochloric acid. The resulting solution was evaporated to the dry amine hydrochloride which was heated for two hours on the steam bath with 25 ml. of acetic anhydride and 1 gm. of sodium acetate. The acetyl derivative was isolated as described above. Fractional distillation yielded a 0.45 gm. fraction of a material which soon crystallized. After two recrystallizations from ether – Skellysolve C the substance melted at 55°–59°C. with $[\alpha]_D$ −10° (*c*, 0.33 in ethanol) and +21° (*c*, 0.33 in chloroform). Nujol mulls of the material and L-1-acetamido-2-acetoxypentane showed identical infrared spectra (Fig. 2). The material, 14 mgm., was mixed with 13 mgm. of L-1-acetamido-2-acetoxypentane and the mixture was recrystallized from ether – Skellysolve C. The yield was 20 mgm., 74%, of crystals which melted at 73°–74°C. and this melting point was not changed on admixture of DL-acetamido-2-acetoxypentane, m.p. 73.5°–74°C.

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CHEMICAL EFFECTS OF THE $Cl^{35}(\gamma, n)Cl^{34}$ REACTION IN SODIUM CHLORATE[1]

By K. J. McCallum and O. G. Holmes[2]

Abstract

The distribution of Cl^{34} among different valence states following the $Cl^{35}(\gamma,n)Cl^{34}$ reaction in solid sodium chlorate has been investigated, using a betatron as the source of gamma rays. The percentage of the activity in the hypochlorite and perchlorate fractions differed from zero by less than the experimental error; the small activity separated with the chlorite fraction could be accounted for by an exchange reaction between chloride and chlorite ions. The major part of the activity, $91 \pm 2\%$, was present in the chloride fraction, the remainder of the activity being present as chlorate ion. One-quarter of the activity in the chlorate fraction could be accounted for by an exchange reaction between chloride and chlorate ions. The results were not affected by an alteration in the peak energy of the gamma rays or by a change in the amount of radiation. The results are compared with those following the $Cl^{37}(n,\gamma)Cl^{38}$ reaction in the same compound.

Introduction

In 1934 Szilard and Chalmers (12) observed that, when ethyl iodide was bombarded with slow neutrons, a considerable fraction of the radioactive iodine atoms formed by the neutron capture process appeared in the form of free iodine or iodide ions and could be separated from the unchanged ethyl iodide. The fraction of the radioactive species which remains combined in the form of the original bombarded material has been termed the retention. In recent years, a study of the Szilard–Chalmers effect following neutron bombardment has been made on a wide variety of organic and inorganic compounds (3).

The expulsion of the radioactive atom from the molecule as a result of the nuclear reaction is usually ascribed to the momenta of the gamma rays emitted in the neutron capture process. In most cases, the recoil energy imparted to the nucleus, calculated on the assumption that one gamma ray only is emitted, is greater than chemical bond energies. Although the total recoil energy is not available for bond rupture (8), in most cases, breakage of the bond is to be expected. However, if the total gamma ray energy is distributed over several quanta, emitted in cascade, the resultant recoil of the nucleus may be much less, depending upon the number and directions of the emitted gamma rays. In cases where the recoil energy is insufficient to cause immediate bond rupture, sufficient activation energy may be present to initiate a chemical reaction. When solids and liquids are bombarded, it is often found that the retention is greater than zero, even in compounds where bond rupture occurs in every case. The nonzero retention often found for the effect in condensed

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media has been explained by Libby (8) as due to the re-entry of the high energy recoiling atom by a reaction with neighboring molecules during the later stages of its cooling down process.

The chemical effects of the $Cl^{37}(n, \gamma)Cl^{38}$ reaction in chlorates have been studied by Amaldi and co-workers (1), D'Agostino (4), and Libby (9). These results showed that nearly all of the induced Cl^{38} activity could be separated from the chlorate in the form of chloride ion. The energy of the gamma radiation accompanying the reaction, as calculated from the masses of the neutron and the chlorine isotopes (6), is 6.2 Mev. If this is emitted as a single photon, the recoil energy imparted to the chlorine nucleus is about 540 ev.

The (γ, n) reaction is another type of nuclear reaction which involves no change in atomic number. To produce this reaction, the energy of the gamma rays used in the irradiation must be larger than a characteristic threshold value. In most cases, the momentum of the gamma ray, which is transferred to the target nucleus, is itself large enough to produce recoil energies larger than bond energies. In addition, the excess energy of the gamma ray over the threshold value appears as excitation energy of the product nucleus plus kinetic energies of the product nucleus and the ejected neutron. When the excitation energy is small compared to the kinetic energies, the recoil energy of the product nucleus may be several orders of magnitude greater than the recoil energy imparted to a nucleus of comparable mass in the neutron capture reaction. This is illustrated by the following example. For the reaction $Cl^{35}(\gamma, n)Cl^{34}$, with the Cl^{34} nucleus in its ground state, the threshold energy as calculated from the masses of the neutron and the nuclei (6) is approximately 11 Mev. If gamma rays of 24 Mev. energy are used, and the product nucleus formed in its ground state, the recoil energy of the Cl^{34} nucleus due to the ejection of the neutron is approximately 370,000 ev., compared to the recoil energy of 540 ev. for the Cl^{38} nucleus from the $Cl^{37}(n, \gamma)Cl^{38}$ reaction.

Considerable chemical effects can be expected to follow photoneutron reactions. In only a few cases have such effects been reported (2, 7). This paper reports a study of the $Cl^{35}(\gamma, n)Cl^{34}$ reaction in sodium chlorate.

Procedure and Results

The irradiations were performed with the betatron at the University of Saskatchewan. Crystals of the cubic form of sodium chlorate were irradiated in a small Pyrex test tube which was shielded by 1 mm. of cadmium foil and 5 cm. of Lucite. The amount of irradiation was measured by a Victoreen air chamber r-meter, shielded by 5 cm. of Lucite. The sample dosage measured in this way is thus not a direct measurement in roentgens of the quantity of energy absorbed by the sample of sodium chlorate, but is roughly proportional to the number of incident photons.

The decay of an irradiated sample of sodium chloride was followed in order to characterize the activity produced. The sample was irradiated with 1600

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roentgens of 24 ± 0.5 Mev. peak energy gamma rays for a five minute period. The activity decayed with a half-life of 32 min. over a period of four half-lives. The half-life of Cl^{34} is reported to be 32 ± 1 min. (5). Only one active component could be detected. It was conceivable that some activity due to Cl^{38}, caused by neutron contamination of the beam, could have been produced, but the presence of the cadmium foil around the irradiated material ensured that slow-neutron induced activities were negligible compared to the activity of Cl^{34}.

In the experiments with sodium chlorate, the activities of the various chlorine fractions were determined by counting the fraction as a silver chloride precipitate mounted on an aluminum disc. The corrections for the self-absorption of the Cl^{34} radiation in silver chloride were determined experimentally. In the calculation of the percentages of the activity found in the different fractions, corrections were applied for the decay of the active isotope during the course of the experiment, for self-absorption and for the fraction of the materials present which were taken for counting. The uncertainties reported in Table I include statistical errors in counting and estimates of the uncertainties in the self-absorption correction and in the determination of the percentage of the given chlorine fraction which was taken for counting.

TABLE I

DISTRIBUTION OF Cl^{34} FOLLOWING THE $Cl^{35}(\gamma,n)Cl^{34}$ REACTION IN SODIUM CHLORATE

Expt. No.	Irradiation* treatment	Percentage of activity in fractions separated				
		Cl^-	Cl^-+OCl^-	ClO_2^-	ClO_3^-	ClO_4^-
1	1600 r. at 24 Mev.	91 ± 2	93 ± 2		9 ± 2	0 ± 1
2	1600 r. at 24 Mev.				7 ± 2	
3	1600 r. at 24 Mev.	91 ± 2		1 ± 0.5	8 ± 2	
4	3200 r. at 24 Mev.	91 ± 2			9 ± 2	
5	3200 r. at 24 Mev. plus 3200 r. at 12 Mev.	91 ± 2			9 ± 2	
6	1600 r. at 18 Mev.	92 ± 3			8 ± 3	
7	3200 r. at 24 Mev. then heated five min. at 125°C.	90 ± 2			10 ± 2	
8	3200 r. at 24 Mev. then heated five min. at 125°C., then 1600 r. at 12 Mev.	89 ± 2			11 ± 2	

**The dosage is expressed as roentgens measured on a Victoreen air chamber r-meter. The energy value is the peak energy of the gamma rays from the betatron, with an uncertainty of 0.5 Mev.*

1. Determination of Distribution of Activity

Chemical treatment of the irradiated sodium chlorate was carried out to determine the chemical form in which the radioactive chlorine appeared.

In Experiment 1, 1 gm. of sodium chlorate was irradiated with 1600 roentgens of gamma rays of peak energy 24 ± 0.5 Mev. over a period of ten minutes. The sample was dissolved in 5 ml. of distilled water containing 2.5 mgm.

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chlorine as chloride and 2.5 mgm. chlorine as perchlorate. The chloride was then precipitated with silver nitrate, and the precipitate removed by centrifugation. To ensure complete removal of chloride activity, a second chloride fraction was precipitated after the addition of ammonia, chloride carrier and neutralization with nitric acid. The chlorate ion in the filtrate was reduced with sodium nitrite and precipitated as silver chloride. This treatment would also reduce any chlorine compounds of intermediate valence states which might be present. The perchlorate ion remaining in the filtrate was then precipitated with methylene blue.

The four precipitates representing the two chloride fractions, the chlorate plus intermediate states, and the perchlorate fraction were counted for activity using a thin-window Geiger counter. It was found that within the experimental error of the determination, all of the chloride activity was found in the first chloride fraction. The average values for the percentages of the total activity which appeared in the different fractions, as found from duplicate experiments, are given in Table I as Experiment 1.

For Experiment 2, the irradiated sodium chlorate was dissolved in a solution containing both chloride and hypochlorite ions. The hypochlorite ion was reduced to chloride with a small quantity of potassium iodide. Silver nitrate was added to precipitate a mixture of silver chloride and silver iodide. A second chloride fraction and the chlorate fraction were precipitated as in Experiment 1. The results are shown in Table I.

For Experiment 3, the irradiated crystals were dissolved in 5 ml. of a solution containing 2.5 mgm. of chloride ion, and 2.5 mgm. chlorine as chlorite ion. Two chloride fractions were precipitated as before and then the chlorite ion remaining in the filtrate was reduced to chloride with potassium iodide and precipitated with silver nitrate. After removal of the precipitate by centrifuging, the chlorate ion was reduced with sodium nitrite and precipitated as silver chloride. The distribution of activity as found in triplicate experiments is shown in Table I.

In other experiments reported in Table I, the conditions of irradiation or treatment of the crystals were varied. In these tests, separations into only chloride and chlorate fractions were carried out, using the procedure of Experiment 1 but without the addition of perchlorate ion.

In an experiment not reported in Table I, crystals of potassium chlorate were irradiated with 3200 roentgens of gamma rays of peak energy 24 ± 0.5 Mev. The percentage of the total activity which was found in the chlorate fraction was $10 \pm 2\%$.

The results of previous workers on the $Cl^{37}(n, \gamma)Cl^{38}$ reaction in crystals of sodium chlorate were confirmed by the bombardment of the solid with photoneutrons from an antimony–beryllium source, which were slowed down in paraffin. The percentage of the total activity which was found in the chlorate fraction under these conditions was $1.5 \pm 1\%$.

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2. Exchange Reactions

The exchange between chloride ion and chlorine has been shown (10) to be rapid, so that it is not possible to determine whether the activity found in the chloride fraction was present in the solution of the crystals as free chlorine or chloride ion. The chemical separations in the experiments on the distribution of activity were carried out under conditions where the exchange between chloride and chlorite, and between chloride and chlorate are slow (13). This was confirmed by the following experiments.

To obtain a solution containing radioactive chloride ion, crystals of irradiated sodium chlorate were dissolved in distilled water containing 0.5 mgm. of chloride ion. This solution was shaken with a solution of 1.0 mgm. of chlorine in carbon tetrachloride. Because of the rapid exchange between chloride ion and chlorine, a portion of the activity was extracted into the organic layer. The carbon tetrachloride solution was next shaken with an aqueous solution containing 1.5 mgm. chloride ion. The activity was exchanged further with 2.0 mgm. chlorine in carbon tetrachloride and then back into 5 ml. of water containing 2.5 mgm. chloride ion.

To investigate the exchange between chloride and chlorate ions, 1 gm. of unirradiated sodium chlorate was dissolved in the above solution. The chloride and chlorate fractions were separated and counted as silver chloride, following the separation procedure described previously. The chlorate fraction was found to contain $2 \pm 1\%$ of the total activity.

The exchange between chloride and chlorite ions was investigated by adding unirradiated sodium chlorate and 2.5 mgm. chlorine as chlorite ion to a solution of radioactive chloride ion prepared in the manner described above. The fractions were separated as described in Experiment 3. The chlorite fraction was found to contain $1.5 \pm 0.5\%$ of the total activity.

3. Investigation of Decomposition of Sodium Chlorate on Irradiation

Attempts were made to determine whether gamma radiation of the intensities used in these experiments produced a chemically detectable decomposition of sodium chlorate into chlorine compounds of lower valence.

To test for the formation of chloride ion, the turbidities produced by the addition of silver nitrate solution to solutions of known chloride ion concentration, to solutions of unirradiated sodium chlorate crystals, and to solutions of irradiated sodium chlorate were compared by means of a nephelometer. Both chlorate solutions were found to contain 0.05 ± 0.02 mgm. of chloride ion per gram of sodium chlorate.

Treatment of solutions of irradiated sodium chlorate with potassium iodide and acetic acid liberated no detectable free iodine under conditions where 0.04 mgm. of chlorine as chlorine dioxide, chlorite ion, hypochlorite ion, or free chlorine per gram of sodium chlorate could have been detected.

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It thus appears that decomposition of sodium chlorate by 1600 roentgens of gamma rays of peak energy 24 ± 0.5 Mev. yields less than 0.02 mgm. chloride ion and less than 0.04 mgm. chlorine as compounds of intermediate valence.

Discussion of Results

The results of Experiments 1, 2, and 3 indicate that on solution of irradiated crystals of sodium chlorate, 91 ± 2% of the total activity appears as the chloride ion or a chemical form rapidly exchangeable with it. The value of the percentage activity in the hypochlorite fraction, 2 ± 3%, does not differ from zero by more than the experimental error in its determination. The small amount of activity found in the chlorite fraction in Experiment 3 can be accounted for by an exchange process between chloride and chlorite ion, as was shown by direct experiment. Exchange between chloride and chlorate ion, however, is insufficient to account for all of the activity isolated in the chlorate fraction. No activity could be detected in the form of perchlorate.

The neutron capture reaction in sodium chlorate leads to a value of the retention of 1.5 ± 1%, all of which can be accounted for by an exchange between chloride and chlorate ions in solution or during the separation process. It thus appears that the retention is significantly greater for the (γ, n) than for the (n, γ) reaction in solid sodium chlorate.

The betatron produces a continuous spectrum of gamma rays with energies up to a selected maximum value. The recoil energies of the Cl^{34} nuclei will also be continuous up to a maximum value of 370,000 ev. for gamma rays of 24 ± 0.5 Mev. peak energy and up to 200,000 ev. for gamma rays of peak energy 18 ± 0.5 Mev. As shown in Table I, the retentions are the same within experimental error for irradiations with gamma rays of either peak energy.

The recoil energies in the (γ, n) reaction are due both to the momenta of the incident photon and, more important, the emitted neutron. If the product nucleus is left in an excited state which is stabilized by subsequent gamma emission a recoil on stabilization will also occur. Since the values of the recoil energy are greater than for the (n, γ) reaction, the increased retention in the (γ, n) process cannot be due to failure to rupture the bonds.

There are several possible reasons for the difference in retention values between the (γ, n) and the (n, γ) reactions in sodium chlorate. In the first place, the intensity of ionization produced in the crystal by radiation effects is much greater when the substance is exposed to the gamma ray beam than when bombarded with neutrons from a small neutron source. It is conceivable that radiation effects could bring about the re-entry into the chlorate ion form of the radioactive chlorine after its kinetic energy has been reduced to thermal

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values. No evidence for this effect is found in the results of Experiments 4 and 5. Experiment 4 shows that doubling the dosage of radiation did not alter the values of the retention within experimental error. Also, no change in this value was observed after postirradiation treatment of the crystals with low energy gamma rays, as shown in Experiment 5. The slight decreases in the percentage of the activity found in the chloride fraction after heat treatment of previously irradiated crystals at 125°C. for five minutes with or without subsequent exposure to low energy gamma rays are less than the experimental uncertainties, as shown by Experiment 7 and 8.

A second possibility is that the greater re-entry of the chlorine activity into the chlorate form in the gamma induced reaction, as compared to the neutron capture reaction, is due to the greater recoil energy in the former case. When the energy of the recoiling Cl^{34} atom is greater than about 34,000 ev., it is to be expected (8) that the recoiling atom will lose energy partially by producing ionization in the medium through which it moves. When the energy falls below this value, the recoiling particle can lose energy by two processes; first, by generating lattice waves which eventually degenerate into thermal motion, and second, by ejecting atoms from their normal lattice positions, thereby forming vacancies and interstitial atoms. It has been shown (11) that the fraction of the energy dissipated by the displacement of atoms decreases slowly as the energy of the particle decreases.

The energy dissipated in lattice vibrations effectively causes a local heating of the crystal in the vicinity of the cooling recoil atom. Reactions activated by this high temperature may have some bearing on the form in which the cooling atom is eventually frozen into the lattice. An exchange reaction between the chlorine atom and the chlorate ion under these conditions would lead to re-entry of some of the radioactive chlorine into the chlorate ion form.

Re-entry by means of the billiard-ball type of collision process discussed by Libby (8) is conceivable. In this mechanism, the recoiling chlorine atom, on ejecting an inert chlorine atom from a chlorate ion, has a certain probability of being left in the vicinity of the three oxygen atoms, with insufficient energy remaining to escape from the lattice cage, and so eventually reacts to form radioactive chlorate.

It cannot be decided from the present experimental evidence whether re-entry is to be attributed to any one or all of these processes.

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ISOTHERMS OF SULPHUR HEXAFLUORIDE IN THE CRITICAL TEMPERATURE REGION[1]

By K. E. MacCormack[2] and W. G. Schneider

Abstract

Measurements of the P-V isotherms for sulphur hexafluoride in a small temperature range of approximately 1.5°C. in the critical region have been made to determine the validity of some theoretical considerations recently proposed. No evidence has been found to support the postulates of Mayer with respect to anomalous second order transitions over a finite temperature range above the temperature of disappearance of a liquid meniscus designated T_m. All isotherms above the latter are found to have a finite slope and it is not possible to conclude that the T_m isotherm has a finite horizontal portion or "flat top". These conclusions are borne out by the nature of the isometrics which have been plotted and discussed qualitatively in relation to the existing theories.

The temperature of meniscus disappearance T_m is estimated to be 45.547 ± 0.003°C. and at the previously determined critical density (1) of 0.7517 gm./cm.^{3} the corresponding pressure is found to be 37.113 ± 0.003 atm. The critical density was found to be approximately 0.73 gm./cm.^{3}

Introduction

Investigations of the true nature of the critical region of a gas have now reached the stage where only extremely careful measurements of the physical properties of such a system will yield data sufficiently accurate to support or invalidate the several theoretical considerations put forward in recent years. The theory of Mayer (5) predicts a so-called "derby hat" region at the critical temperature. Whether such a region actually exists has so far not been conclusively demonstrated. The "derby hat" region is characterized by a flat-topped liquid–vapor coexistence curve. The temperature corresponding to this flat top, designated by T_m, is the temperature at which the visible meniscus disappears on heating. Above T_m there is a finite temperature interval in which the PV isotherms have zero slope but which show no marked discontinuity in slope such as that which occurs below T_m. The highest temperature at which the slope $\left(\frac{\partial P}{\partial V}\right)_T$ is still zero, but above which it is finite, is designated as the true critical temperature, T_c.

Several attempts have been made to determine the shape of the coexistence curve near the critical temperature experimentally (1, 3, 4, 10), and at present the question as to whether the top of the coexistence curve is flat, or rounded as in the classical theory, must be regarded as unsettled.

Measurements of the PV isotherms for carbon dioxide in the immediate neighborhood of the critical point have been reported by Michels, Blaisse, and

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Michels (7). Within the accuracy of their measurements, $\left(\frac{\partial P}{\partial V}\right)_T$ was finite above 31.04°C. this temperature having been deduced from the measurements and defined as the critical temperature. However, since simultaneous observations of the meniscus disappearance were not made, it is not clear whether this temperature is to be identified with the temperature T_m or T_c. No correction appears to have been made for the effect of "vapor head" on the measured pressures. Owing to the high density of the vapor near the critical point, the hydrostatic head of the vapor (and also of the liquid when the system is confined above a mercury column) is not negligible and as shown below can seriously alter the slopes of the measured isotherms. Measurements of PV isotherms for the system ethylene near the critical point were carried out by McIntosh, Dacey and Maass (6) who reported zero slopes of the isotherms in a small temperature interval above the temperature of meniscus disappearance, although within the accuracy of the measurements the existence of a small but finite slope could not be excluded (8).

Sulphur hexafluoride was chosen for the present measurements both because of its convenient critical properties and also because the coexistence curve for this substance had been measured previously (1). The experiments were designed so that:

(i) The system could be stirred.

(ii) Observations of the temperature of meniscus disappearance could be made.

(iii) The necessary data for making a "vapor head" correction to the measured pressures could be obtained.

Method

The arrangement of the apparatus is shown schematically in Fig. 1. The gas is confined to the thick-walled Pyrex glass bomb, A, whose volume, 29.855 cc. was determined by the gas expansion method described by Kaminsky and Blaisdell (2). With valves V_1 and V_2 closed, the pressure within the bomb is transmitted to a dead weight piston gauge via the mercury U-tube, C, the mercury being adjusted to electrical point contacts at the level B by means of the injector and balancing weights. Under these circumstances, it is evident that all measured pressures refer to this particular level. This level, relative to the bomb, was determined by means of a cathetometer; the dimensions are indicated in Fig. 1. The implications of these dimensions will be discussed later. The system V_1, V_2, V_3, A, C, was totally immersed in a rapidly stirred oil bath automatically controlled to $\pm$ 0.002° by means of a Wheatstone bridge – photocell arrangement. During the course of an actual measurement this could be improved by temporary manual control. Temperatures were measured with an accuracy of $\pm$ 0.001°C. by a platinum resistance thermometer in conjunction with a Leeds and Northrup Type G-2 Mueller bridge.

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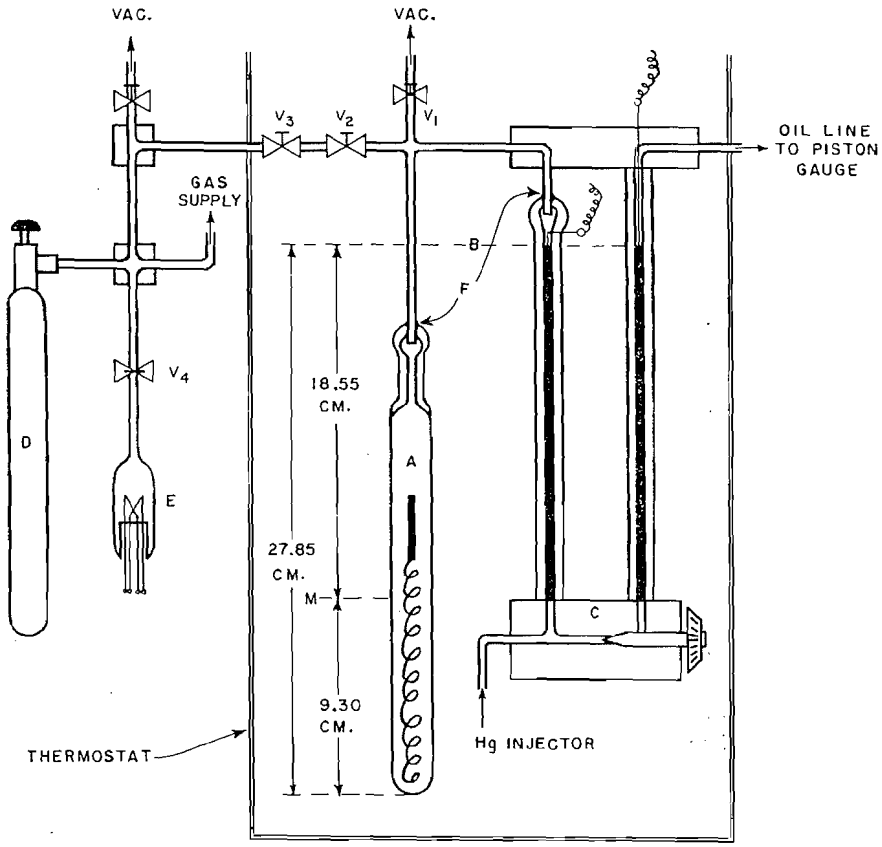

FIG. 1. *Schematic diagram of apparatus.*

Pressures were measured using a piston gauge of the type designed by F. G. Keyes and corrections applied as described in a previous paper (9). The sensitivity of this instrument was 2×10^{-4} atm., but temperature fluctuations of $\pm$ 0.001°C. gave rise to pressure fluctuations of $\pm$ 0.001 atm. and these must therefore be considered the limits of accuracy of the pressure measurements.

Sulphur hexafluoride which had been purified and analyzed by mass spectrometer as described previously (1) was condensed into the evacuated bomb A from the previously weighed pressure container D. Valve V_2 was closed and gas remaining in the connecting lines was recondensed in D at liquid air temperature. Vessel D was reweighed to 1 part in 2×10^5 (total wt. $\doteq$ 200 gm.) and the difference amounts to the mass of the filling in A. Small increments of gas could be removed from A by expanding into the small volume between valves V_2 and V_3 and condensing into D before weighing. One expansion served to remove approximately 0.1 gm. of SF_6. The end point of such a condensation process was determined by opening valve V_4 to a thermocouple gauge E and measuring the line pressure. A McLeod gauge could not be used here because

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of the possible condensation of mercury vapor in D. Glass-Kovar seals were employed at F in order to eliminate introduction of impurities from the alternative metal–glass packing arrangements. The high-pressure valves V_1 and V_2 were so arranged that gas was not in contact with the Teflon packings when closed. The bomb A was equipped with a glass stirrer, as shown, to the upper end of which was sealed a piece of soft iron encased in glass. This was agitated by means of an external D.C. coil with a variable make-break interval of approximately 0.5 sec.

In all cases where a liquid meniscus could be observed, the level was measured by means of the cathetometer relative to the level B and also the base of the bomb. On completion of the experiments the bomb was calibrated using distilled water so that liquid volumes could be estimated with an accuracy of 0.1 cc. by measuring the height of liquid SF_6 in the bomb.

Treatment of Data

(*a*) *Liquid Volume Measurements*

In the two-phase system at constant temperature,

$$V_L + V_G = V_T \tag{1}$$

where V_L, V_G, and V_T are the liquid, vapor, and total volumes respectively. If v_L and v_G are the equilibrium specific volumes (reciprocal densities) of the liquid and vapor respectively, and $\bar{v}$ is the over-all specific volume of the particular mass filling, then the ratio of the masses of the vapor and liquid phases is given by,

$$\frac{m_G}{m_L} = \frac{\bar{v} - v_L}{v_G - \bar{v}} = \frac{V_G v_L}{V_L v_G}$$

$$\therefore \quad V_G = V_L \left(\frac{\bar{v} - v_L}{v_G - \bar{v}}\right) \frac{v_G}{v_L} \tag{2}$$

Combining Equations (1) and (2),

$$V_L = V_T \frac{v_L}{\bar{v}} \left(\frac{v_G - \bar{v}}{v_G - v_L}\right)$$

or

$$V_L = \frac{k}{\bar{v}} - C \tag{3}$$

where $k = V_T(v_L v_G / v_G - v_L)$

and $C = V_T(v_L / v_G - v_L)$

This means that the liquid volume should be directly proportional to the over-all specific density and since V_T is known, it becomes possible to estimate v_L and v_G for a given isotherm by plotting V_L vs. $1/\bar{v}$. At the temperature for which v_L becomes equal to v_G, the slope k of the isotherm will become infinite and the over-all specific volume at which this occurs will be the critical volume. All the isotherms will intersect at this value of $\bar{v}$.

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(*b*) *P-V-T Measurements*

As mentioned earlier, the effect of gravity on a column of gas is sufficiently large to influence the interpretation of P-V-T relations measured in a system such as that described. The approximate expression for the difference in pressure between two points in a vertical column of fluid of height h(cm.) having a mean density $\bar{\rho}$ (gm./cm.^{3}) is given by,

$$\Delta P(\text{atm.}) = \frac{h\bar{\rho}}{76\ \rho_{Hg}}$$

where ρ_{Hg} is the density of mercury at 0°C. and 1 atm. Applying this relation to the present system as depicted in Fig. 1, it can be shown for example that for $\bar{\rho} = 0.73$ gm./cm.^{3} the ΔP between level B and the bottom of the bomb is approximately equal to 0.020 atm. This is far larger than the accuracy with which P can be measured at level B. It is evident then that, in the case of all homogeneous systems measured, pressures must be corrected to correspond to the level M at which the critical meniscus would occur for it is this level which has a density equal to the mean density of the over-all mass filling. This level can be estimated from the point of intersection of isotherms plotted according to Equation (3). In calculating this correction, however, it must be assumed that the mean density in the upper regions of the tube is the same as the over-all mean density. In actual fact it will be somewhat less than this value.

It is next necessary to consider the nature of isotherms lying below the critical temperature, i.e., an isotherm such as that marked XY on the conventional P-V diagram, Fig. 2. Here the rounded curve represents the liquid–vapor coexistence envelope. Let us suppose that $\bar{V}_1$ is the measured mean specific volume which in reality occurs only at the level M in the fluid column. The volume designated v_L is larger than $\bar{V}_1$ and is the volume at that par-

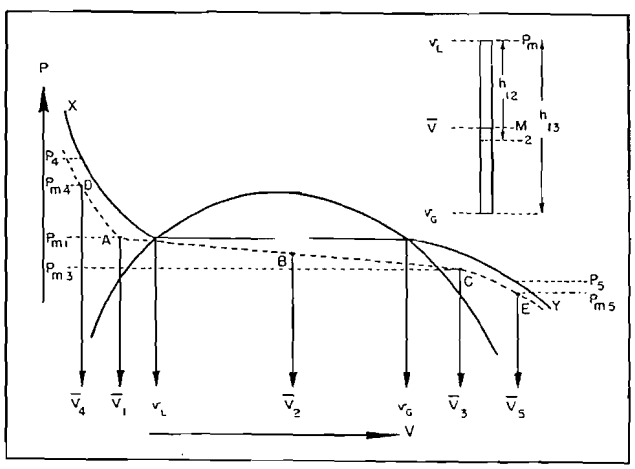

FIG. 2. *Diagram showing the effect of "vapor head" on the shape of a subcritical P-V isotherm. Measured DABCE. Correct—XY.*

ticular temperature at which the first bubble of vapor would appear at the top of the column on lowering the temperature by a very small amount. If the pressure were measured at this point it would be plotted at (P_{m_1}: $\bar{V}_1$) marked A. As $\bar{V}_1$ is increased to $\bar{V}_2$ the liquid level falls in the bomb to level 2 (see inset Fig. 2) and $P_{m_2} < P_{m_1}$ by virtue of the vapor head which is approximately equal to $h_{12}\rho_G$. This point (P_{m_2}: $\bar{V}_2$) is plotted at B. As $\bar{V}$ is further increased the liquid finally becomes a small drop at the base of the bomb where v_G is the saturated vapor volume and the pressure is P_{m_1}, since v_L and v_G are true equilibrium volumes. P_{m_3}, the measured pressure, is less than P_{m_1} by the amount $h_{13}\rho_G$ and v_G is smaller than the over-all measured volume $\bar{V}_3$. This point (P_{m_3}: $\bar{V}_3$) is thus plotted at C.

It now remains to consider the trend of the isotherm to the left of A and right of C where the system is homogeneous, liquid, and gas respectively. If the measured volume be $\bar{V}_4$, $P_{m_4} < P_4$ since P_4 refers to the level M near the center of the column where the volume is actually $\bar{V}_4$. This point is thus plotted at D. Finally, $\bar{V}_5$ should refer to P_5 whereas the measured pressure $P_{m_5} < P_5$ by an amount approximately equal to $\frac{1}{2}h_{13}\rho_5$. This point is plotted at E.

Since $(P_4 - P_{m_4}) \doteq \frac{1}{2}h_{13}\rho_4$ is always greater than $\frac{1}{2}(P_{m_1} - P_{m_3})$ the measured isotherm AD will never become coincident with the true isotherm. Conversely, $(P_5 - P_{m_5}) \doteq \frac{1}{2}h_{13}\rho_5$ is always less than $\frac{1}{2}(P_{m_1} - P_{m_3})$ and as ρ_5 decreases the curve CE should ultimately coincide with the true isotherm.

It becomes evident then that isotherms measured in this way will produce a diagram quite unlike the classical shape, for the tie-line ABC will have a slope depending on the saturation vapor density ρ_G and the level above the liquid meniscus at which the pressure is measured. This will, of course, be negligible in all cases far below the critical temperature where the density of the saturated vapor is much less than that of the liquid.

Results

The maximum temperature of coexistence, T_m, for sulphur hexafluoride was reported (1) to be 45.555°C. Isotherm measurements were confined to a range of temperature extending 1.5°C. above this temperature and to one lower temperature, 45.500°C. where two phases could be distinguished quite clearly by visual observation. The range of specific volume extended from 1.183 to 1.604 cm.^{3}/gm., i.e., a density range 0.8451 to 0.6233 gm./cm.^{3} For all temperatures and densities the measured pressures at the level B are recorded in Table I. Corrections have been applied to each of these pressures according to the methods outlined in the previous section. This may be summarized by the following relations:

(*a*) Homogeneous cases,

$$\Delta P(\text{atm.}) = h_{B-M}\,\bar{\rho}/76\,\rho^\circ_{\text{Hg}}$$

(*b*) 2-phase case (corrected to meniscus level),

$$\Delta P(\text{atm.}) = h_{B\text{-meniscus}}\,\rho_G/76\,\rho^\circ_{\text{Hg}}$$

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TABLE I

MEASURED AND CORRECTED PRESSURES AT VARIOUS VOLUMES AND TEMPERATURES FOR SF_6

V cm.³/gm.	45.500°C.		45.550°C.		45.600°C.		45.680°C.		45.800°C.		46.000°C.		46.500°C.		47.000°C.	
	Meas'd.	Corr. (*b*)	Meas'd.	Corr. (*a*)	Meas'd.	Corr. (*a*)	Meas'd.	Corr. (*a*)	Meas'd.	Corr. (*a*)	Meas'd.	Corr. (*a*)	Meas'd.	Corr. (*a*)	Meas'd.	Corr. (*a*)
1.183	37.095		37.142	37.157	37.188	37.203	37.262	37.277	37.375	37.390						
1.188	37.088		37.137	.152	37.180	.195	37.254	.269	37.366	.381						
1.221	37.073		37.118	.133	37.164	.179	37.234	.249	37.342	.357						
1.221	37.070		37.116	.131	37.162	.177	37.231	.246			37.517	37.532	37.971	37.986	38.434	38.449
1.263	37.064	37.070	37.107	.121	37.147	.161	37.219	.233	37.322	.336	37.496	.510	37.935	.949	38.377	38.391
1.318	37.064	37.073	37.105_6	.119	37.147	.161	37.213	.227	37.313	.327	37.481	.495	37.903	.917	38.328	38.342
1.379	37.059	37.072	37.099	.112	37.141	.154	37.208	.221	37.304	.317	37.469	.482	37.875	.888	38.282	38.295
1.438	37.059	37.074	37.099	.111	37.139	.151	37.201	.213	37.297	.309	37.455	.467	37.848	.861	37.242	38.254
1.490	37.058	37.075	37.096_5	.108	37.135	.147	37.196	.208	37.289	.301	37.444	.456	37.826	.838	38.206	38.218
1.556	37.049		37.086_5	.097	37.124	.135	37.184	.195	37.273	.284	37.421	.432	37.789	.801	38.154	38.165
1.604	37.038		37.073_6	.084	37.110	.121	37.166	.177	37.252	.263	37.397	.408	37.752	.763	38.108	38.119

where $\bar{\rho}$ is the mean density of the mass filling and ρ_G is the saturation vapor density for the particular temperature. For each temperature in Table I, the corrected pressures are given in the right-hand column. In order to compute correction (*b*) an estimate of ρ_G was made from liquid volume measurements and the application of Equation (3) at the temperature 45.500°C. By carrying out similar measurements at two lower temperatures, 45.000° and 45.300°C., it was possible to estimate the level of the liquid, at its maximum temperature of coexistence with vapor from the point of intersection of the liquid volume isotherms plotted in Fig. 3. This is the level marked M in Fig. 1 and was found to be 18.55 cm. below the measuring level B. If the coexistence curve shows a unique value for the critical density this from Fig. 3 should again correspond to the density at the point of intersection, i.e., 0.73 gm./cm.^{3} This cannot be expressed with any greater accuracy by virtue of the limitations involved in estimating liquid volumes by cathetometric methods in a nonsymmetrical bomb. The same limitations are, of course, involved in the estimate of the B–M distance but a 5% error would cause an error in ΔP no greater than the error

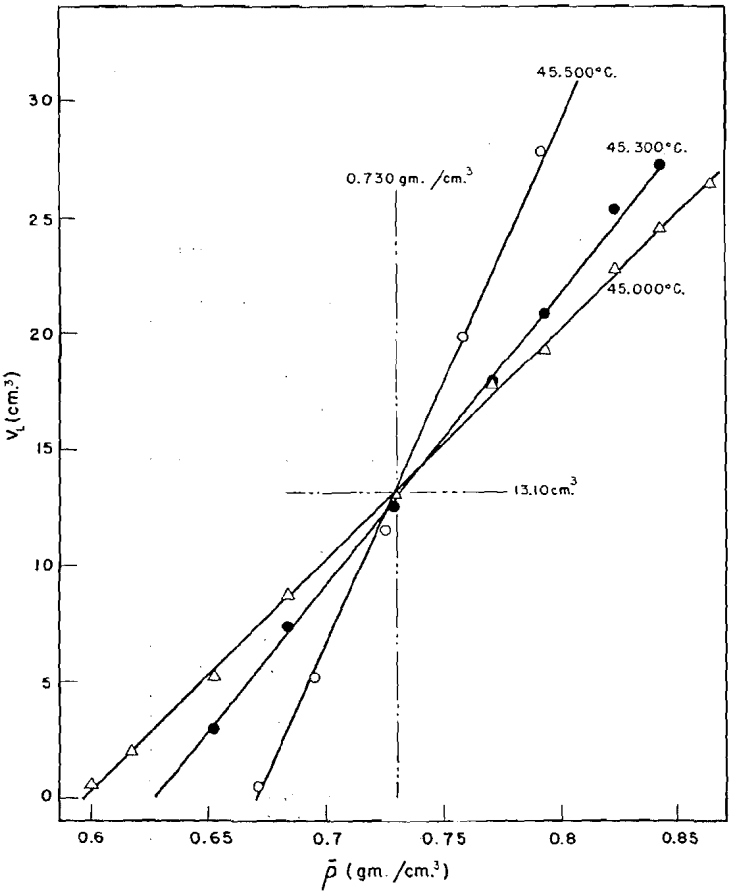

FIG. 3. *Plots of total liquid volume vs. mean specific density.*

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involved in measuring the pressure. It is estimated, therefore, that the limits of error in P(Table I) should be $\pm$ 0.0015 atm.

The measured isotherms have been plotted as broken lines in Figs. 4 and 4A the solid lines referring to the corrected data. The qualitative nature of the opalescence at each point on these isotherms has been indicated by appropriate symbols for the sake of interest and the position of the opalescent envelope has been shown approximately by the broken line, A. It should be emphasized that efficient stirring was maintained during pressure measurements and no attempt was made to determine the coexistence curve as measured earlier by Atack and Schneider (1). By interpolation, their coexistence curve has been

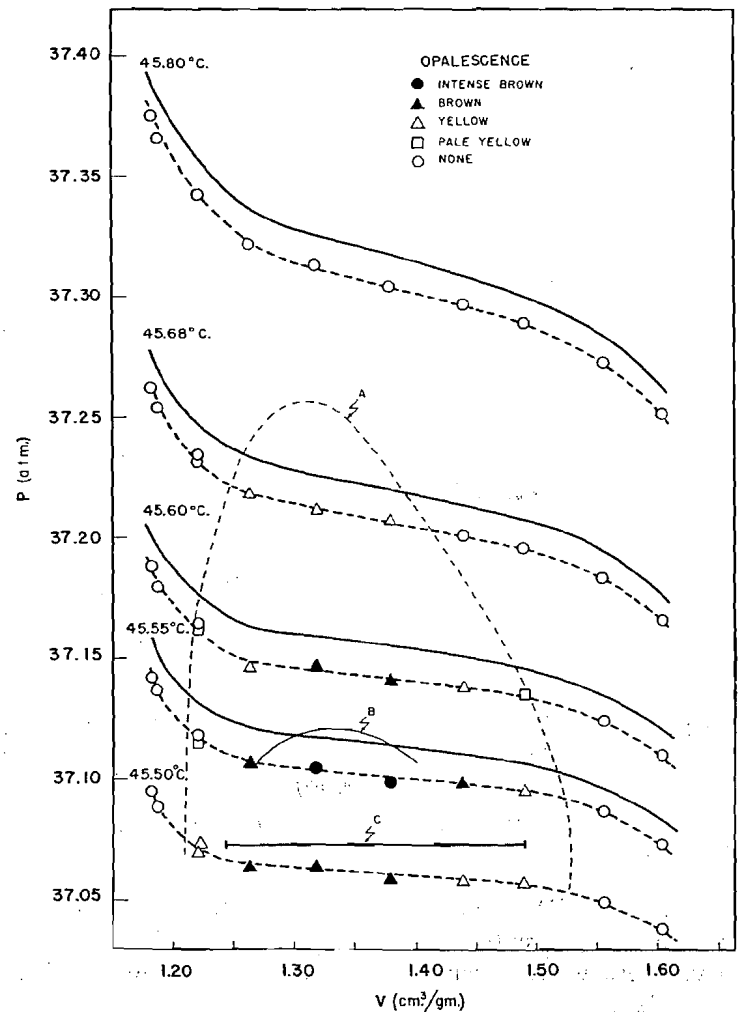

FIG. 4. *P-V isotherms for SF_6 showing the opalescence boundary—A; B, critical coexistence curve (Ref. (1)); C, corrected isotherm for two-phase range of specific volume. Measured isotherms shown as broken lines. Corrected isotherms shown as solid lines.*

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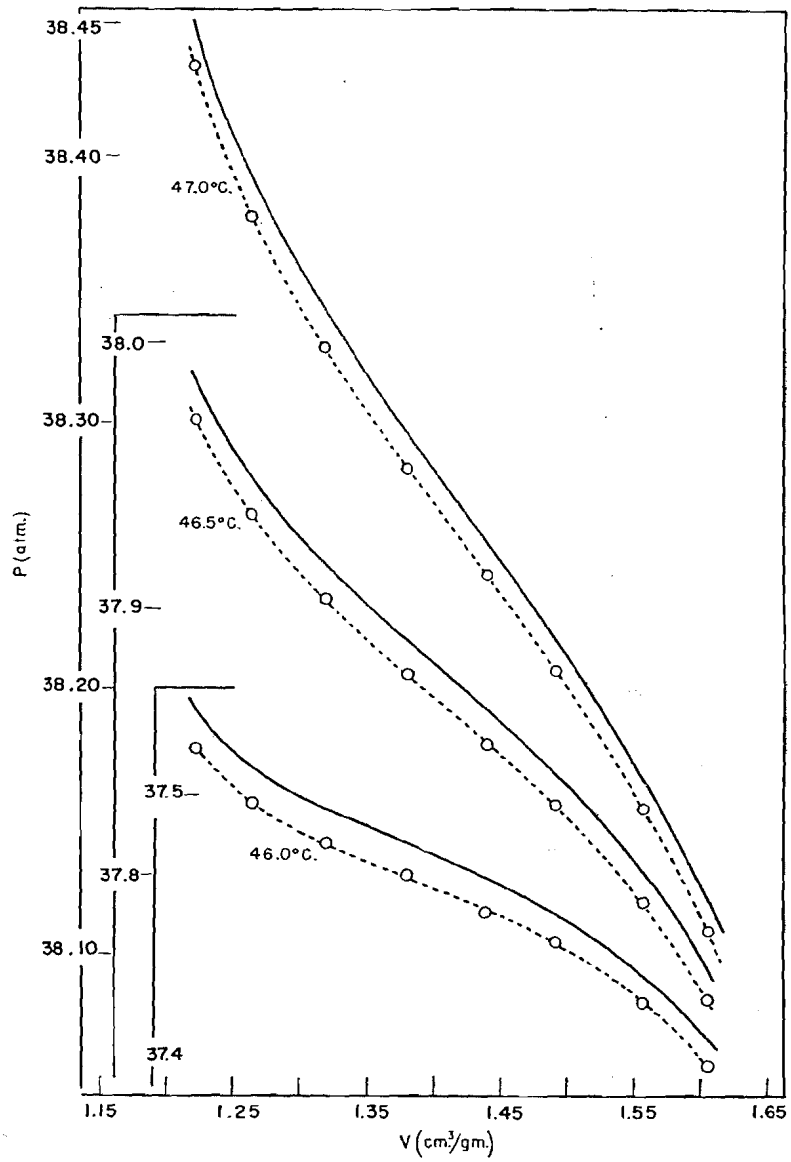

FIG. 4A. *P-V isotherms for SF_6. Measured and corrected isotherms shown as broken and solid lines respectively.*

included in Fig. 4 (line B) showing that it lies slightly above the isotherm at 45.550°C. where an apparently homogeneous system exists over the whole density range. There are two points on this isotherm, however, which showed very intense opalescence.

During the time in which stirring was maintained this opalescence appeared to be of uniform intensity. The system of specific volume 1.379 cm.^{3}/gm. did,

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however, show a definite tendency to settle down on long standing (one-two hours) in the absence of stirring, giving rise to a gradient of increasing opalescence from top to bottom of the bomb. Although the corrected isotherm lies just within the coexistence curve B the failure to establish a definite liquid meniscus at this temperature might be due to the existence of a discrepancy of two or three thousandths of a degree in the temperature measurements of the coexistence curve B (1) and those involved in the present work. A reduction in temperature of 0.005°C. caused the definite establishment of two phases separated by a meniscus.

With reference to the isotherm at 45.500°C., where two definite phases could be observed over the volume range 1.244 to 1.490 cm.^{3}/gm., it is interesting to note that pressure corrections over this particular range serve to establish a horizontal isotherm as expected from conditions imposed by thermodynamic equilibrium. This should also be an indication of the high degree of purity in the sample.

From the data presented the value of T_m is estimated to be 45.547 $\pm$ 0.003°C. and the corresponding pressure is 37.113 $\pm$ 0.003 atmospheres.

Finally it may be said quite certainly that within the limits of experimental accuracy each point showed very good reproducibility independent of thermal history or time effects during a measurement.

Discussion

From the isotherms plotted in Fig. 4 it can be concluded that the isotherm at 45.50° where a meniscus was definitely present at intermediate densities is horizontal when corrected for vapor head. At 45.55° which is very near the critical temperature, designated as T_m the isotherm is not horizontal; at all temperatures above T_m the slope of the isotherms is finite. Hence the present measurements do not support the theory of Mayer with respect to the slope of the isotherms above T_m. Likewise, the measurements on the coexistence curve of sulphur hexafluoride reported previously (1) indicate that the top of the coexistence curve is not flat. Thus for sulphur hexafluoride at least it appears that the "derby hat" region at the critical point does not exist. It should be emphasized, however, that these conclusions do not necessarily invalidate the concept of molecular clustering at the critical temperature.

The above conclusions appear to offer at least partial confirmation of the views expressed by O. K. Rice (8). On the basis of a thermodynamic treatment he has developed the theory to explain the "flat top" nature of the isotherm at T_m. It is almost impracticable, however, to establish the T_m isotherm and thereby investigate the validity of the "flat top" coexistence curve by the method described in this paper. The theory further predicts that the isotherms above T_m should have the finite slope observed in the present work.

Since the value of $(\partial P/\partial V)_T$ must reach a zero value at the temperature estimated to be 45.547°C. independent of the shape of the coexistence curve, it

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is therefore interesting to determine the nature of temperature dependence of $(\partial P/\partial V)_T$ in the immediate vicinity of T_m. Michels and co-workers (7) who measured isotherms for carbon dioxide in the neighborhood of the critical point estimated the critical temperature, i.e., the temperature for which $(\partial P/\partial V)_T = 0$, by plotting the values of $(\partial P/\partial V)_T$ at the inflection points of the isotherms as a function of T. Only three points were used extending approximately over 1.5°C. above the critical temperature. The linearity of the relationship was claimed to be sufficiently good to warrant extrapolation of the line to the point where $(\partial P/\partial V)_T = 0$ in order to estimate the critical temperature and the results were not considered to support doubts as to the validity of the classical theory of the coexistence region. The present data for SF_6 covers approximately the same temperature range, including five isotherms only 0.5° above the coexistence temperature. In Table II, the inflection values of $(\partial P/\partial V)_T$ are presented for each isotherm and these are plotted in Fig. 5. It is evident from the latter that

TABLE II

INFLECTION VALUES OF $(\partial P/\partial V)_T$

T,°C.	$(\partial P/\partial V)_T$ atm. gm. cm.$^{-3}$
45.500	0.000
45.550	0.057
45.600	0.067
45.680	0.110
45.800	0.139
46.000	0.223
46.500	0.440
47.000	0.690

a linear relationship such as observed for carbon dioxide could not be assumed in this case over the whole temperature range. Furthermore, the curve does not pass through the estimated coexistence temperature when $(\partial P/\partial V)_T = 0$. In fact an extrapolation to zero $(\partial P/\partial V)_T$ would cut the temperature axis at approximately 45.4°C. which is far below the observed coexistence temperature 45.547°C. This means that the compressibility of the system is less than that which would be expected from classical theory for any given temperature within this particular range, i.e., 45.547 to 46.000°C. Moreover, it appears necessary for an abrupt change to occur in the temperature dependence of the compressibility when T_m is reached in order to establish the condition of zero $(\partial P/\partial V)_T$.

In Table III data for the isometrics (constant volume) are presented for two or three values of specific volume on each side of the critical volume. The corrected pressures are used and these have been plotted as a function of temperature over a range of approximately 0.5°C. in Fig. 6. For the sake of clarity only five isometrics are plotted. Over this short range these plots are definitely linear within the limits of experimental error, On a much larger scale it is possible to include the full temperature range of 1.5°C. and it is quite clear

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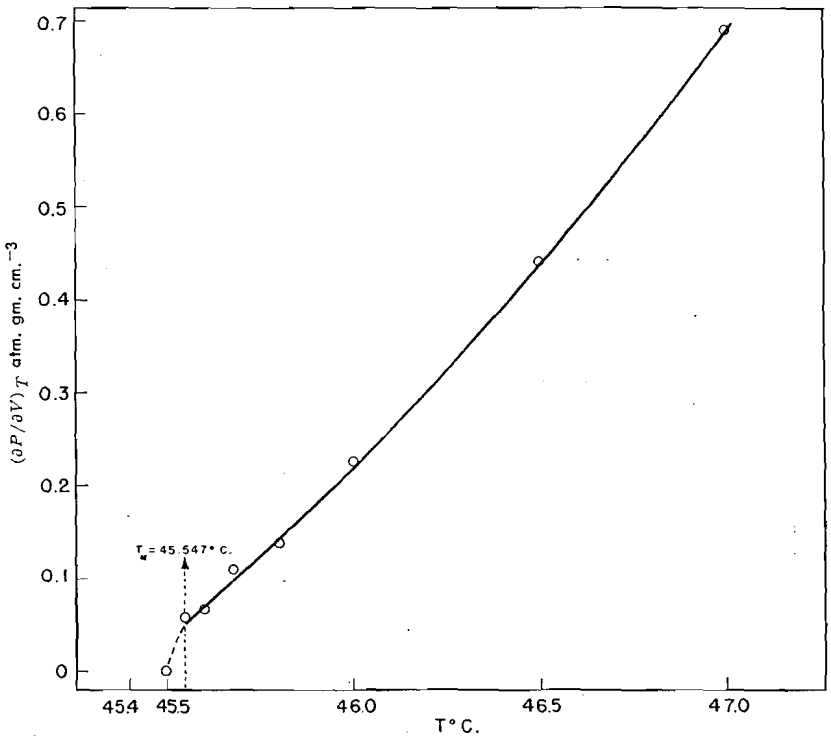

FIG. 5. *Plots of* $(\partial P/\partial V)_T$ *vs. temperature.*

TABLE III

ISOMETRIC DATA FOR THE CRITICAL REGION OF SF_6
(ALL PRESSURES CORRECTED AS DESCRIBED)

V cm.^{3}/gm.	T,°C.						
	45.550	45.600	45.680	45.800	46.000	46.500	47.000
1.190	37.150	37.195	37.268	37.381			
1.270	37.121	37.163	37.233	37.335	37.507	37.944	38.384
1.290	.120	.161	.229	.330	.501	.932	38.366
1.330	.117	.159	.225	.324	.492	.911	38.332
1.370	.115	.156	.221	.319	.483	.892	38.301
1.550	.098	.136	.196	.286	.434	.804	38.170
1.590	.088	.126	.182	.270	.415	.775	38.134

that the isometrics on the high density side are concave upwards and conversely downwards on the low density side. The isotherm at a specific volume of 1.37 cm.^{3}/gm. is linear over the whole range. If a "flat top" did occur over an appreciable volume range, it should be possible to observe one point of intersection at the temperature T_m for all isometrics within this range. This is illustrated in Fig. 7, case (A), where isometrics over the volume range b to d all intersect at T_m. The branching should occur at lower temperatures for all

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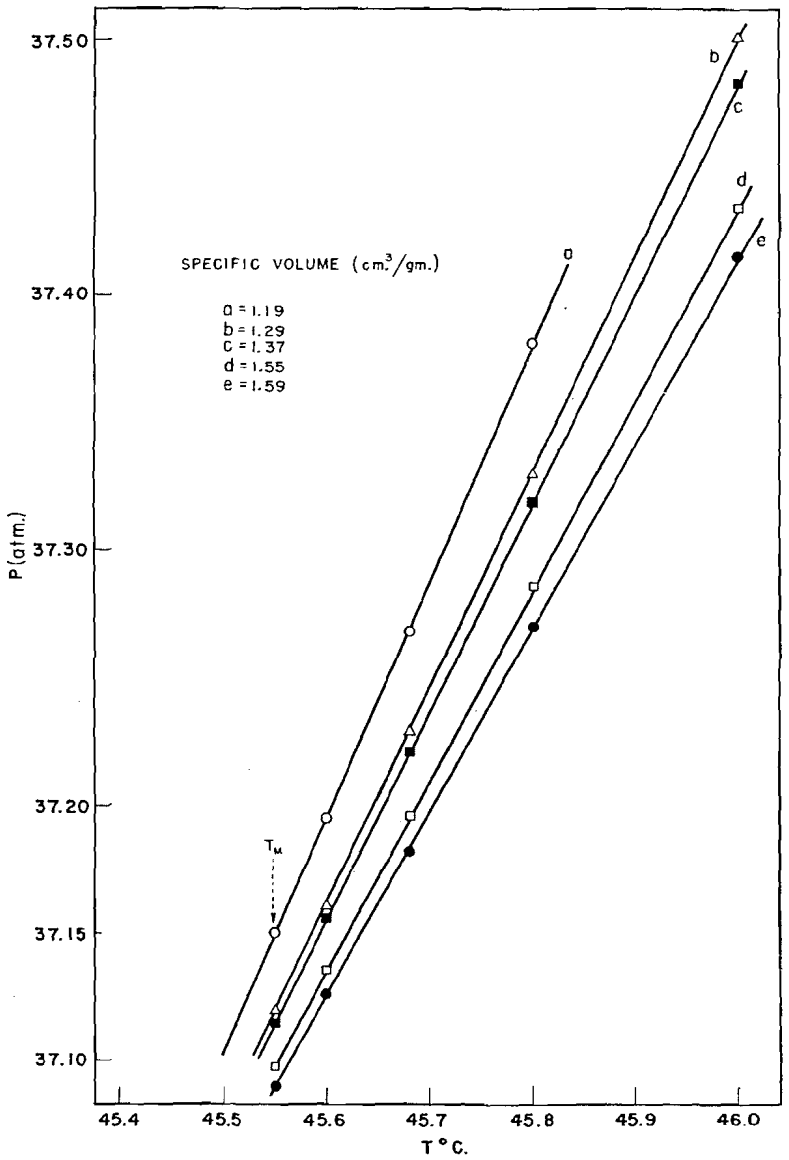

FIG. 6. *Isometric plots.* (*Pressure vs. temperature at constant volume.*)

other isometrics. If the P-V isotherms above T_m did in fact possess a horizontal portion, it would be expected that isometrics would show a tendency to branch above the estimated value of T_m. This is illustrated in Fig. 7, case (B), showing the occurrence of branching between T_m and T_c. It is clear, however, from Fig. 6 that the values of $(\partial P/\partial T)_v$ do not change very much over a fairly wide volume range and it would be difficult to decide whether in fact there were a small volume range for which intersections all occur at the value T_m. It does seem clear, however, that there is no tendency to branch above the temper-

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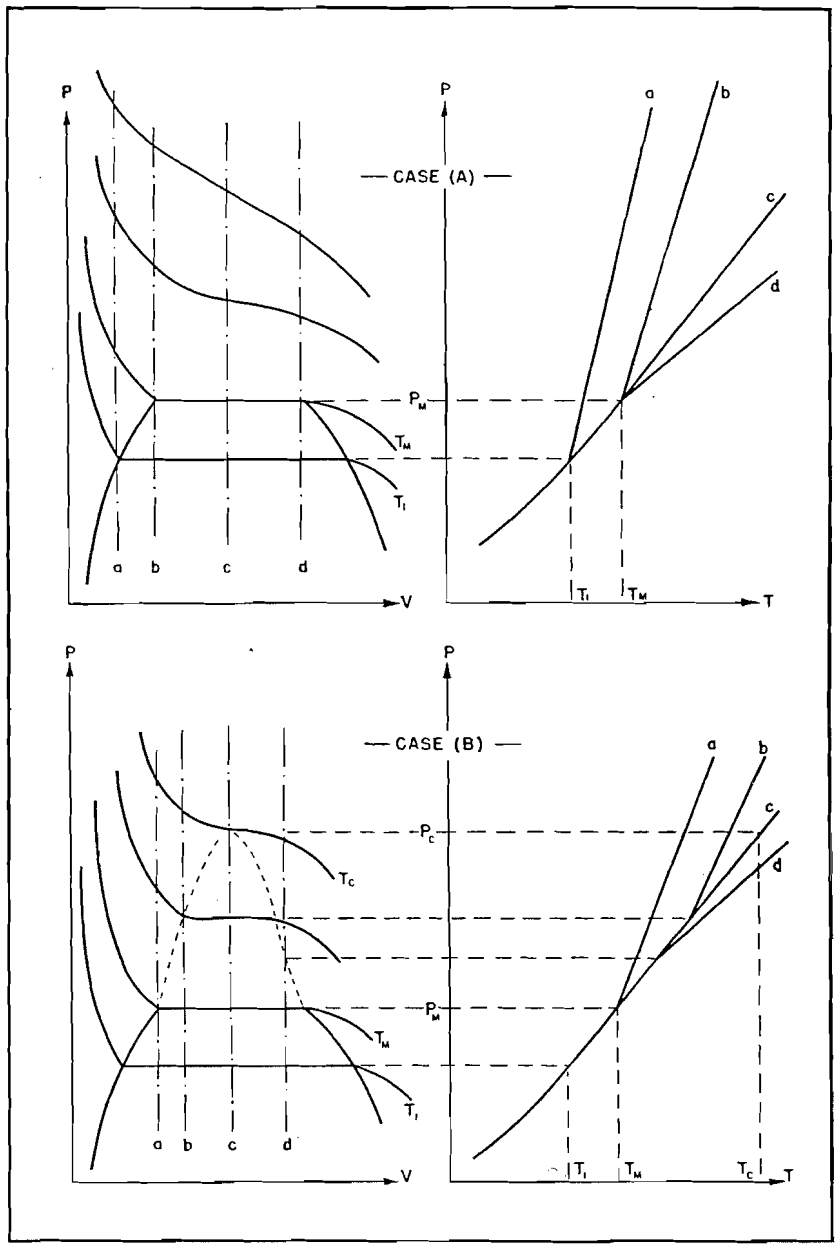

FIG. 7. *Diagrams showing relationship between isotherms and isometrics.*

ature 45.547°C. estimated for T_m earlier. Indeed the three isometrics at specific volumes of 1.29, 1.33, and 1.37 cm.³/gm. which all lie very close to the critical value previously determined (see Fig. 4) appear to intersect well below 45.547°C. It would seem then that no "flat top" could extend over a range of density so broad.

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Acknowledgments

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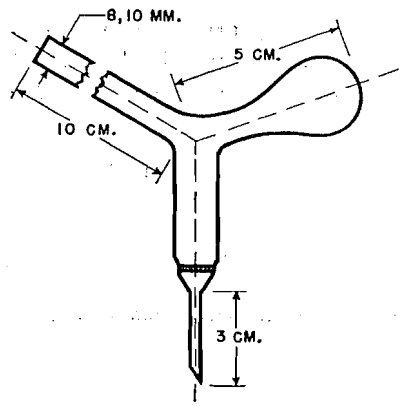
NOTES

A Semimicro Filtration Apparatus*

This device is a modification of the sidearm test tube described by Wright (1) and others, and has been in use in this laboratory for several years. Its main function is the removal of insoluble impurities from organic compounds, prior to their crystallization for elementary analysis, measurement of infrared and ultraviolet spectra, optical rotation, etc. It is simply constructed by blowing a pear-shaped bulb on the end of a length of 8 or 10 mm. Pyrex tubing, bending the tubing at an angle of 120° about 5 cm. from the bottom of the bulb, and sealing a small sintered glass filter tube to the bent portion, rather closer to the bulb than to the open end of the tube. (See illustration.) The bulb may be



of any desired capacity, usually between 2 and 5 ml., depending on the amount of material to be handled and the solubility of the material. The filter tubes are normally available** in three porosities, the most useful for this purpose being 'medium,' though it is desirable to have one 'coarse' for more viscous solutions. In addition, the volume of the funnel above the filter disc may be varied, a short barrel affording readier preheating by refluxing solvent.

In use, the apparatus may be held by hand or in a clamp, or suspended in a $2\frac{1}{2}$ in. retort ring, with the bulb pointing down. The sample to be recrystallized is placed in the bulb, along with the appropriate solvent, and heated over a hot plate until dissolved. The long neck acts as an air condenser, while the refluxing solvent serves to preheat the filter plate. Bumping is prevented by the addition of a small boiling chip, or by swirling the contents of the bulb, while concentration may be effected by inclining the apparatus so that some

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** *These micro filter tubes with fritted disc are made by the Corning Glass Works, and are easily available from the usual agencies.*

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of the solvent distills off through the neck. When the substance has completely dissolved, the apparatus is removed from the hot plate, tilted so that the filter tube is pointing down, and the solution forced into the crystallizing vessel by air pressure applied either by mouth, or with a rubber hand-bulb. If necessary, a silica gel moisture trap may be attached by means of rubber tubing. The fritted disc may be washed with a few drops of fresh solvent, while, if a precipitant is required, such as petroleum ether, it may be added in the same way.

The main advantages of this piece of equipment are as follows:

1. Permanent all-glass construction avoids contamination of the specimen by stopper, filter material, etc.

2. The sintered glass disc may be preheated by refluxing solvent.

3. Filtration is under pressure, with the result that evaporation even of volatile solvents is cut to a minimum. This also avoids clogging of the filter by premature crystallization, and permits the use of more concentrated solutions, with consequent high recovery.

4. Since most compounds being prepared for analysis are already pure, the apparatus is easily cleaned with standard solvents, while insoluble impurities, such as accumulated dust particles, may be removed periodically with cleaning solution.

1. WRIGHT, G. F Can. J. Research, B, 17: 302. 1939.

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Some Observations on the Copper Oxide Oxidation of Cholesterol

In 1904, Diels and Abderhalden (5) reported that cholesterol treated at 300°C. with finely divided copper oxide was oxidized to cholestenone in 60% of the theoretical yield. This ketone was characterized by melting point determination and by combustion analysis. In addition, the oxime, semicarbazone, phenylhydrazone, and 2,4-dinitrophenylhydrazone were prepared and characterized. More recently, the oxidation of cholesterol was carried out in a similar manner by Diels, Gadke, and Kording (6), who characterized their reaction product by melting point determination only.

This oxidation procedure was repeated a number of times in the present investigation. A crystalline product obtained by extraction of cooled reaction mixtures with diethyl ether melted at 80°C. after several recrystallizations and formed the expected phenylhydrazone melting at 145°C. However, selective ethanolic extraction of the reaction mixtures gave in a number of instances

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another crystalline product (in yields as high as 40% of the theoretical), which also melted at 80°C. after recrystallization but failed to form a phenylhydrazone. This second reaction product gave a positive color test with the sulphuric acid–acetic anhydride (Liebermann–Burchard (2,11)) reagent (in agreement with the qualitative findings of Diels and Abderhalden for their reaction product), while cholestenone prepared by us according to Oppenauer (13) and carefully characterized gave no color with this reagent. Subsequent ultraviolet absorption and optical rotation measurements characterized the product which formed the phenylhydrazone as the expected cholestenone (cholesten-4-one-3, $[\alpha]_D$ + 88.0°, ϵ_{max} = 15,725 at 240 mμ) which, as a 17-alkyl-substituted 4:5-unsaturated 3-ketosteroid, gives a negative Liebermann–Burchard color reaction (3). The reaction product which failed to form a phenylhydrazone but gave a positive Liebermann–Burchard reaction was the better known of the intramolecular dehydration products of cholesterol, cholesterilene (cholestadiene-3,5, $[\alpha]_D$ − 90.0°, ϵ_{max} = 18,450 at 235 mμ, with lesser ϵ_{max} at 229 and 243 mμ).

It is evident that the reaction product described by Diels and Abderhalden contained the ketone cholestenone, because these workers prepared the derivatives listed above (oxime, semicarbazone, etc.); however, they made no mention of quantitative recovery of these derivatives. It is further apparent that the product obtained by these investigators also contained one or more steroids which give a positive Liebermann–Burchard color reaction. One such steroid might have been unchanged cholesterol, while a second, in the light of the present findings, might have been cholesterilene.

This dehydration of cholesterol observed by us is not particularly surprising when one considers the observations of other researchers in the steroid field. For example, the simple heating of cholesterol has been shown by a number of investigators (1, 7, 14, 15, 17) to give either cholestenone or cholesterilene or both. In addition, one or both of these steroids have resulted from the distillation of cholesterol either alone or in the presence of zinc, nickel, copper, or other suitable metal catalyst (8, 9, 10, 12, 16). (Metallic copper is formed by the reduction of the copper oxide in the oxidation procedure under consideration.)

Although our experimental observations are not entirely unexpected in the light of these past researches, they strongly suggest that any product of the copper oxide "oxidation" of cholesterol should be carefully characterized. Combustion analysis is not the ultimate for such characterization because of the relatively high molecular weights of the compounds involved. Characterization by melting point determination is also unsatisfactory, because both cholestenone and cholesterilene melt at approximately 80°C.; furthermore, there is little depression evidenced in mixed melting point determinations. The physical measurements of choice are those of optical rotation and ultraviolet absorption, as may readily be seen by comparing the experimentally determined values for the respective steroids. (A graphic comparison of the

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ultraviolet absorption spectra of cholestenone and cholesterilene has been made by Cox and Spencer (4) in a consideration of the molecular structure of enol esters of cholestenone.)

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Part of this work was done during the tenure of a Life Insurance Medical Research Fund Student Fellowship by one of us (R.H.C.).

Aryldiguanidines*

Some aryldiguanidines were prepared by treating aryldiamines with cyanamide. These are described below in the experimental section.

Experimental**

Tolyl-2,5-diguanidine

Fifteen grams (0.077 mole) of 2,5-diaminotoluene dihydrochloride and 7.3 gm. (0.174 mole) of cyanamide were covered with 35 cc. of absolute alcohol. Dry, oxygen-free nitrogen was bubbled through the reaction mixture while it was heated on a steam bath for eight hours. After the reaction mixture had cooled in the refrigerator, the solid was removed by filtration and washed with ethanol. The purplish-white solid melted at 283°–295°C. with decomp., yield 18.09 gm. (84.3%). Two crystallizations from 95% ethanol raised the melting point of the 2,5-diguanidinotoluene dihydrochloride to 294°–295°C. with decomp. This dihydrochloride was previously reported (1) as melting at 290°–292°C. with decomp.

* *Issued as DRCL Report No. 64.*
** *All melting points were determined on a Kofler block and are corrected.*

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ultraviolet absorption spectra of cholestenone and cholesterilene has been made by Cox and Spencer (4) in a consideration of the molecular structure of enol esters of cholestenone.)

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Anal.*** Calc. for $C_9H_{16}Cl_2N_6$: C, 38.80; H, 5.74; N, 30.11.
Found: C, 38.90; H, 5.67; N, 29.88.

An aqueous solution of 1 gm. of tolyl-2,5-diguanidine dihydrochloride on treatment with a saturated aqueous picric acid solution gave 1.96 gm. (82.4%) of a yellow picrate melting at 170°–175°C. One crystallization from water raised the melting point to a constant value of 177.5°–177.9°C., yield 1.72 gm.

Anal. Calc. for $C_{21}H_{20}N_{12}O_{14}$: C, 38.00; H, 3.03; N, 25.30.
Found: C, 37.96; H, 3.50; N, 25.15.

Tolyl-3,4-diguanidine

3,4-Diaminotoluene dihydrochloride (15 gm., 0.077 mole) and 7.3 gm. (0.174 mole) of cyanamide in 35 cc. of absolute alcohol were heated as above for three hours. No solid was obtained on cooling the solution to 4°. A black, tarry residue remained after the alcohol was removed *in vacuo* under nitrogen. The tar was dissolved in 100 cc. of water and the solution almost saturated with potassium carbonate. The solution was allowed to stand at 4° several hours after which the tolyl-3,4-diguanidinium carbonate (17.55 gm.; 85.0%) was removed by filtration. The crude carbonate melted with decomposition at 101°–104°C. with shrinkage at 95°. This melting point could not be improved by crystallization, therefore a sample (1.12 gm.) was dissolved in water and converted to the picrate in the usual manner. One crystallization from water gave 1.32 gm. (47.7%) of a yellow crystalline picrate melting at 238.5°–239.5°C.

Anal. Calc. for $C_{21}H_{20}N_{12}O_{14}$: C, 38.00; H, 3.03; N, 25.30.
Found: C, 38.20; H, 3.11; N, 25.11.

Anisyl-2,4-diguanidine

Cyanamide (7.56 gm., 0.18 mole) and 15 gm. (0.071 mole) of 2,4-diaminoanisole dihydrochloride in 32 cc. of absolute ethanol were treated in the same manner as described above for the preparation of 3,4-diguanidinotoluene. The carbonate was obtained in 25.8% (5.2 gm.) yield. It melted over a range of 165°–170°C. with decomp. A 250 mgm. portion of this product gave 512 mgm. (85.4%) of a crystalline picrate which melted at 252°–256°. One crystallization from water raised the melting point to a constant value of 259.4°–260.2°C.

Anal. Calc. for $C_{21}H_{20}N_{12}O_{15}$: C, 37.06; H, 2.97; N, 24.69.
Found: C, 36.88; H. 3.02; N, 24.55.

Phenol-2,4-diguanidine

A mixture of 6.4 gm. (0.152 mole) of cyanamide and 13.05 gm. (0.066 mole) of 2,4-diaminophenol dihydrochloride in 32 cc. of absolute ethanol was refluxed under nitrogen for four hours. The alcohol was removed *in vacuo* to give a purple colored, semisolid residue. This residue was treated with aqueous sul-

*** *Microanalyses by C. W. Beazley, Skokie, Ill.*

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phuric acid solution which contained 6.11 cc. of sulphuric acid (sp. gr. 1.84) in 110 cc. of water. An immediate precipitate of phenol-2,4-diguanidinium sulphate was obtained in 69.8% (14.12 gm.) yield. The crude product appeared to decompose at 282°–286°C. When this material was crystallized from 5% sulphuric acid solution, crystals were obtained which charred at 287°–289°C. The decomposition point was indefinite.

Anal Calc. for $C_8H_{14}N_6O_5S$: C, 31.40; H, 4.58; N, 27.46.
Found: C, 31.16; H, 4.89; N, 27.65.

A 1 gm. sample of the sulphate was dissolved in water and converted to the picrate in the usual manner. The melting point of 210°–220°C. of the crude picrate was raised to a constant value of 219.5°–220°C. by two crystallizations from water, yield 0.47 gm.

Anal. Calc. for $C_{20}H_{18}N_{12}O_{15}$: C, 36.00; H, 2.73; N, 25.20.
Found: C, 35.83; H, 2.91; N. 25.01.

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THE PAPILIONACEOUS ALKALOIDS

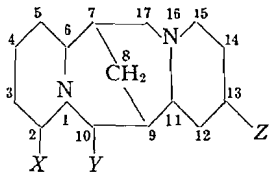
XIII. IDENTITY OF OCTALUPINE WITH HYDROXYLUPANINE[1,2]

BY LÉO MARION AND BRYCE DOUGLAS[3]

Abstract

Octalupine has been shown to be identical with hydroxylupanine by means of a comparison of the physical properties of the bases and corresponding derivatives and also by a direct comparison of the infrared absorption spectra of both alkaloids.

The alkaloid octalupine occurs in *Lupinus sericeus* var. *flexuosus* C. P. Smith (1). It is described by Couch as a hygroscopic base, m.p. 167.5–169.5°, which forms a dihydrochloride, a monohydrochloride, an aurichloride, and a methiodide (1). On electrolytic reduction in sulphuric acid, octalupine gives rise to a mixture of bases assumed to consist of *d*-lupanine and *l*-sparteine. On the basis of these results Couch (1) suggested that octalupine was a 2,10-diketosparteine, I(*a*). It seemed of interest to undertake a further examination of the structure of the base.



I (*a*) $X = O$; $Y = O$; $Z = H$
(*b*) $X = H$; $Y = H$; $Z = OH$
(*c*) $X = O$; $Y = H$; $Z = OH$

Dr. J. F. Couch kindly provided us with a generous sample of octalupine for this work. When sublimed and recrystallized from dry acetone, the base was anhydrous and melted at 169–170°, but from aqueous acetone it separated as a hydrate melting at 76–77°. Analysis suggested the empirical formula $C_{15}H_{24}O_2N_2$ and not $C_{15}H_{22}O_2N_2$ as previously assigned (1). The infrared absorption spectrum of octalupine taken in chloroform solution with a calcium fluoride prism showed an absorption band at 3607 cm.$^{-1}$ indicative of the

[1] *Manuscript received April 30, 1951.*
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[2] *The paper published by L. Marion and N. J. Leonard. Can. J. Chem. 29: 335. 1951 is considered as Part XII of this series.*
[3] *National Research Council of Canada Postdoctorate Fellow.*

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presence of a hydroxyl group, and a band at 1625 cm.$^{-1}$ in the carbonyl absorption region. The latter band was at the same wave number as that occurring in the spectrum of *d*-lupanine indicating that the carbonyl group of octalupine is probably lactamic and part of an α-piperidone ring. The catalytic hydrogenation of octalupine in 2*N* hydrochloric acid over Adams' catalyst reduced the lactamic oxygen and gave rise to a hydroxy compound, the infrared spectrum of which still showed the presence of a hydroxyl group, but no longer contained the carbonyl band. The analytical figures, melting point, and optical rotation of this compound were identical with those reported for hydroxysparteine, I(*b*) ($C_{15}H_{26}ON_2$), obtained in a similar way from hydroxylupanine I(*c*), by Galinovsky and Pöhm (2).

A comparison was made of the properties of octalupine, its hydrate, methiodide, and benzoyl derivative with the properties of the corresponding derivatives of hydroxylupanine. The close agreement obtained strongly suggested the identity of the two bases.

Dr. F. Galinovsky and Dr. V. Deulofeu kindly supplied us with authentic samples of hydroxylupanine. On admixture of these samples with octalupine there was no depression in the melting point. One of the samples (Galinovsky) was sublimed and recrystallized and its infrared absorption spectrum determined in carbon disulphide solution using a rock-salt prism. This spectrum was compared with that of octalupine taken under similar conditions and found to be exactly superposable (Fig. 1). Octalupine, therefore, is identical with hydroxylupanine I(*c*).

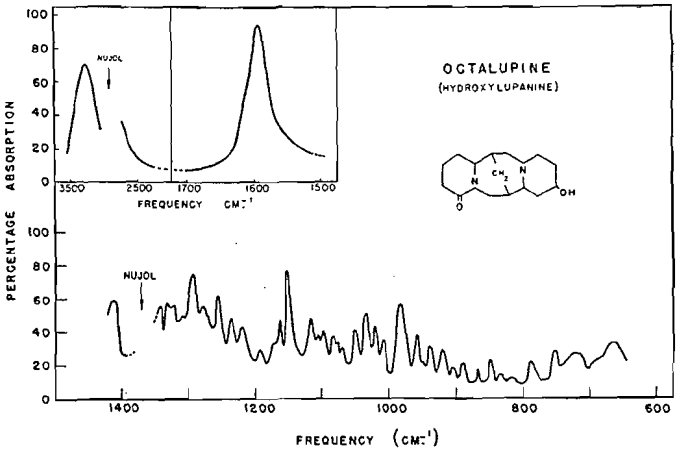

FIG. 1. *Infrared spectra measured on Perkin–Elmer 12B single beam spectrometer with sodium chloride prism. The alkaloids were in Nujol Mulls.*

Experimental[4]

Octalupine

The free base was isolated from a crude extract of *Lupinus sericeus* var. *flexuosus* C. P. Smith, supplied by Dr. J. F. Couch, by the method previously

[4] *All melting points are corrected, unless otherwise stated.*

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described (1). The alkaloid was sublimed and recrystallized from dry acetone to yield thin colorless plates, m.p. 169–170°. Admixture with the free base supplied by Dr. Couch showed no depression. $[\alpha]_D^{20} = +45.6 \pm 1.5°$ (*c*, 1.49, ethanol); $+ 65.1 \pm 1°$ (*c*, 1.09, water) Calcd. for $C_{15}H_{22}O_2N_2$: C, 68.68; H, 8.45; N, 10.68. $C_{15}H_{24}O_2N_2$: C, 68.15; H, 9.15; N, 10.60. Found: C, 67.86; 68.20; H, 9.03; 8.92; N, 10.63, 10.60%. Hydroxylupanine (Galinovsky and Pöhm) has m.p. 173–174°, $[\alpha]_D^{20} = +64.1°$ (*c* = 3.59, water).

Octalupine Hydrate

Octalupine (m.p. 169–170°) was recrystallized from a small volume of 10% aqueous acetone to yield clear prisms m.p. 76°. This melting point was observed by inserting the specimen in the apparatus at 73–74°. The melt resolidified immediately and remelted at 169–170°.

Octalupine hydrate is unstable and readily loses water, as shown by the analytical results. Calcd. for $C_{15}H_{24}O_2N_2.H_2O$: C, 63.8; H, 9.28. $C_{15}H_{24}O_2N_2.1\frac{1}{4}\ H_2O$: C, 62.8; H, 9.0. $C_{15}H_{24}O_2N_2.2H_2O$: C, 60.0; H, 9.39. Found: C, 62.39; H, 8.84%. According to the literature (2) hydroxylupanine dihydrate melts at 76°.

Octalupine Methiodide

Octalupine, dissolved in acetone, was treated with an excess of methyl iodide and allowed to stand at room temperature for one hour and finally in the refrigerator for one further hour. The deposited crystalline solid was collected and washed with acetone to give a crystalline product m.p. 236–243°. Recrystallization three times from methanol–ether gave small needles m.p. 254–255°. Calcd. for $C_{15}H_{24}O_2N_2.CH_3I$: C, 47.30; H, 6.70; N, 6.90. Found: C, 47.61, 47.04; H, 6.76, 6.93; N, 6.88, 7.04%. The reported melting point of hydroxylupanine methiodide is 258–259° (2).

Benzoyloctalupine

Octalupine (50 mgm.), pyridine (0.5 cc.), and benzoylchloride (0.1 cc.) were heated together in a sealed tube at 100° for four hours. The reaction mixture was diluted with chloroform (20 cc.) and extracted with 5*N* hydrochloric acid. The acid solution was made alkaline with sodium hydroxide solution and exhaustively extracted with chloroform. The dried (sodium sulphate) chloroform extract was concentrated under vacuum to yield an oil which solidified (71 mgm.). Recrystallization from acetone yielded needles which were sublimed (170°/10^{-5} mm.) to give a small initial fraction m.p. 112–113° and a main fraction m.p. 190–197°. Recrystallization of the main fraction yielded hard clear prismatic needles m.p. 199–200°. The specimen for analysis was dried at 80° under vacuum over phosphorus pentoxide for six hours. Calcd. for $C_{22}H_{28}O_3N_2$: C, 71.71; H, 7.66. Found: C, 71.88, 71.96; H, 7.41, 7.62%. The literature (2) records m.p. 202–203° for benzoylhydroxylupanine.

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Hydrogenation of Octalupine

Octalupine (140 mgm.) dissolved in 2*N* hydrochloric acid (10 cc.) was treated with hydrogen at 24° and atmospheric pressure in the presence of Adams' platinum oxide catalyst (100 mgm.). The theoretical volume for two moles of hydrogen was taken up in 27 hr. The catalyst was removed by filtration, the solution made alkaline with sodium hydroxide solution and extracted exhaustively with ether. The dried extract (sodium sulphate) was concentrated to yield a white solid (97 mgm.) m.p. 146–148°. Recrystallization three times from ether yielded short colorless needles, m.p. 150–151°. $[\alpha]_D^{20} = -24.3° \pm 0.9$ (*c*, 1.11, ethanol). Calcd. for $C_{15}H_{26}ON_2$: C, 71.95; H, 10.47; N, 11.20. Found: C, 72.05, 72.33; H, 10.16, 10.34; N, 11.20%. Hydroxysparteine prepared by Galinovsky and Pöhm has m.p. 154–155° and $[\alpha]_D^{20} = -25.4°$ (*c*, 5.43, ethanol).

Acknowledgment

Our indebtedness to Dr. James F. Couch, Eastern Regional Research Laboratory, Philadelphia, Dr. F. Galinovsky, II. Chemischen Laboratorium, University of Vienna, and Dr. V. Deulofeu, Laboratorio de Quimica, Facultad de Ciencias Exactas, Fisicas y Naturales, Buenos Aires, is hereby acknowledged. Our thanks are also due to Dr. R. N. Jones and Mr. R. Lauzon, of these laboratories for the infrared absorption spectra.

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STUDIES ON RDX AND RELATED COMPOUNDS

V. THE EFFECT OF DELAYED ADDITION OF AMMONIUM NITRATE, AND THE RATE OF DISAPPEARANCE OF HEXAMINE, IN THE BACHMANN REACTION[1]

By A. O. Ralph, J. G. MacHutchin, and C. A. Winkler

Abstract

Ammonium nitrate can be withheld from the Bachmann reaction at 35°C. for several hours without reducing the yield of RDX below approximately 50% of the normal value for the given amount of ammonium nitrate added. The rates of formation of RDX, on the addition of ammonium nitrate from 15 min. to five hours after the reaction has started in its absence, are approximately the same and are approximately one-half that when ammonium nitrate is present initially. A low temperature analysis for hexamine in the Bachmann mixture, by precipitating hexamine as the styphnate, indicates that hexamine disappears from the reaction mixture within five seconds at 35°C., either in the presence or absence of ammonium nitrate.

Introduction

Data presented in a previous paper (4) indicated that certain minimum concentrations of ammonium nitrate were necessary for maximum yields of RDX in the nitrolysis of hexamine by the Bachmann reaction (1). It therefore became of interest to determine the effect of delaying the addition of ammonium nitrate to such reaction mixtures, in an effort to obtain, if possible, information on the part played by ammonium nitrate during the nitrolysis. This study in turn emphasized the importance of getting at least a rough estimate of the rate of disappearance of hexamine in the reaction mixture. The present paper describes the results obtained in the two investigations.

The Effect of Delayed Addition of Ammonium Nitrate on the Rate of Formation and Yield of Total Solids and RDX

The reactions were allowed to take place in glass stoppered Erlenmeyer flasks, shaken in a thermostat at 35 ± 0.05°C.

Experiments were first made to determine the effect on the yield of RDX of adding various amounts of ammonium nitrate at definite time intervals after the reaction had been started in its absence. Reaction was allowed to proceed for an additional three hours at 35°C. following addition of the nitrate, at the end of which time the RDX yield was determined by diluting the reaction mixture with an equal volume of water, boiling it for one hour, diluting it further to 250 cc., and allowing the RDX to crystallize over night. The product was filtered, dried for three hours at 95°C., and weighed.

The sequence and quantities of reagents used were:

1. Acetic anhydride, 0.24 mole.
2. Nitric acid, 0.05 mole.
3. Hexamine, 0.008 mole in acetic acid, 0.32 mole.
4. Ammonium nitrate, 0.003, 0.006, 0.012, and 0.024 mole.

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The results with 0.024 mole ammonium nitrate, shown in Table I, are quite typical of the behavior observed in all the experiments except that the yields of RDX obtained were less at the lower ammonium nitrate levels.

TABLE I

EFFECT ON THE YIELD OF RDX OF WITHHOLDING THE ADDITION OF AMMONIUM NITRATE

Time before addition of 0.024 mole ammonium nitrate, min.	RDX yield, mgm.
0	1198
5	931
10	863
20	840
30	870
42	792
120	762
180	787
300	570

Experiments were then made to determine the effect on rate of production of total solids and of RDX when ammonium nitrate was withheld from the reaction for various periods of time. Total solids were estimated by diluting a portion of reaction mixture, after which the precipitated solids were filtered off, dried for 24 hr. at 95°C., and weighed. The amount of RDX produced was determined by dilution of a second portion of the reaction mixture. After the diluted mixture had been boiled for one hour, it was allowed to stand over night, when the RDX was filtered off, dried, and weighed. The difference between the weight of total solids and the weight of RDX at any time should correspond approximately to the amount of BSX formed (1).

The quantities and sequence of addition of the reagents in the rate experiments were the same as in the previous yield experiments, except that a given quantity (0.024 mole) of ammonium nitrate was used. The experimental results are shown in Table II.

Examination of the data in Table I reveals immediately that the yield of RDX when ammonium nitrate is withheld for as long as five hours may remain as much as 50% of the yield obtained when ammonium nitrate is added initially. It is also readily seen from Table II that if the addition of ammonium nitrate is delayed for 15 min. (or less) the rate of production of RDX is reduced to approximately one-half the rate when the nitrate is added initially. However, withholding the ammonium nitrate for as much as five hours apparently caused no further reduction in rate.

The results of these studies indicated either that some hexamine persisted in the system for prolonged periods under the experimental conditions, or that "fragments" or intermediates of moderate stability were formed, which could be converted to RDX in the presence of ammonium nitrate. A rough estimate of the rate of disappearance of hexamine from such systems was therefore sought.

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TABLE II

EFFECT ON RATE OF FORMATION AND YIELD OF RDX AND TOTAL SOLIDS OF WITHHOLDING THE ADDITION OF AMMONIUM NITRATE

Time of reaction after addition of ammonium nitrate, min.	Yield, mgm.	
	RDX	Total solids
A. Ammonium nitrate not withheld		
20	288	538
40	609	796
60	668	1276
120	953	1843
180	1078	2095
B. Ammonium nitrate withheld 15 min.		
20	140	453(366)
40	345	860(795)
60	547	1157(1084)
120	725	1666(1652)
180	795	1518
C. Ammonium nitrate withheld 45 min.		
20	179,176	675(680)
40	304	1013(729)
60	480	1342(1301)
120	679	1804(1882)
180	800	2059(2103)
D. Ammonium nitrate withheld for 90 min.		
20	142	933(779)
40	296	1200
60	422	1320(1420)
120	721	1850(1950)
180	743	2040(1982)
E. Ammonium nitrate withheld 300 min.		
20	140	—
40	350	—

Rate of Disappearance of Hexamine

Estimation of the hexamine content of a reaction mixture was based on the observation that hexamine may be precipitated under suitable conditions as a styphnate (3).

Styphnic acid was prepared according to Beilstein (2), and used in ethanol solution. Precipitation of hexamine as the styphnate was found to be 98% complete from glacial acetic acid solution, assuming 1: 1 molar ratio of hexa-

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mine and styphnic acid in the complex. Difficulty was experienced, however, in adapting the method to estimation of hexamine in the presence of both nitric acid and acetic anhydride. It was finally found possible to obtain satisfactory precipitation at sufficiently low temperatures, and the following procedure was adopted to determine the rate of disappearance of hexamine in the Bachmann mixture containing no ammonium nitrate.

To acetic anhydride (11.25 ml.), cooled to the desired low temperature, was added nitric acid (1.0 ml.), followed by the hexamine–acetic acid solution (9.50 ml. AcOH containing 0.58 gm. hexamine) at 14°C. The reaction was allowed to proceed at the mixture temperature for various periods of time, after which was added the styphnic acid solution (20.0 ml. ethanol containing 1.18 gm. styphnic acid), mixed with an equal volume of water and previously cooled to 0°C. The temperature of the system was then dropped to about −60°C., maintained there for one-half hour, and finally raised to 0°C., at which temperature the solution was filtered after a five minute period.

The rate of disappearance of hexamine in Bachmann type systems, without ammonium nitrate present, was measured for HNO_3–Ac_2O solution temperatures of −55°C., −30°C., and −15°C. with the results shown in Table III.

The weights of hexamine styphnate recorded are corrected for the appreciable solubility of the styphnate in the reaction mixture at 0°C., the temperature of filtration. Since the solubility of the styphnate in the mixture varied with the amount of styphnic acid present in solution, it was necessary to determine the magnitude of the correction appropriate to the calculated amount of unused styphnic acid in each mixture. The correction was only approximate, but sufficiently good for the purpose at hand.

Obviously, the very short reaction times and the technical difficulties of the procedure precluded more than a rough estimate of the rates of hexamine disappearance. Lack of accuracy in making the measurements was, fortunately, of no real consequence as far as the main point at issue was concerned. The data are adequate to demonstrate the very rapid disappearance of hexamine in the systems studied.

The rate of disappearance of hexamine was also examined in the absence and presence of ammonium nitrate at 35°C. Ammonium nitrate (0.98 gm.) was added to the nitric acid – acetic anhydride mixture at 35°C., five minutes before the addition of the hexamine – acetic acid solution, also at 35°C. For the short periods studied the reaction occurred essentially at 35°C. The reaction was stopped by adding the usual amount of styphnic acid – ethanol – water solution at 0°C., after which the mixture was cooled to −60°C., and treated as described previously. After two seconds reaction time, the amount of hexamine styphnate obtained was 0.2 gm. (average of four determinations) instead of 1.6 gm. to be expected had no reaction occurred. When the reaction time was extended to five seconds, a minute trace only of precipitate was obtained. In the absence of ammonium nitrate at 35°C., 0.25 gm. hexamine styphnate (average of four determinations) was obtained after a two

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TABLE III

RATE OF DISAPPEARANCE OF HEXAMINE IN BACHMANN TYPE REACTION MIXTURES IN THE ABSENCE OF AMMONIUM NITRATE

Time of reaction, sec.	Weight hexamine styphnate, gm.
A. Nitric acid – acetic anhydride at −55°C. (mixture temp. approx. −20°C.)	
0.0	1.61
2.0	1.23
7.5	1.16
15.0	0.98
22.0	0.95
30.0	0.87
40.0	0.81
60.0	0.83
90.0	0.48
110.0	0.43
120.0	0.21
160.0	0.20
180.0	0.17
B. Nitric acid – acetic anhydride at −30°C. (mixture temp. approx. −8°C.)	
0.0	1.61
2.0	1.07
5.0	0.98
10.0	0.80
20.0	0.57
40.0	0.43
60.0	0.47
80.0	0.35
90.0	0.28
120.0	0.11
140.0	0.02
C. Nitric acid – acetic anhydride at −15°C. (mixture temp. approx. 0°C.)	
0.0	1.61
2.0	0.50
5.0	0.44
7.5	0.32
10.0	0.17
12.5	0.36
15.0	0.22
17.5	0.15
20.0	0.32
22.5	0.24
25.0	0.29

second reaction time. The very rapid rate of hexamine disappearance in Bachmann mixtures, together with the results for the effect of delayed addition of ammonium nitrate on the yield and initial rate of formation of RDX, leave little doubt that in the Bachmann reaction one molecule of RDX is obtained by nitrolysis of hexamine introduced originally, and a second molecule from a resynthesis of fragments in the presence of ammonium nitrate.

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Acknowledgment

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STUDIES ON RDX AND RELATED COMPOUNDS

VI. THE HOMOGENEOUS HYDROLYSIS OF CYCLOTRIMETHYLENETRINITRAMINE (RDX) AND CYCLOTETRAMETHYLENETETRANITRAMINE (HMX) IN AQUEOUS ACETONE, AND ITS APPLICATION TO ANALYSIS OF HMX IN RDX(B)[1]

By S. Epstein and C. A. Winkler

Abstract

Measurements of the rates of alkaline hydrolysis of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) in aqueous acetone show these two reactions to involve consecutive steps, the first of which is second order and rate controlling. Activation energies were estimated as 14 and 25 kcal. respectively. By establishing calibration curves, and controlling temperature, alkali concentration relative to concentration of explosive, and reaction time, the differential hydrolysis permits analysis of the HMX content of RDX(B) with an error of approximately ±0.2% HMX.

The present paper presents the results of a study on the alkaline hydrolysis of cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) in homogeneous systems. On the basis of the data obtained, a satisfactory method for determining the HMX content of RDX has been established.

Experimental and Results

(*a*) *The Hydrolysis of Pure RDX and HMX*

The RDX* and HMX were dissolved in acetone to which was added an appropriate amount of aqueous sodium hydroxide solution. The relative proportions of the solutions were chosen to prevent precipitation of the solids and the alkali solution was always below approximately 0.6 *N* to ensure its miscibility with acetone.

Accurately weighed samples of RDX and HMX contained in 250 ml. Erlenmeyer flasks were dissolved in the required amounts of acetone and placed in the thermostats. These consisted of a well stirred ice bath for experiments at 0°C., melting acetic acid for experiments at 15.5°(±0.2°C.), and an ordinary regulated water bath for experiments at 27°C.(±0.05°C.). The sodium hydroxide solutions were brought to thermostat temperatures before being added to the RDX or HMX solutions. The reaction was stopped at different intervals of time by adding sufficient glacial acetic acid to neutralize the alkali present. The acetone was distilled off until the volume of liquid was reduced to about one-fifth its original value and the resulting mixture diluted slightly with water, cooled, and permitted to stand for about an hour to precipitate RDX and HMX. The resulting precipitate was filtered, washed, dried, and weighed.

[1] *Manuscript received May 22, 1951.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

* *The product from the direct nitrolysis of hexamine, containing insignificant amounts of HMX.*

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The reactions with HMX were slow and amounts reacted in the reaction times used were small enough that its solubility would have introduced a relatively large error. Therefore a correction factor experimentally evaluated as about 10 mgm. was applied.

The data indicated that RDX consumed approximately three moles and HMX four moles of sodium hydroxide per mole of explosive hydrolyzed. The initial rates of both reactions, however, were well represented by the second order expression

$$\frac{dx}{dt} = [\mathrm{Na^+ OH^-}] \begin{matrix}[\mathrm{RDX}] \\ \text{or} \\ [\mathrm{HMX}]\end{matrix}$$

for the range of concentration investigated. These second order constants are recorded in Tables I and II. Apparently the complete hydrolysis of RDX or HMX occurs by a series of consecutive reactions, probably the first of which is second order and rate controlling.

Measurements with RDX at 27°C. were ignored in estimating the temperature coefficient, since at this temperature the reaction is much too fast to permit satisfactory estimates of the initial rates.

TABLE I

RATE CONSTANTS FOR HYDROLYSIS OF RDX IN AQUEOUS – ACETONE – SODIUM HYDROXIDE SOLUTIONS

Temp., °C.	Concentration in moles per liter		k(liter-moles^{-1} min.$^{-1}$)
	RDX	NaOH	
0.0	0.010	0.0280	5.1
0.0	0.010	0.0145	5.1
0.0	0.005	0.0145	5.1
15.5	0.010	0.0280	21.7
15.5	0.010	0.0145	21.8
15.5	0.005	0.0145	21.8

TABLE II

RATE CONSTANTS FOR HYDROLYSIS OF HMX IN AQUEOUS – ACETONE – SODIUM HYDROXIDE SOLUTIONS

Temp., °C.	Concentration in moles per liter		k(liter-moles^{-1} min.$^{-1}$)
	HMX	NaOH	
0.0	0.00645	0.116	0.0074
0.0	0.00645	0.058	0.0081
15.5	0.00645	0.116	0.065
15.5	0.00645	0.058	0.064
15.5	0.00322	0.058	0.064
27.0	0.00645	0.116	0.46
27.0	0.00645	0.058	0.46
27.0	0.00322	0.058	0.50

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The activation energies for the hydrolysis of RDX and HMX, estimated from mean k values, were found to be approximately 14 kcal. per mole and 25 kcal. per mole respectively. The data are not sufficiently extensive to permit a closer evaluation.

(*b*) *A Method for Determining Percentage HMX in RDX from the Bachmann Reaction*

The large difference in the rates of hydrolysis of RDX and HMX in acetone – aqueous sodium hydroxide solutions encouraged the use of differential hydrolysis in the homogeneous systems to analyze for HMX in RDX obtained from the Bachmann reaction. Known mixtures of pure RDX and HMX were first hydrolyzed at a controlled temperature (0°C. and 27°C.) with various concentrations of sodium hydroxide for various periods of time to establish the sodium hydroxide concentration and the reaction time necessary for complete hydrolysis of RDX. The experimental procedure was the same as that employed in the kinetic studies with pure HMX and pure RDX. Using the appropriate sodium hydroxide concentrations and reaction times, calibration curves were established with RDX – HMX mixtures of known composition, formed by dry mixing or coprecipitation by water from acetone solution.

Analysis of RDX samples of unknown HMX contents required merely that the identical conditions and procedure used for establishing the calibration curves be applied to the analytical sample. With samples containing more than 2% HMX, it was possible to determine the HMX content with a precision of $\pm 0.2\%$ HMX. With samples containing less than 2% HMX, the same precision was obtained only by adding a known quantity (2%) of pure HMX before analysis, and deducting the known amount added from the analytically determined value for the sample.

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THE FORMATION OF LIGNIN IN WHEAT PLANTS[1]

By J. E. Stone, M. J. Blundell, and K. G. Tanner

Abstract

Wheat plants were harvested approximately every two weeks after emergence from the soil. Determination of the lignin content by the 72% sulphuric acid method showed a rapid increase between the period 45–70 days from seeding, and there was a corresponding increase in the yield of vanillin and syringaldehyde, obtained by alkaline nitrobenzene oxidation. The *p*-hydroxybenzaldehyde yield remained low at all times and seemed to be derived from a different system. It is suggested that the source of this aldehyde is not the lignin, but the tyrosine associated with the protein. The ratios of vanillin to syringaldehyde did not remain constant from plants of different ages, the percentage of syringaldehyde being lower than vanillin in the young plants and higher in those which were more mature. This is qualitatively in agreement with an increase in the methoxyl content of the lignin.

When the yield of aldehydes from mature plants is taken as the criterion for the amount of lignin present, the youngest plants have a lignin content of about 0.13%, a value much lower than other bases for calculation would indicate.

Oxidation of the whole plant and of the plant which had been extracted with alcohol–benzene, water, and 1% hydrochloric acid, gave similar percentages of aldehydes, owing partly to the removal of aldehyde-producing substances and partly to the degradation of the lignin during the extraction process. Oxidation of the extracts gave no trace of aldehyde in the hydrochloric acid extract, a trace in the water extract, and appreciable percentages in the alcohol–benzene extract. This latter extract consisted of two portions, a red water soluble, alcohol–benzene insoluble fraction and the main alcohol–benzene soluble fraction. The former gave rise to vanillin and *p*-hydroxybenzaldehyde on oxidation, the amount being a maximum at the first harvest and decreasing to zero after lignification had occurred. The latter, that is, the alcohol–benzene soluble extract, gave rise to syringaldehyde as well as the others, the amounts being low at first and increasing during lignification in the same way as the main body of the plant. It is believed that the alcohol–benzene removes a soluble portion of the lignin since the relative proportions of the aldehydes are very similar to those obtained from lignin itself.

Introduction

The work of Phillips *et al.* (10, 11, 12) showed that wheat, oat, and barley seedlings contained a small amount of lignin and that a rather rapid increase took place about 40 days after the plants had emerged from the soil. The lignin was determined by the fuming hydrochloric acid method and characterized by its methoxyl content. In all cases the young lignin had a lower methoxyl content than the older material. Phillips concluded (12) that this was definite evidence against Klason's (6) hypothesis that the plant synthesizes lignin from coniferyl alcohol (or aldehyde) by a process of polymerization for, it was argued, Klason's theory would require a constant methoxyl content at all stages of the phytochemical synthesis. This argument may be questioned on two grounds. Firstly, the cereal straws are angiosperms and the lignin is

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Contribution from the National Research Council, Prairie Regional Laboratory, Saskatoon, Sask. Issued as Paper No. 121 on the uses of Plant Products and as N.R.C. No. 2495.

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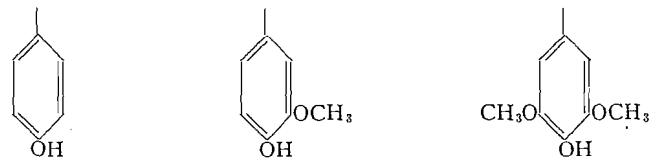
consequently made up of syringyl and guaiacyl units, as shown by Hibbert *et al.* (4). Moreover, the same school produced evidence that monocotyledons give rise to some *p*-hydroxybenzaldehyde on oxidation with alkaline nitrobenzene (4, 5). The lignin in cereal straws might therefore be considered as built up from *p*-hydroxyphenyl (I), guaiacyl (II), and syringyl (III) units.



I II III

A change in the ratio of these building units during the growth of the plant could account for any variations in methoxyl content found in the lignin and does not eliminate the possibility that coniferyl alcohol played a part in the formation of II. Secondly, there is the possibility that the low methoxyl content found by Phillips in the lignin of young seedlings was due to the presence of humic acid, formed from the protein and carbohydrate during the isolation of lignin with strong mineral acid. Certain oat seedlings contained more than 40% protein ($N \times 6.25$) and the nitrogen content of the isolated lignin indicated that much protein was present there also in the form of humic acid. A correction for ash and protein gave what Phillips described as "pure" lignin, but it took no account of carbohydrate matter in the humic acid so that any carbohydrate present, being unaccounted for, would lower the methoxyl content accordingly.

The present work was undertaken in order to clarify these points. An alkaline nitrobenzene oxidation carried out on plants at various stages of growth followed by quantitative determination of vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde so formed, should provide evidence as to the relative amounts of the guaiacyl, syringyl, and *p*-hydroxyphenyl units present in the lignin. The amounts of aldehyde derivable from the plant should also provide a good indication of the amount of lignin present, unconfused by the presence of protein, carbohydrate, or any other plant constituent.

Experimental

Thatcher wheat was seeded on May 15, 1950, emerged from the soil about a week later, and the first harvest taken 17 days after seeding. The plants were then about 10 cm. high and in the early second-leaf stage. The dates of subsequent harvests and descriptions of the plants are given in Table I. The plants were prepared for analysis by removing the roots (and the heads when the latter had formed), washing them briefly, air-drying at 45°C., and grinding them in a Wiley Mill to pass a 60-mesh screen. The material was then extracted with solvents according to the scheme shown in Fig. 1.

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TABLE I

Harvest	Date	Age of plants (days from seeding)	Height of plants (cm.)	Description
1	June 1	17	10	Early two-leaf stage
2	June 15	31	17–20	
3	June 30	46	38–42	Head starting to form
4	July 17	63	67–70	Head well formed
5	July 28	74	70–75	
6	Aug. 11	88	70–80	Ripening
7	Aug. 25	102	70–80	

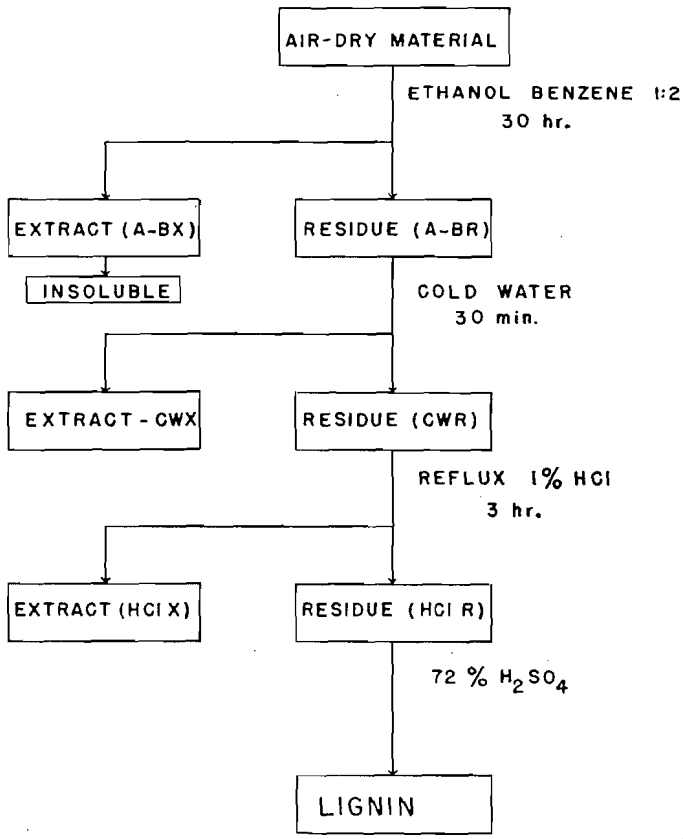

FIG. 1. *General scheme of analysis.*

Alcohol–Benzene Extraction

The air-dry material was extracted for 30 hr. with ethanol–benzene 1:2 in a Soxhlet extractor. The extract was poured off into a Petri dish, the solvent evaporated, and the dried extract weighed. A red, water soluble, alcohol–benzene insoluble substance was found to be extracted from the plant by the alcohol–benzene. After pouring off the solvent, this red material was dissolved

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in water, filtered, dried, and weighed. The extracted plant material was air-dried at room temperature and the dry weight calculated by oven drying a weighed portion of it.

Cold Water Extraction

This extraction was carried out in a Waring Blendor for 30 min., using 150 ml. water for each gram of plant material used. The extract was clarified by centrifuging, evaporated to dryness, and weighed. The residue was dried by lyophilization, weighed, a portion retained for analysis and the remainder extracted with 1% hydrochloric acid.

1% Hydrochloric Acid Extraction

The material was refluxed for three hours with 150 ml. of 1% hydrochloric acid for each gram of substance used. The extract and residue were separated, dried, and weighed as in the cold water extraction. The purpose of using lyophilization for drying the residues was to retain the plant material in a finely divided form.

Lignin Determination

The 72% sulphuric acid method was used since it is convenient and has been shown by Adams and Castagne (1) to be suitable for cereal straws.

Analysis of Extracts and Residues

Each extract and residue, as well as the original unextracted plant material and the final lignin, was analyzed for ash, nitrogen, and methoxyl. An alkaline nitrobenzene oxidation with a quantitative determination of the vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde so formed, was also carried out, using a rapid microtechnique especially devised for this purpose and described in detail in another publication (13). A brief description is given here for the sake of clarity.

Alkaline Nitrobenzene Oxidation

Into a 2 ml. stainless steel bomb were placed 50–100 mgm. plant material, 0.06 ml. nitrobenzene, and 1.00 ml. of 2*N* sodium hydroxide. The bomb was heated with shaking for 2½ hr. at 160°C., cooled, and centrifuged. An aliquot (0.2 ml.) was removed, spotted along the base line of a paper chromatogram, acidified by fuming with acetic acid, and the chromatogram developed with a mixture of petroleum ether and *n*-butyl ether (6:1) saturated with water. The individual aldehydes were extracted from the paper with alcohol and the amount of each determined by the density of absorption of ultraviolet radiation using the Beckman DU spectrophotometer.

Results and Discussion

The relative amounts of the extractives and lignin at various stages of growth are shown in Fig. 2. The results are calculated on an ash-free basis and while

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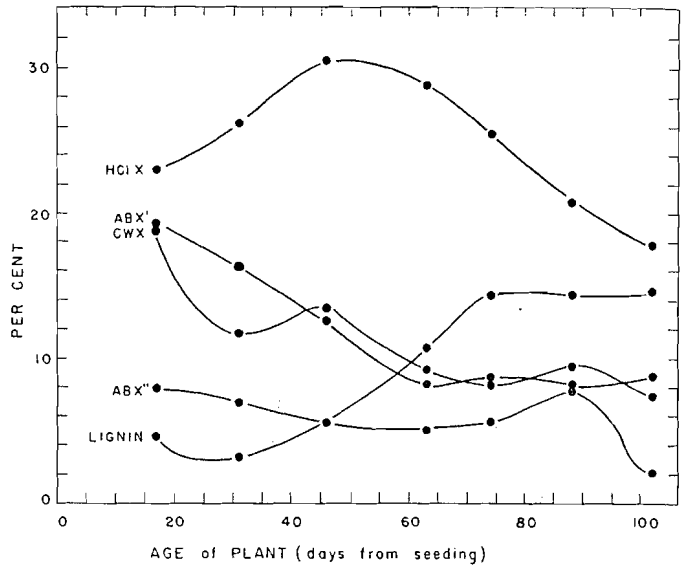

FIG. 2. *Per cent of lignin and extractives (ash free) at various growth stages.*

the curves are not quite regular there is a general tendency for the amount of material extracted by alcohol–benzene and by water to fall steadily with increasing age of the plant, and for the lignin to increase in amount.

Percentage of Lignin

In Fig. 3, Curve 1 shows the crude analytical values for the lignin content of the plants, corrected for ash in Curve 2 and for ash and protein in Curve 3. Curve 3 corresponds to the "pure lignin" of Phillips, and its considerable divergence from the other two indicates the importance of correcting for ash and protein when calculating the lignin content of this type of plant material.

The percentage of lignin is low in the young plants, rises rapidly about midway through the life cycle, during the period when heading-out is in progress, and then rises more slowly as the plant reaches the final stages of maturity.

The methoxyl content of the lignin represented by Curve 3 is not constant, but rises with increasing age of the plant. This is shown in Fig. 4. Also shown in Fig. 4 are the yields of vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde derivable from this lignin. The alkaline nitrobenzene oxidations which led to these results were carried out, not on the isolated lignin itself, but on the plant material which had been extracted with alcohol–benzene, water, and 1% hydrochloric acid. The yield of aldehydes was then recalculated on the basis of the Klason lignin content. The reason for doing this was that oxidations on the isolated lignin itself gave very poor results, presumably owing to its insolubility in sodium hydroxide, whereas the extracted plant material represents, in theory, chiefly cellulose and lignin, and the latter has not been modified in a way that prevents aldehyde formation.

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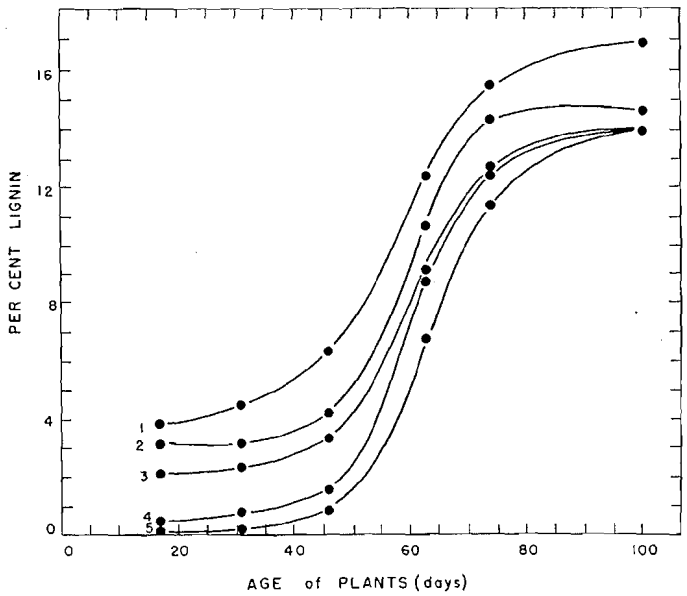

FIG. 3. *Per cent of lignin calculated on various bases:*
(*1*) *Crude 72% sulphuric acid lignin.*
(*2*) *Corrected for ash.*
(*3*) *Corrected for ash and protein.*
(*4*) *Lignin content based on methoxyl content of young plants and 72% sulphuric acid lignin content of mature plants.*
(*5*) *Lignin content based on vanillin and syringaldehyde yield from young plants and 72% sulphuric acid lignin content of mature plants.*

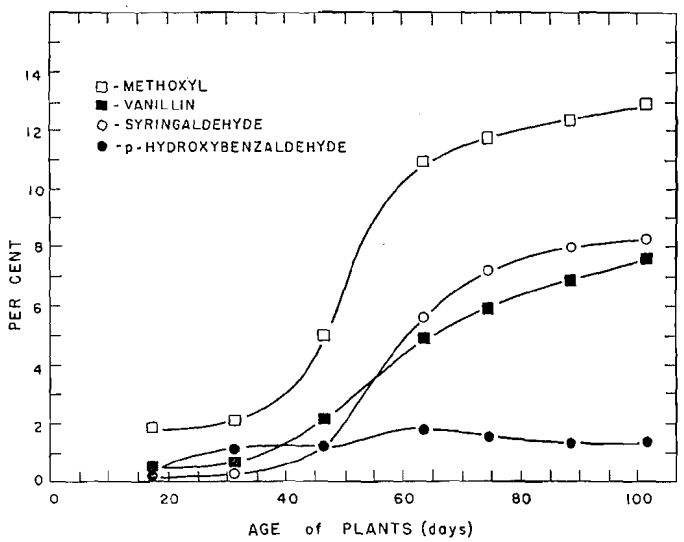

FIG. 4. *Methoxyl content of 72% sulphuric acid lignin and aldehydes obtained from hydrochloric acid residue and calculated as a percentage of 72% sulphuric acid lignin.*

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There are several noteworthy points in connection with Fig. 4. Firstly, the percentage of vanillin and syringaldehyde increases rapidly at the stage of growth where lignification occurs, following the methoxyl content in this respect. The conclusion might be drawn that the young lignin is very different from the more mature material, since if it had been the same, the percentage of methoxyl and of aldehydes would have remained constant throughout the growth of the plant and this would have been shown in Fig. 4 by parallel and horizontal straight lines. A simpler explanation is that the brown amorphous powder isolated from young plants actually consists largely of humic acid. This would account for the low methoxyl content and the low aldehyde yield and is a more reasonable explanation than assuming the existence of two types of lignin so different in structure that one yields 20 times as much vanillin as the other on nitrobenzene oxidation. It is to be expected that very young tissue with a high protein content will give rise to more humic acid than mature straw and it is felt that any estimation of lignin in young plant tissue, based on the weight of a residue formed under the action of strong mineral acid, should be treated with caution. MacDougall and DeLong (8) have shown that removal of nitrogenous constituents from plant tissues prior to a lignin determination reduces the amount of lignin obtained by the 72% sulphuric acid method; so that an extraction such as theirs to remove proteinaceous material would seem to be obligatory if the gravimetric estimation of lignin in young tissue is to have significance. Possibly the methoxyl content of the brown amorphous powder would be a better indication of the true lignin content, and Curve 4 in Fig. 3 represents the lignin content of growing wheat plants calculated on this basis. The assumptions have been made that (*a*) a mature lignin (ash- and protein-free) contains no humic acid, and (*b*) the methoxyl content of young lignin is the same as that of mature lignin. Actually, both these assumptions are probably incorrect, but since correcting the error of (*a*) would give an even lower lignin content to young plants, and (*b*), as will be seen in the next paragraph, would increase the lignin content, it is possible that compensating errors might render Curve 4 in Fig. 3 a closer approximation to the actual lignin content than does Curve 3.

Fig. 4 shows that the ratios of *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde, obtained by oxidation, changes with the growth of the plant. In the early stages the order of abundance is as above, whereas at maturity the order is reversed, syringaldehyde now being predominant. This may be taken to mean that there is, indeed, a basic difference in the nature of the lignin at various growth stages, and the early predominance of the aldehyde with no methoxyl groups followed by the later predominance of the doubly methoxylated unit is qualitatively in agreement with an increase in the methoxyl content of the lignin.

Just as the lignin content of young plants was calculated from the methoxyl content of the mature material, so may the lignin be estimated using the aldehyde yield as the basis for calculation. And whereas the methoxyl group is not a characteristic of lignin alone, vanillin and syringaldehyde may be

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considered as derived uniquely from lignin. The difference in the ratio of the two aldehydes at various stages requires a separate calculation for each, as though there were a guaiacyl and a syringyl type lignin, each giving rise to a certain percentage of vanillin and syringaldehyde upon oxidation. This is simply expressed algebraically:

$$N = M\,\frac{(a+b)}{(x+y)}$$

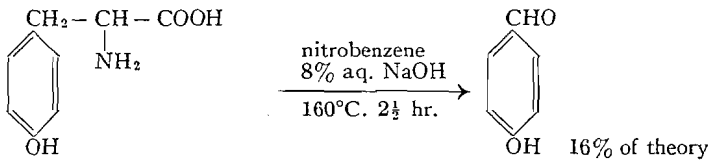
where N = required lignin content of plant material at any growth stage,
M = percentage Klason lignin (ash- and protein-free) of mature plant, determined by normal gravimetric procedure,
a, b = percentages of vanillin and syringaldehyde respectively at any growth stage,
x, y = percentages of vanillin and syringaldehyde respectively at maturity.

Calculating the lignin content of the plants on this basis gives rise to Curve 5 in Fig. 3. The percentage of lignin in the youngest plants, 0.13%, obtained in this way is considerably lower than the other bases for calculation indicate, and it is to be noted that the value would be reduced still further if the presence of humic acid or other impurity gave M an inflated value. It is considered that Curve 5, representing as it does the "aromaticity" of the plant, is the closest approach to the true lignin content. The low aldehyde yield from the young tissue may be compared with the absence of cyclohexyl derivatives from hydrogenated spruce buds, noted by Bower, Cooke, and Hibbert (2).

Significance of p-Hydroxybenzaldehyde

The methoxyl group is usually considered to be a characteristic of lignin and the percentage is important when attempting to assign a structure to the lignin molecule, using guaiacyl or guaiacyl and syringyl units. The production of *p*-hydroxybenzaldehyde, as well as vanillin and syringaldehyde, by oxidizing monocotyledons was demonstrated by Hibbert *et al.* (4, 5) and this indicated that a nonmethoxylated building unit might have to be considered in structural theories. The mere absence of methoxyl groups in a plant or plant extract could not be taken as indicating the absence of ligninlike substances, since one could conceive the existence of a completely unmethoxylated lignin built up of *p*-hydroxyphenyl units.

It occurred to the present authors that the source of the *p*-hydroxybenzaldehyde obtained on alkaline nitrobenzene oxidation of wheat plants might be, not the lignin, but the tyrosine associated with the protein. An oxidation of tyrosine (*dl*) was carried out under standard conditions and a yield of *p*-hydroxybenzaldehyde of 16% of theory was obtained.



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It would seem from this that some, if not all, of the *p*-hydroxybenzaldehyde obtained from wheat plants is derived from the protein fraction. It is perhaps significant that those plants shown by Hibbert to give rise to *p*-hydroxybenzaldehyde, that is the monocotyledons, are those which are high in proteinaceous material. Considering the present data, the 31-day-old plants gave rise to 0.13% *p*-hydroxybenzaldehyde (Fig. 5). Assuming a similar yield from

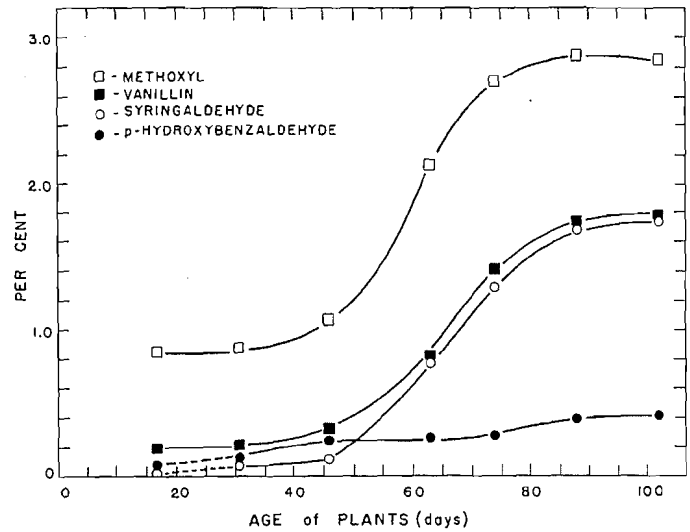

FIG. 5. *Methoxyl content and aldehyde yield from unextracted whole plants.*

protein as was obtained from tyrosine, the tyrosine content of the plant would be about 0.8%. The protein content of 37.50% (6.0 × 6.25) means that tyrosine would constitute about 2.1% of the plant protein according to the present data. This agrees well with the data of Lugg (7) who showed that the protein of the Gramineae contains 2.3–2.5% tyrosine. It would therefore appear likely that all the *p*-hydroxybenzaldehyde obtained on oxidizing wheat plants with alkaline nitrobenzene is derived from proteinaceous material. Further evidence that *p*-hydroxybenzaldehyde was derived from a nonlignin source is the shape of the curves in Fig. 4, 5, 6, and 7, which show that the production of vanillin and syringaldehyde at various growth stages follows a much different path from that of the nonmethoxylated aldehyde.

Oxidation of Extractives

It was considered that very immature plants might contain lignin or lignin precursors in a form that was soluble to some extent in the solvents used for extraction, prior to the actual lignin determination. The oxidation of these extracts with alkaline nitrobenzene, followed by a qualitative and then quantitative determination of aldehydes, provides a valuable tool in following the solubility properties of lignin or lignans. A lot depends upon the definition of the word "lignin", and in the present case the criterion of whether lignin was present or absent from any particular fraction was the production, or

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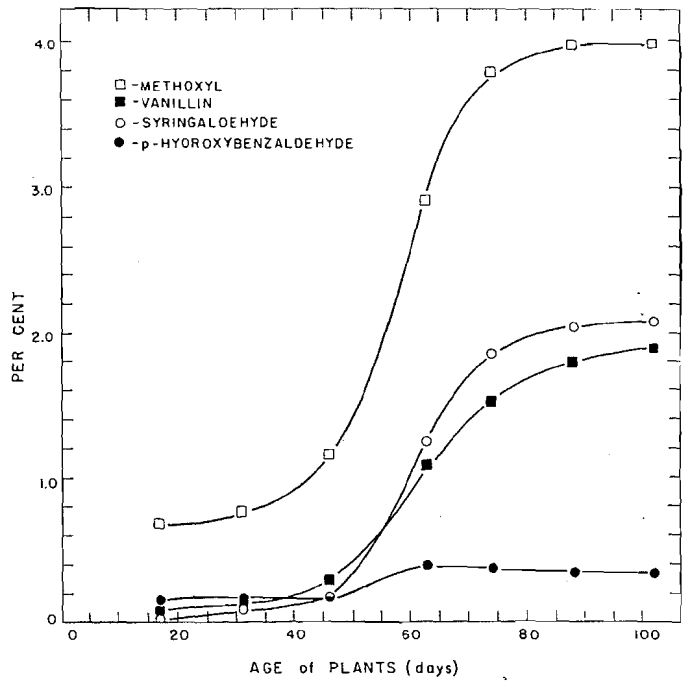

FIG. 6. *Methoxyl content and aldehyde yield from fully extracted plants (hydrochloric acid residue.)*

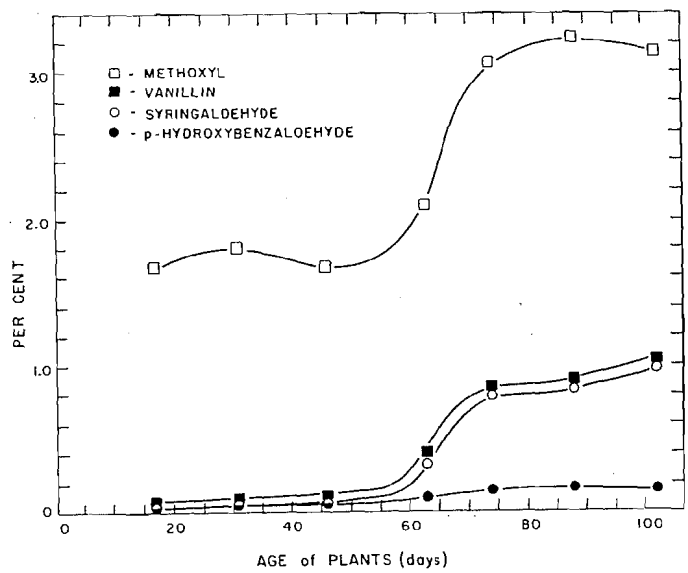

FIG. 7. *Methoxyl content and aldehyde yield from alcohol–benzene extract (alcohol–benzene soluble ABX').*

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nonproduction, of vanillin and syringaldehyde. Consequently oxidations were performed on the material that had been extracted from the plant by alcohol–benzene, by cold water, and by 1% hydrochloric acid. An oxidation was also performed on the air-dry, unextracted material and on the residues at each stage of extraction.

Fig. 5 shows the results obtained from the original, unextracted material and the curves may be compared with Fig. 6, obtained from the fully extracted plant. The yield of aldehydes obtained is seen to be similar in both cases, notwithstanding the fact that the extraction process removes a large percentage of supposedly nonlignin material. The relative amounts of vanillin and syringaldehyde differ somewhat in the two cases. Two explanations would account for this; (*a*) the extraction process removes some aldehyde-producing substances, (*b*) the extraction process polymerizes or changes the lignin so that lower yields of aldehyde are produced from it on oxidation. It would seem from the present work that both these explanations are valid since although some lignin was found to be extracted by alcohol–benzene, it was insufficient to account for the lowered aldehyde yield obtained from the hydrochloric acid residue.

The material extracted by hot alcohol–benzene consisted of a principal fraction (ABX′), soluble in alcohol–benzene, and a second fraction (ABX″) that was only very slightly soluble in this solvent, accumulating at the bottom of the flask during the course of the extraction. It was water soluble and consisted largely of sucrose. Oxidations of these two fractions gave the curves shown in Figs. 7 and 8. The similarity of Fig. 7 to those shown previously indicates that the substance removed by alcohol–benzene and responsible

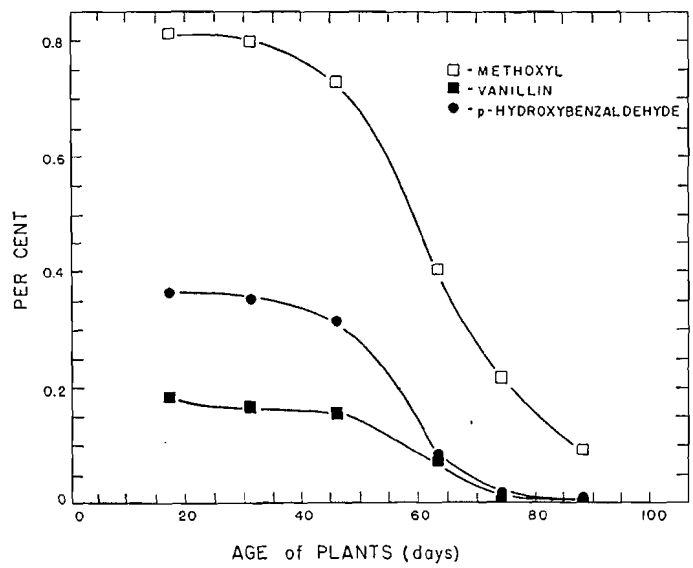

FIG. 8. *Methoxyl content and aldehyde yield from alcohol–benzene extract (alcohol–benzene sparingly soluble ABX″).*

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for these aldehydes is closely related to lignin. Not only does the amount increase during the same growth period as lignification, but the relative amounts of vanillin and syringaldehyde are too similar to the yields from lignin to be derived from a heterogeneous mixture of lignans and other phenolic bodies. It may be compared with Brauns' "native" lignin (3) isolated from wood by ethanol at room temperature, and is similar to the lignin isolated from mature wheat straw by Marion (9) using methanol–benzene (1:1) as solvent.

The red, water soluble material extracted from young plants by alcohol–benzene (ABX″) gave rise to small percentages of vanillin and *p*-hydroxybenzaldehyde on oxidation (Fig. 8). But plants harvested beyond the period of lignification, that is, after the fourth harvest, produced no aldehyde so far as could be detected. The extract itself gave a positive reaction for phenols and an attempt was made to determine how many phenols were present. Paper chromatography using *n*-butanol saturated with water as solvent gave two distinct spots when the paper was sprayed with ferric chloride. After lignification, at the stage where no vanillin was produced on oxidation, no phenols could be detected chromatographically. This observation is to receive further study.

Small quantities of vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde were obtained from an oxidation of the cold water extract but the results were irregular and little significance can be attached to them at this time. No aldehydes could be obtained from the hydrochloric acid extract at any stage of maturity of the plants.

Acknowledgment

The authors wish to express their thanks to Dr. L. H. Shebeski of the Field Husbandry Department, University of Saskatchewan, for supplying the wheat plants used in this work.

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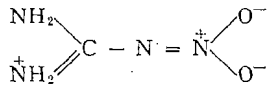
THE STRUCTURES OF NITROGUANIDINE AND ITS DERIVATIVES[1]

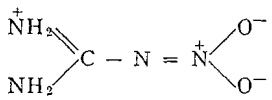
By A. F. McKay, J. P. Picard, and P. E. Brunet

Abstract

The ultraviolet absorption spectra of a number of derivatives of nitroguanidine were determined. An analysis of the effects of substituents on the absorption spectrum of nitroguanidine has led to the conclusion that it exists as a resonance hybrid of several structures including (*a*) and (*b*).



(*a*)



(*b*)

The bearing of these structures on the nomenclature of nitroguanidine and its derivatives is discussed. Also the structures of some of the derivatives of nitroguanidine have been interpreted from their absorption spectra.

I. Introduction

In 1892, Thiele (18) considered the evidence for the symmetrical (I) and nonsymmetrical (II) structures of nitroguanidine at some length before deciding in favor of the unsymmetrical form. Since then the latter form has been used almost exclusively. Further experience with nitroguanidine and its derivatives led to some doubts concerning the accepted structures so the author (A.F.M.) initiated a study of the ultraviolet absorption spectra of derivatives of nitroguanidine. Over a period of four years some sixty compounds have been examined. The results of these studies indicate that certain types of substitution in nitroguanidine lead to decided spectral changes while others have very little effect. An analysis of these spectral changes has been employed in elucidating the structures of nitroguanidine and its derivatives.

$NH_2C(N.NO_2)NH_2$ — I

$NH_2C(NH)NHNO_2$ — II

Previous to this work Jones and Thorn (7) described the ultraviolet absorption spectra of nitroguanidine in neutral, acid, and alkaline media. The spectrum of nitroguanidine was described also by Baly and Desch (1).

II. The Structure of Nitroguanidine

An examination of the ultraviolet absorption spectra of nitroguanidine and its derivatives has led to the conclusion that nitroguanidine exists as a hybrid of the electronic structures I, III, and IV.

[1] *Manuscript received April 18, 1951.*
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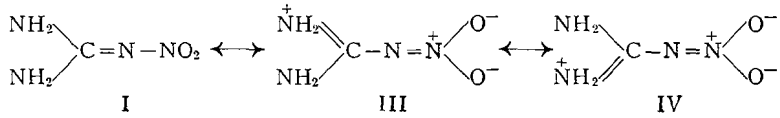
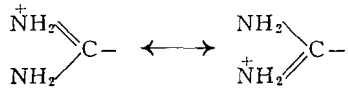


I III IV

If the $-N\rbrack=\overset{+}{N}\langle^{O^-}_{O^-}$ group is considered to be the chromophore responsible for the absorption maximum and the attached group



is considered as a modifier[2] of the absorption characteristics, then the ultraviolet absorption spectra of nitroguanidine and its derivatives are readily interpretable in terms of structure. It is undoubtedly true that there exists interaction between the unbonded electrons of the amino groups and the chromophore group. Thus the molecule as a whole is responsible for the absorption spectrum. However, as long as the nitramino group in derivatives of nitroguanidine is free to form a double bond between the two nitrogens the absorption characteristics vary only slightly. A replacement of one of the hydrogens of the modifier group by an alkyl or aralkyl group produces no major change in the shape of the absorption curve or λ_{max} as shown by a comparison of Curve A, Fig. 1 for nitroguanidine with Curves A and B, Fig. 2.

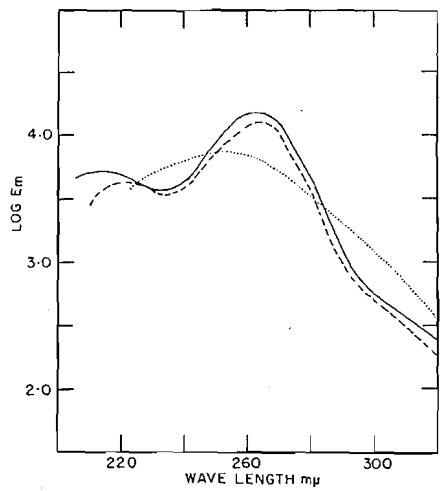


FIG. 1. *Curve A —— Nitroguanidine (ethanol). Curve B – – – Nitroguanidine (N HCl). Curve C . . . . Nitroguanidine (N KOH).*

[2]*The nitroguanidine molecule is divided here into two groups, the chromophore* $-N=\overset{+}{N}\langle^{O^-}_{O^-}$ *and modifier group* $H_2N\rangle\overset{+}{C}=H_2\overset{+}{N}$ *– for convenience in discussion. In this way the effect of substituents in each of the two groups can be discussed separately.*

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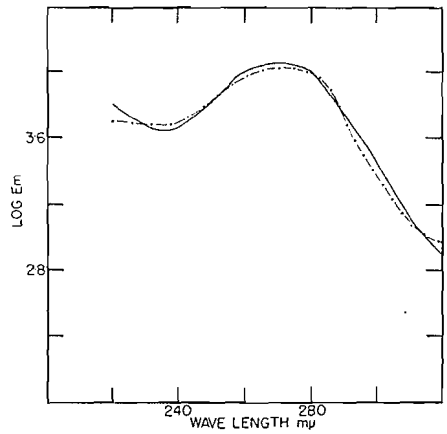
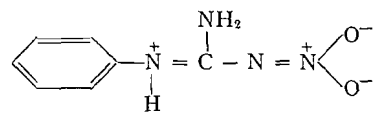


FIG. 2. *Curve A* —— *N-Benzyl-N′-nitroguanidine (ethanol).*
Curve B – · – *N-Cyclohexyl-N′-nitroguanidine (ethanol).*

Table I shows that a considerable variation in the substituents has little effect on the wave length of the absorption maximum or the extinction coefficient.

When an aryl group replaces one of the hydrogens of the modifier group then conjugation of the double bond of the chromophore with the double bonds of the aryl group can occur as shown in (V).



V

TABLE I

ABSORPTION SPECTRA OF N-ALKYL- AND N-ARALKYL-N′-NITROGUANIDINES

Compound*	Solvent	Absorption maxima		E_{max}/** 16,000
		λ,mμ	E_{max}	
N-Methyl-N′-nitroguanidine (3)	Ethanol	269	15,600	0.97
N-Ethyl-N′-nitroguanidine (3)	Ethanol	271	15,700	0.98
	Water	267	15,380	
N-*n*-Butyl-N′-nitroguanidine (3)	Water	270	14,490	
N-iso-Amyl-N′-nitroguanidine (4)	Ethanol	270	16,600	1.03
N-Allyl-N′-nitroguanidine (9)	Ethanol	270	16,300	1.02
N-β-Methoxyethyl-N′-nitroguanidine (11)	Ethanol	269	15,600	0.97
N-Cyclohexyl-N′-nitroguanidine (9)	Ethanol	271	15,500	0.97
N-Benzyl-N′-nitroguanidine (3)	Ethanol	271	16,000	1.00
N-*dl*-α-Phenylethyl-N′-nitroguanidine (9)	Ethanol	273	16,700	1.04
N-β-Phenylethyl-N′-nitroguanidine (9)	Ethanol	271	16,200	1.01

* *The numbers in parentheses refer to the references at the end of this paper in which the preparation and properties of the compounds are described.*

** *The values tabulated in this column are presented to illustrate the relative constancy of the molar extinction coefficient (see Jones and Thorn, reference 7).*

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An examination of Table II indicates that in general this results in bathochromic and hyperchromic shifts. The absorption maxima lie in the range of 272-280 mμ with an average molar extinction coefficient of 16,400. Part of this increase in extinction coefficient is undoubtedly due to the additive effect of aryl absorption. A second absorption maximum has a tendency to appear with *p*-substituted phenyl nitroguanidines. It occurs at a wave length of 224-225 mμ with a slightly lower extinction coefficient than the main absorption maxima at 272-278 mμ. This is indicated in the absorption curve for N-*p*-anisyl-N′-nitroguanidine in ethanol (Curve A, Fig. 3). Typical absorption curves of this group of compounds are recorded in Fig. 3.

TABLE II

ABSORPTION SPECTRA OF N-ARYL-N′-NITROGUANIDINES

Compound	Solvent	Absorption maxima		E_{max}/ 16,400
		λ,mμ	E_{max}	
N-*p*-Tolyl-N′-nitroguanidine (9)	Ethanol	276	15,000	0.91
N-*m*-Tolyl-N′-nitroguanidine (9)	Ethanol	278	14,700	0.89
N-*o*-Tolyl-N′-nitroguanidine (9)	Ethanol	272	16,600	1.01
N-*p*-Anisyl-N′-nitroguanidine (9)	Ethanol	275	16,900	1.03
		(225)	(12,900)	
N-*m*-Anisyl-N′-nitroguanidine (9)	Ethanol	277	18,700	1.14
N-*o*-Anisyl-N′-nitroguanidine (9)	Ethanol	274	15,800	0.96
N-*p*-Phenetyl-N′-nitroguanidine (9)	Ethanol	275	16,700	1.02
N-*m*-Phenetyl-N′-nitroguanidine (9)	Ethanol	277	17,200	1.05
N-*o*-Phenetyl-N′-nitroguanidine (9)	Ethanol	274	13,600	0.83
N-*p*-Chlorophenyl-N′-nitroguanidine (9)	Ethanol	278	17,500	1.06
N-*m*-Chlorophenyl-N′-nitroguanidine (9)	Etnanol	279	17,200	1.05
N-*o*-Chlorophenyl-N′-nitroguanidine (9)	Ethanol	274	19,040	1.16
N-*p*-Bromophenyl-N′-nitroguanidine (9)	Ethanol	280	15,300	0.93
N-*m*-Bromophenyl-N′-nitroguanidine (9)	Ethanol	279	16,400	1.00
N-*p*-Hydroxyphenyl-N′-nitroguanidine (12)	Ethanol	278	15,300	0.93
		(224)	(11,700)	
N-*p*-tert. Amylphenyl-N′-nitroguanidine (9)	Ethanol	278	17,000	1.03

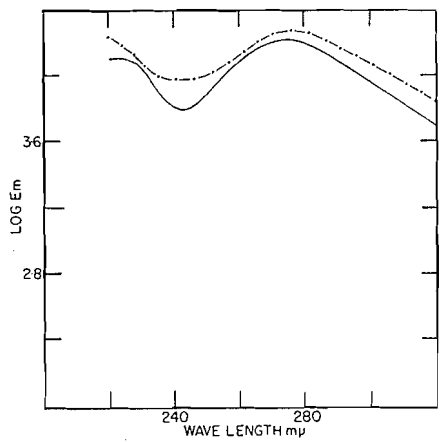

FIG. 3. *Curve A* —— *N-p-Anisyl-N′-nitroguanidine (ethanol).*
Curve B – · – *N′-m-Anisyl-N′-nitroguanidine (ethanol).*

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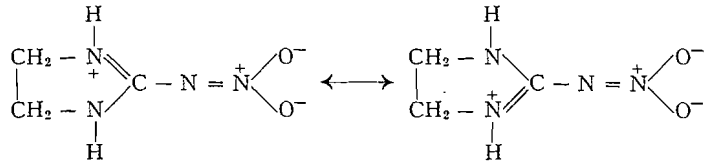
If two or three hydrogen atoms of the modifier group are replaced to give a cyclic compound such as 2-nitramino-2-imidazoline (VI) or a substituted



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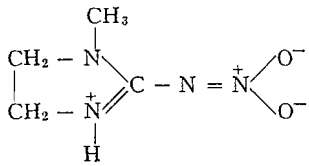
cyclic structure like 1-methyl-2-nitramino-2-imidazoline (VII) the wave length



VII

of the absorption maxima are not changed from the usual values of 269-273 mμ. Also the curves presented in Fig. 4 show the type of absorption to be the same as exhibited by the compounds in Tables I and II. Table III lists a number of cyclic nitroguanidine derivatives of this type. The molar extinction coefficient is higher (17,100-17,700) for the 2-nitramino-1, 3-diaza-2-cycloalkenes than the unsymmetrically substituted N-alkyl-, and N-aralkylnitroguanidines. This may not be due entirely to ring formation because sym.-dibenzylnitroguanidine (8) has an E_{max} of 18,000 at λ_{max} 274. Dibenzylnitroguanidine is perhaps not a good example for this comparison because the absorptions of the two phenyl groups would be expected to appear as additive factors in its extinction coefficient. In comparison with more closely related compounds, e.g., ethylnitroguanidine, it is evident that ring formation results in a slightly increased absorption.

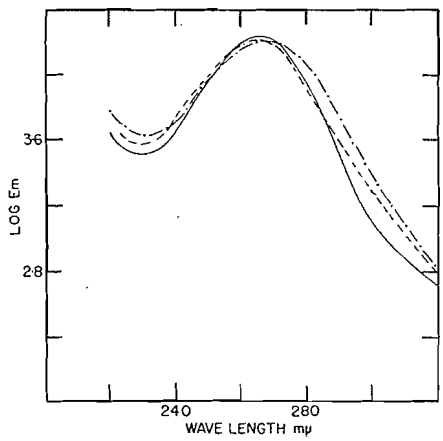


FIG. 4. *Curve A* —— *2-Nitramino-2-imidazoline (ethanol).*
Curve B – · – *2-Nitramino-2-tetrahydropyrimidine (ethanol).*
Curve C – – – *2-Nitramino-2-imidazoline (N HCl).*

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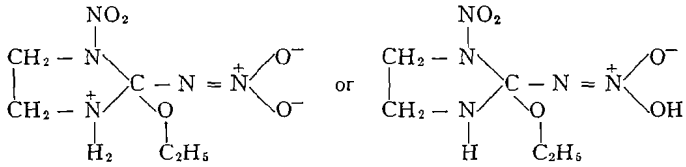
TABLE III

ABSORPTION SPECTRA OF CYCLIC NITROGUANIDINES—CLASS I

Compound	Solvent	Absorption maxima	
		λ,mμ	E_{max}
2-Nitramino-2-imidazoline (14)	Ethanol	267	17,700
	N Hydrochloric acid	264	16,600
2-Nitramino-4 (or 5)-methyl-2-imidazoline (14)	Ethanol	265	17,700
2-Nitramino-2-tetrahydropyrimidine (14)	Ethanol	271	17,400
	Water	267	16,600
	N Hydrochloric acid	265	15,500
2-Nitramino-4 (or 6) methyl-2-tetrahydropyrimidine (14)	Ethanol	271	17,700
	N Hydrochloric acid	266	15,150
2-Nitramino-5-hydroxy-2-tetrahydropyrimidine (14)	Ethanol	271	17,100
2-Nitramino-1, 3-diaza-2-cycloheptene (14)	Ethanol	273	15,300
1-Methyl-2-nitramino-2-imidazoline (16)	Ethanol	269	15,600
1-Ethyl-2-nitramino-2-imidazoline (16)	Ethanol	270	16,400
1-β-Hydroxyethyl-2-nitramino-2-imidazoline (16)	Ethanol	270	16,800
1-β-Nitroxyethyl-2-nitramino-2-imidazoline (16)	Ethanol	269	17,600
1-Benzyl-2-nitramino-2-imidazoline (8)	Ethanol	271	17,400
1-Nitro-2-nitramino-2-imidazoline (15)	Ethanol	270	13,300
1-Nitro-4-methyl-2-nitramino-2-imidazoline (6)	Ethanol	269	11,600

It will be noted in Table III that a nitro group in position 1 of 2-nitramino-1, 3-diaza-2-cycloalkenes does not affect λ_{max} but the E_{max} is lowered to 11,600-13,300. This would be expected, because the nitro group in this position interferes with resonance in the modifier group. Even a higher degree of substitution as exhibited by compound (VIII) has no effect on λ_{max} but once again the value of E_{max} is lowered to 13,340. Thus it is evident that the number



VIII

and kind of substituents on the modifier group may be varied considerably without affecting the spectral characteristics of nitroguanidine. On the other hand, any substitution which interferes with the chromophore assuming the structure $-N=\overset{+}{N}\begin{matrix}O^-\\O^-\end{matrix}$ changes the ultraviolet absorption spectrum of nitroguanidine profoundly.

When nitroguanidine is substituted in a manner to include the nitramino group in a heterocyclic ring, the absorption curve takes the form illustrated in Fig. 5, Curve A. Other compounds of this type are given in Table IV along

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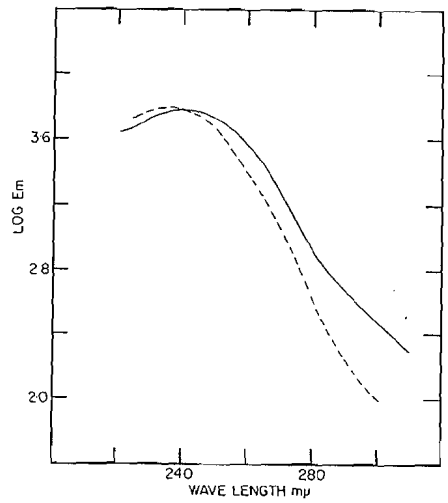


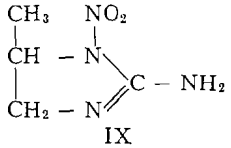
FIG. 5. *Curve A* —— *1-Nitro-2-amino-4-methyl-2-imidazoline hydrochloride (95% ethanol).* *Curve B* – – *1-Nitro-4-methyl-2-imidazolidone (ethanol).*

TABLE IV

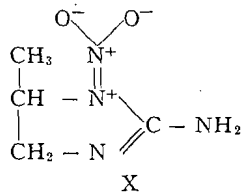
ABSORPTION SPECTRA OF CYCLIC NITROGUANIDINES—CLASS II

Compound	Solvent	Absorption maxima	
		λ,mμ	E_{max}
1-Nitro-2-amino-2-imidazoline (11)	Ethanol	230	4500
1-Nitro-2-amino-2-imidazolinium bromide (11)	Ethanol	244	6300
1-Nitro-2-amino-4-methyl-2-imidazolinium chloride (6)	Ethanol	243	6300
1-Nitro-2-amino-4-methyl-2-imidazolinium (6)	Ethanol	240	6100

with their absorption maxima. In compound (IX), which is typical of this class, it is apparent that the nitramino group cannot take the form $-N=\overset{+}{N}\begin{matrix}O^-\\O^-\end{matrix}$. This would result in the two adjoining nitrogens carrying a positive charge as



IX



X

illustrated in (X), which is an unstable state (17). Furthermore, any attempt to force the nitramino group to take the form of the chromophore in nitroguanidine by the addition of alkali causes a rupture of the ring. The cyclic structure of this class of compounds is opened also by standing in excess acid at room temperature (8). A comparison of Curves A and B in Fig. 5 shows that the spectra of this class of compounds is similar to the spectra of secondary nitramines (Table V).

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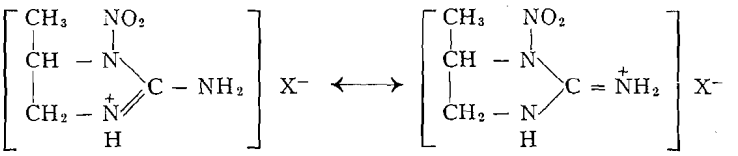
TABLE V

ABSORPTION SPECTRA OF SECONDARY NITRAMINES

Compound	Solvent	Absorption maxima		E_{max}/5500
		λ,mμ	E_{max}	
1-Nitro-4-methyl-2-imidazolidone (13)	Ethanol	237	6200	1.13
1, 3-Dinitro-4-methyl-2-imidazolidone (10)	Ethanol	236	11,300	2.05
1, 3-Dinitro-2-hexahydropyrimidone (15)	Ethanol	243	10,400	1.89
1-β-Nitroxyethyl-3-nitro-2-imidazolidone (16)	Ethanol	244	7800	1.42*
1, 3-Dinitro-5-nitroxy-1, 3-diaza-2-cyclohexanone (10)	Ethanol	233	13,400	1.21*

* *These high values for E_{max}/5500 are due to the presence of the nitroxy group. A similar observation was made previously by Jones and Thorn (7).*

Even the salts (XI) of compound (IX), which fulfill the requirements for resonance do not change the shape of the absorption curve (Fig. 5, Curve A)



XI

to the type given by nitroguanidine (Fig. 1, Curve A). Salt formation does cause a bathochromic shift from 230 mμ to 240 mμ.

Another class of compounds in which the chromophore group is held in the nitrimino form $= N - N\langle^{O}_{O}$ by suitable substitution of the nitroguanidine nucleus gives ultraviolet absorption spectra (Fig. 6 and Table VI) much different than nitroguanidine.

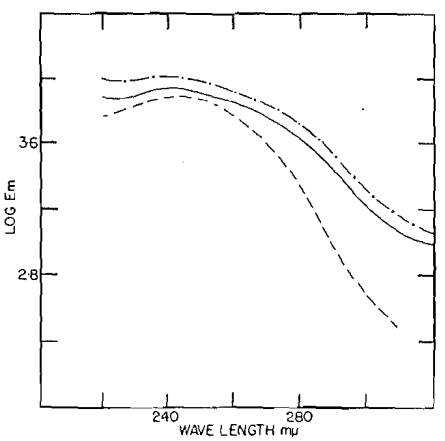


FIG. 6. *Curve A —— 1-Ethyl-2-nitrimino-3-nitroimidazolidine (ethanol).*
Curve B – – 1-Methyl-2-nitrimino-3-nitroimidazolidine (ethanol).
Curve C – · – 1-β-Nitroxyethyl-2-nitrimino-3-nitroimidazolidine (ethanol).

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TABLE VI

ABSORPTION SPECTRA OF CYCLIC NITROGUANIDINES—CLASS III

Compound	Solvent	Absorption maxima	
		λ,mμ	E_{max}
1-Methyl-2-nitrimino-3-nitroimidazolidine (16)	Ethanol	241	7700
1-Ethyl-2-nitrimino-3-nitroimidazolidine (16)	Ethanol	242	8800
1-β-Nitroxyethyl-2-nitrimino-3-nitroimidazolidine (16)	Ethanol	240	10,700

The Spectra of Nitroguanidine and Its Derivatives in N Hydrochloric Acid Solution

Nitroguanidine forms salts in concentrated acid solutions, but these salts are very unstable. On standing in the air the atmospheric moisture is sufficient to hydrolyze them (2). A dilute acid solution of nitroguanidine might be expected to consist mainly of a hybrid of the "zwitterion" structures (III and IV) along with, possibly, very little of the cation XIII. The structures (XIII and XIV) contributing to the cation are very similar to the "zwitterion" structures for

XIII XIV

nitroguanidine except for the association of the H ion. Thus one might expect the absorption curves for nitroguanidines in acid and neutral solution to be quite similar. This can be seen to be the case with nitroguanidine (Fig. 1, Curve B) and those of its derivatives examined (Fig. 4, Curve C, cf. Table III).

The Spectra of Nitroguanidine and Its Derivatives in Alkaline Solution

Two types of absorption curves are observed for nitroguanidine and its derivatives in alkaline solution. The first type is exemplified by Curve C, Fig. 1 of nitroguanidine and Curve A, Fig. 8 of 2-nitramino-2-imidazoline. The second type of absorption curve is observed with unsymmetrically substituted nitroguanidines, e.g., N-ethyl-N′-nitroguanidine, N-isoamyl-N′-nitroguanidine, N-*m*-chlorophenyl-N′-nitroguanidine (Curves A, B, and C respectively, Fig. 7). This type of curve is also obtained for the six- and seven-membered ring compounds in alkaline solution, e.g., 2-nitramino-1, 3-diaza-2-cyclohexene and 2-nitramino-1, 3-diaza-2-cycloheptene (Curves B and C, Fig. 8). The second type curve approaches more closely to that of a nitramine (cf. Curve D, Fig. 7). Jones and Thorn (7) have shown that the ultraviolet absorption curves of primary nitramines in 95% ethanol and alkaline solution are similar with the exception that the absorption maxima have a higher extinction coefficient in alkaline solution.

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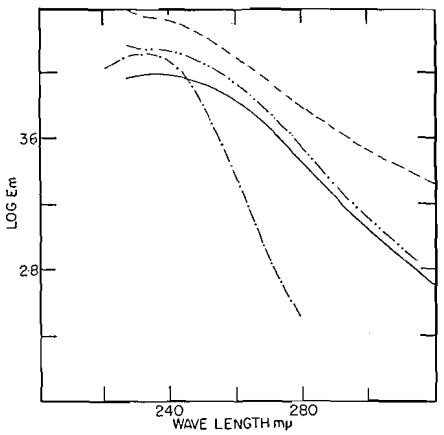


FIG. 7. *Curve A* —— *N-Ethyl-N'-nitroguanidine (N KOH).*
Curve B – ·· – *N-iso-Amyl-N'-nitroguanidine (N KOH).*
Curve C – – – *N-m-Chlorophenyl-N'-nitroguanidine (N KOH).*
Curve D – · – *1, 3-Dinitraminopropane (ethanol).*

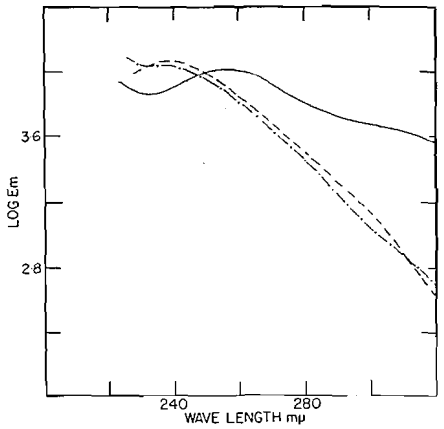
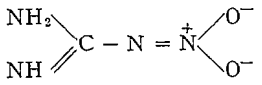


FIG. 8. *Curve A* —— *2-Nitramino-2-imidazoline (N KOH).*
Curve B – – – *2-Nitramino-1, 3-diaza-2-cycloheptene (N KOH).*
Curve C – · – *2-Nitramino-1, 3-diaza-2-cyclohexene (N KOH).*

In alkaline solution the mesomeric form of nitroguanidine and its derivatives would be expected to change into the anion form (XV).



XV

If this occurs immediately there should be no further change in the absorption curves in alkaline solution with time. An examination of Curves B and C, Fig. 9 show that the shape of the curves and absorption maxima change very little with time. However, there is a decrease in the extinction coefficient which

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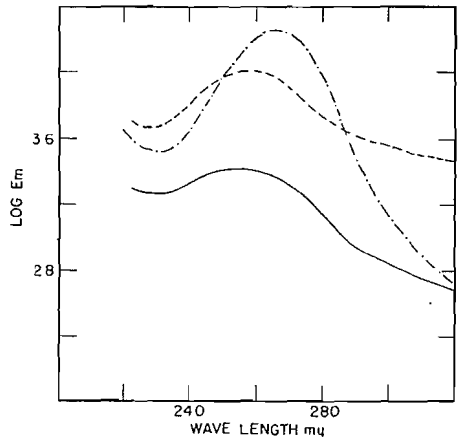

FIG. 9. *Curve A – · – 2-Nitramino-4 (or 5)-methyl-2-imidazoline (ethanol).*
Curve B – – – 2-Nitramino-4 (or 5)-methyl-2-imidazoline (N KOH determined immediately).
Curve C —— 2-Nitramino-4 (or 5)-methyl-2-imidazoline (N KOH determined after standing in alkaline solution 24 hr.).

indicates a decrease in concentration of the absorbing species. The same behavior was noted with methyl nitroguanidine in alkaline solution. These decreases in extinction coefficients occur on hydrolyses of these nitroguanidine derivatives to the corresponding ureas. Ethylene urea and urea exhibit no absorption in this region of the spectrum in which the nitroguanidine derivatives absorb. The only conclusion possible is that under the conditions employed, nitroguanidine and its derivatives are changed first into the corresponding anions which are hydrolyzed slowly in the alkaline solution to the corresponding ureas. It is also apparent that the species responsible for absorption in neutral and alkaline solution are different. Further work is in progress on the absorption spectra of nitroguanidine derivatives in alkaline solution.

Structures of Compounds Formed by the Addition of Ammonia, Amines, and Alcohols to 1-Nitro-2-Nitramino-2-Imidazoline

The ultraviolet absorption curve for N-β-nitraminoethyl-N′-nitrourea exhibits two maxima at 230 mμ and 260 mμ. As shown in Table VII and Fig. 10,

TABLE VII

Compound	Solvent	Absorption maxima	
		λ, mμ	E_{max}
N-β-Nitramino-α-methylethyl-N′-nitrourea (13)	Ethanol	230 260	13,300 11,600
N-β-Nitraminoethyl-N′-nitroguanidine (16)	Ethanol	232 271	13,500 20,000
N-β-Nitramino-α-methylethyl-N′-nitroguanidine (6)	Ethanol	232 271	12,000 18,200

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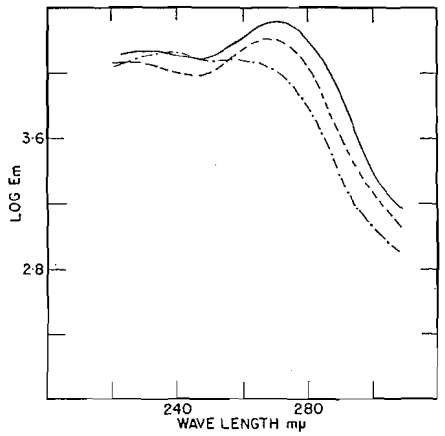
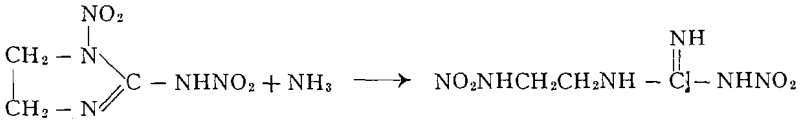


FIG. 10. *Curve A* —— *N-β-Nitraminoethyl-N-nitroguanidine (ethanol).*
Curve B – – – *N-β-Nitramino-α-methylethyl-N'-nitroguanidine (ethanol).*
Curve C – · – *N-β-Nitramino-α-methylethyl-N'-nitrourea (ethanol).*

Curves A, B, and C, the ammonia addition products of 1-nitro-2-nitramino-2-imidazoline and 1-nitro-4-methyl-2-nitramino-2-imidazoline (6) also possess absorption maxima at these wave lengths. Also these latter two compounds give a negative Franchimont Test (5) employing dimethylaniline. All other 2-nitramino-2-imidazolines with the exception of nitroxy derivatives give a pink color in this test. The properties are more in agreement with linear structures than the cyclic structures previously proposed (15). Thus the reaction of ammonia with 1-nitro-2-nitramino-2-imidazoline should be written as follows:



The compound obtained from refluxing 1-nitro-2-nitramino-2-imidazoline with ethanol gives an ultraviolet absorption spectrum typical of the cyclic nitroguanidines of Table III. It also gives a deep red color with the Franchimont test using dimethylaniline. It is therefore assigned structure VIII.

Experimental

The absorption spectra were measured on a Beckman model D.U. ultraviolet spectrometer using a slit width of 20 Å between 220 and 235 mμ and of 10 Å at longer wave lengths. The samples used were analytically pure.

Concluding Remarks

The results of this study of the ultraviolet absorption spectra of the derivatives of nitroguanidine have led to the following conclusions. In nitroguanidine and all its derivatives represented by the compounds listed in

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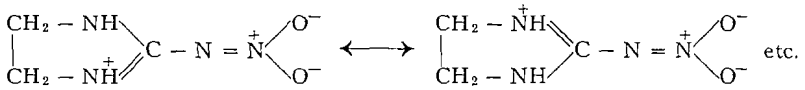
Tables I, II, and III, the nitramino group exists mainly in the form $-N=\overset{+}{N}\begin{smallmatrix}O^-\\O^-\end{smallmatrix}$. When the substituents are such that resonance is permitted, the compounds exist as a resonance hybrid of several structures, e.g., 2-nitramino-2-imidazoline is a resonance hybrid of the electronic structures



Those compounds in which the chromophore group $-N=\overset{+}{N}\begin{smallmatrix}O^-\\O^-\end{smallmatrix}$ is present should not be classed as nitrimines. The term nitrimine should be retained for compounds represented by those in Table VI. It is suggested that the names now used for nitroguanidine and its derivatives be retained.

It should be borne in mind that some of the finer points of structure of nitroguanidines remain to be determined. As an example, there is almost certain to be a high degree of hydrogen bonding in these compounds.

Acknowledgments

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BIOCHEMISTRY OF THE USTILAGINALES

VI. THE ACYL GROUPS OF USTILAGIC ACID[1]

By R. U. Lemieux and R. Charanduk[2]

Abstract

A partition chromatographic technique was established for the estimation of the acetic, *n*-caproic, L-β-hydroxy-*n*-caproic, and L-β-hydroxy-*n*-caprylic acids which are liberated on the hydrolysis of ustilagic acid. The free carboxyl group of ustilagic acid was shown to be derived from the ustilic acid residue. Since fractional precipitation of ustilagic acid did not alter the original composition, it was concluded that ustilagic acid consists of 65-70% of a monoacetyl-mono-L-β-hydroxy-*n*-caproylglucoustilic acid and 25-30% of a monoacetyl-mono-L-β-hydroxy-*n*-caprylylglucoustilic acid.

The alkaline hydrolysis of ustilagic acid was shown (3) to yield an amorphous substance termed glucoustilic acid, acetic acid, L-β-hydroxy-*n*-caproic acid (4), L-β-hydroxy-*n*-caprylic acid (4), and a small amount of *n*-caproic acid.

Ustilagic acid was treated with a large excess of sodium methylate in dry methanol in order to effect transesterification. On the addition of dry ether, sodium glucoustilate was deposited quantitatively. Analysis of the mother liquor showed it to contain two equivalents of ester per equivalent of ustilagic acid degraded and this ester group content was shown, by the chromatographic procedure described below, to be derived from acetic, L-β-hydroxy-*n*-caproic, L-β-hydroxy-*n*-caprylic, and *n*-caproic acids. It was thus evident that the free carboxyl group in ustilagic acid was derived from the ustilic acid residue and that the ester groups of the ustilagic acid mixture were formed from the two β-hydroxyacids as well as the two fatty acids.

A method for the quantitative estimation of the amounts of the various ester groups in ustilagic acid by partition chromatography was established. The technique, an adaptation of the procedures recently described by Neish (7, 8, 9), employed an aqueous static phase supported by acid-washed Celite 535. The chromatography of the entire hydrolysis mixture made unnecessary the separation of the acids to be analyzed from the gelatinous precipitate of glucoustilic acid and allowed a determination with only 50 mgm. of ustilagic acid. The acidified saponification mixture was absorbed on an appropriate amount of Celite and the resulting powder was transferred quantitatively to the top of the chromatographic column where it was packed to yield an additional Celite–water column containing the substances to be fractionated. Of the conditions for development tested, the most favorable involved the successive percolation of 40, 80, and 80 ml. amounts of benzene, chloroform, and 5% butanol in benzene, respectively. The success of the method is illustrated

[1] *Manuscript received June 11, 1951.*
Contribution from the National Research Council, Prairie Regional Laboratory, Saskatoon, Sask. Issued as Paper No. 122 on the uses of Plant Products and as N.R.C. No. 2499.
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by Plots B and C of Fig. 1 which were established by the titration of successive 2 ml. portions of effluent. Plot B shows that these conditions effected satisfactory separation of the various acids derived from the ester groups of ustilagic acid and the identity of the acids in each zone is shown by the plots of Fig. 1, C which were obtained by the chromatography of solutions which contained only one of each of the four acids. Table I shows that the recovery of the various acids from solutions of known concentration was within 3%.

TABLE I

THE RECOVERY OF SOME ACIDS BY PARTITION CHROMATOGRAPHY

No.	Substance	Mgm. added	Mgm. recovered	% recovered
1	Acetic acid	3.44	3.36	97.7
2	L-β-Hydroxy-*n*-caproic acid	9.24	9.06	98.1
3	L-β-Hydroxy-*n*-caprylic acid	7.10	7.05	99.3
4	*n*-Caproic acid	0.56	0.55	98.2

The separation of the lower fatty acids by partition chromatography has been described by several investigators (1, 2, 6). In each case, the acids were extracted before chromatography. In an earlier publication in this series (3), mention was made of the use of the presently described chromatographic technique for the isolation of *n*-butyric and *n*-caproic acids from degradative reaction mixtures. In these experiments, as well as for the determination of Plots A and C of Fig. 1, the sodium salts of the carboxylic acids were decomposed with hydrochloric acid and the aqueous mixture was absorbed on Celite for transfer to the top of the chromatographic column. It is noteworthy at this point that the absorption on dry Celite of an equal weight of a solution or suspension in water of water-soluble materials with subsequent packing into a column forms a convenient means for efficient extractions with any water-immiscible solvent with or without accompanying partition chromatography. The method is especially useful for the manipulation of small amounts of material. Plot A, Fig. 1, shows that the chromatographic technique resolved a mixture of the normal C_1-C_5-fatty acids with a slight overlap for the C_4- and C_5-acid zones.

The analysis of ustilagic acid showed that the ester group content as determined by saponification was accounted for by the four acids separated in the chromatogram. It was thus established that all of the products of the alkaline hydrolysis of ustilagic acid have been detected. Several ustilagic acid preparations have been analyzed and in each case the acyl group contents were in the following ranges: 0.95-1.05 acetyl, 0.65-0.70 L-β-hydroxy-*n*-caproyl, 0.25-0.30 L-β-hydroxy-*n*-caprylyl, and 0.03-0.07 *n*-caproyl groups per neutral equivalent of ustilagic acid. As pointed out previously (3), the products of the alkaline hydrolysis of ustilagic acid cannot be recombined to yield a single substance of appropriate molecular weight and ustilagic acid must therefore be a mixture. So far, all efforts to separate the components have failed, thus

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complicating the problem of more precisely defining the structure of the substances. A forthcoming publication in this series will show that the amorphous substance previously designated glucoustilic acid (3) was a mixture composed almost entirely of di-D-glucosyl substituted dihydroxyhexadecanoic and trihydroxyhexadecanoic acids, the former substance being the major component. It is proposed to continue to use the term ustilagic acid to refer to the mixture of substances and to designate the various components as the ustilagic acids A, B, etc., when the substances have been fully characterized. Similarly, the term glucoustilic acid will designate the mixture obtained on the hydrolysis of the ustilagic acid complex.

Considering the rather unique solubility properties (5) of ustilagic acid, it seemed likely that at least a partial separation of its components could be effected by fractional precipitation. A crude, ash-free sample of ustilagic acid was subjected to fractional precipitation by the successive addition of nonpolar solvents to a methanolic solution. The material was recovered as five fractions in 91% yield (Table II). Fractions 1, 2, 3, and 4 were white powders which represented 20, 44, 18, and 6.2%, respectively, of the original sample. Fraction 5 was an amber-colored oil which contained some insoluble solids and represented only 2.6% of the original sample. No attempt was made to characterize this minor component; however, the material contained an unexpectedly high acetyl group content.

As seen in Table II, the first four fractions were weakly dextrorotatory in pyridine solution and showed essentially identical neutralization and saponification equivalents, acyl group and glucose contents. The saponification

TABLE II

THE FRACTIONAL PRECIPITATION OF USTILAGIC ACID

	Ustilagic acid samples					
	Original sample	Fraction No. 1	Fraction No. 2	Fraction No. 3	Fraction No. 4	Fraction No. 5
% of the original sample	–	20	44	18	6.2	2.6
$[\alpha]_D$ (c, 1 in pyridine)	+5.6°	+7.0°	+6.9°	+7.5°	+5.3°	–
% Acetyl	5.6	5.4	5.6	5.5	5.5	17.4
% L-β-Hydroxy-*n*-caproyl	9.9	8.9	9.6	10.0	8.6	3.2
% L-β-Hydroxy-*n*-caprylyl	4.8	5.2	4.7	4.6	4.1	4.1
% *n*-Caproyl	0.7	0.4	0.3	0.6	0.9	1.2
% Glucose	44	45	45	48	42	–
Neutralization equivalent	801	808	806	784	822	1220
Saponification equivalent (*A*)	396	400	395	392	402	214
Saponification equivalent based on acidity recovered by chromatography (*B*)	390	410	400	400	420	200
2*B*	780	820	800	800	840	–
Acetyl groups per 2*B*	1.01	1.02	1.04	1.01	1.06	–
L-β-Hydroxy-*n*-caproyl groups per 2*B*	0.67	0.64	0.67	0.69	0.62	–
L-β-Hydroxy-*n*-caprylyl groups per 2*B*	0.27	0.30	0.26	0.25	0.24	–
n-Caproyl groups per 2*B*	0.05	0.03	0.02	0.05	0.08	–

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equivalents, B, calculated from the total acidity found in the effluent of the chromatograms, agreed, within ± 4%, with the saponification equivalents, A, determined directly. The number of moles of an acyl group, X, per neutralization equivalent of the ustilagic acid sample was calculated from the relationship:

$$\frac{\text{(Mol. wt. of acyl group) } 100X}{\text{Neutralization equivalent}} = \% \text{ acyl group.}$$

Since glucoustilic acid is composed of structurally closely related compounds, the substance can be considered, for the following arguments, as a pure substance. The analytical results listed in Table II indicate that about 94% of the sample of ustilagic acid consisted of glucoustilic acid substituted by acetyl, L-β-hydroxy-*n*-caproyl, and L-β-hydroxy-*n*-caprylyl groups. Since, as shown in Table II, the fractional precipitation of a sample of ustilagic acid failed to yield fractions of appreciably different acyl group content, the main components of the ustilagic acid complex must certainly each possess two ester groups per mole. Consequently, it is clear that the six substances listed in Table III are the possible components of about 94% of the ustilagic acid

TABLE III

SOME POSSIBLE FORMS OF USTILAGIC ACID

Form	Substituents on glucoustilic acid*	Molecular weight
1	Diacetyl	696
2	Monoacetyl-mono-L-β-hydroxy-*n*-caproyl	768
3	Monoacetyl-mono-L-β-hydroxy-*n*-caprylyl	796
4	Di-L-β-hydroxy-*n*-caproyl	840
5	Mono-L-β-hydroxy-*n*-caproyl-mono-L-β-hydroxy-*n*-caprylyl	868
6	Di-L-β-hydroxy-*n*-caprylyl	896

* *The molecular weight of glucoustilic acid is assumed to be 612 (3).*

complex. If Forms 4, 5, or 6 were present in appreciable amounts in the ustilagic acid preparation, it would follow, since one-half of the substituent acyl groups were acetyl, that an appreciable amount of Form 1 would be present. Since Forms 4, 5, and 6 all have molecular weights more than 21% greater than Form 1, it would be expected that, if ustilagic acid contained one or more of Forms 4, 5, or 6, the fractional precipitation would yield fractions with appreciably different acyl group contents. However, as pointed out above, the fractional precipitation procedure used failed to accomplish any appreciable resolution of the ustilagic acid complex. It therefore seems highly probable that ustilagic acid does not contain Forms 1, 4, 5, or 6 but consists almost entirely of Forms 2 and 3, the monoacetyl-mono-L-β-hydroxy-*n*-caproyl (65-70%) and monoacetyl-mono-L-β-hydroxy-*n*-caprylyl (25-30%) substituted glucoustilic acids—the simplest possible composition for the ustilagic acid complex.

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Experimental

Partition Chromatography

Acid washed Celite No. 535, dried at 500°C. (8), 0.5 gm., was added to a 35 cm. chromatographic tube of 15 mm. inside diameter previously fitted with a perforated porcelain disk which held a cotton plug. This dry Celite was added to prevent any leakage of the aqueous phase into the effluent. A disk of filter paper just barely greater in diameter than the inside diameter of the tube was pushed by means of a plunger to the top of the dry Celite column and the latter was firmly pressed. Five milliliters of 0.01 *N* hydrochloric acid was thoroughly mixed with 5 gm. of the dry Celite and the wet powder was added by means of a funnel to the tube. The chromatographic column was prepared by adding 30 ml. of the benzene developer and packing the wet Celite by means of the plunger to a column about 7 cm. in length. The sides of the tube were swept clean by the addition of a disk of filter paper in the manner described by Neish (7). The excess benzene was percolated through the column with the aid of air pressure until a height of about 4 mm. remained above the column. The acidified saponification mixture absorbed on Celite, prepared as follows, was now added. A weighed sample of ustilagic acid, about 50 mgm., was heated with 0.5 ml. of 0.6 *N* aqueous sodium hydroxide on the steam bath for 15 min. in a loosely stoppered 100 × 14 mm. test tube. The resultant clear solution was cooled and 0.1 ml. of concentrated hydrochloric acid was added. The resultant mixture was a thick slurry due to the precipitation of glucoustilic acid. The test tube was lightly tapped in order to ensure uniform mixing and 0.5 gm. of the dry Celite was added. On thorough mixing the Celite completely absorbed the mixture and dried the test tube. The resulting powdery material was transferred as quantitatively as possible to the top of the chromatographic column. The small amount of the mixture which tended to cling to the inside surface of the chromatographic tube was gathered by means of a filter paper disk as described above. On pressing the Celite mixture with the plunger, an additional 7 mm. section of chromatographic column was formed. The resulting column was developed with 40 ml. of benzene followed by 80 ml. of chloroform and lastly, 80 ml. of 5% *n*-butanol in benzene. These solvents were equilibrated before use with one-fifth their volume of 0.01 *N* hydrochloric acid in the manner described by Neish (7).

In order to determine the positions of the acids in the effluent, successive 2 ml. volumes were titrated with 0.01 *N* sodium hydroxide solutions to the end point of phenol red indicator. The plots in Fig. 1 represent the best curve passing through the points obtained by plotting the volume of alkali in each successive titration against the total volume of effluent at the point of collection. Figs. 1, A and 1, C were established by the chromatography of 0.5 ml. solutions of the sodium salts, acidified with 0.1 ml. of concentrated hydrochloric acid. The salt solution used for Fig. 1, A was approximately 0.06 *N* with respect to each acid. Fig. 1, B shows the results obtained for a sample of ustilagic acid.

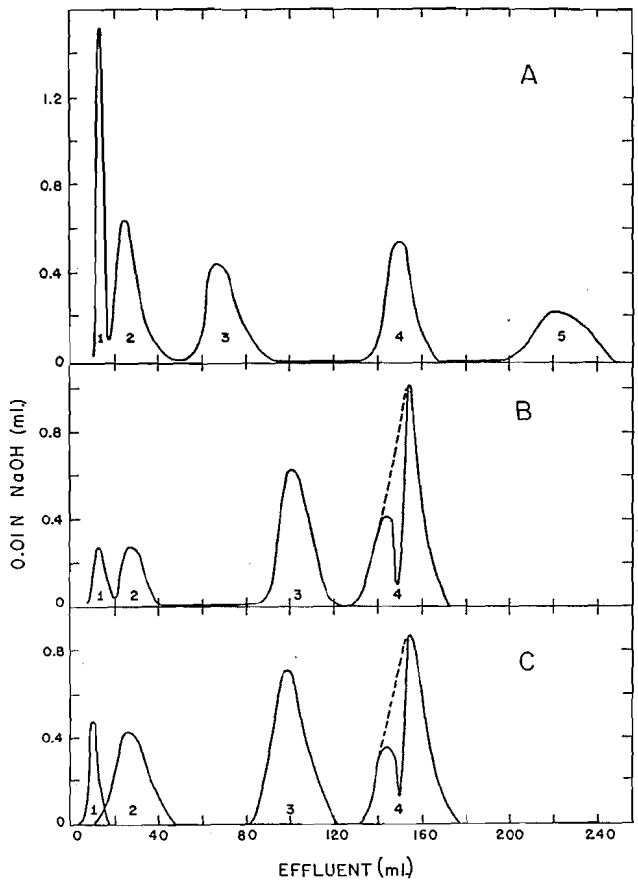

FIG. 1. *The separation of some aliphatic acids by partition chromatography.*
A. The separation of the C_1 to C_5 fatty acids: 1. n-valeric; 2. n-butyric; 3. propionic; 4. acetic; and 5. formic.
B. The separation of the acids formed on the hydrolysis of ustilagic acid: 1. n-caproic; 2. L-β-hydroxy-n-caprylic; 3. L-β-hydroxy-n-caproic; and 4. acetic.
C. The location in the effluent of each of the four acids listed in B.

The results show that the small amount of *n*-caproic acid which occurs in the hydrolyzates of ustilagic acid was adequately separated from the L-β-hydroxy-*n*-caprylic acid. The L-β-hydroxy-*n*-caprylic acid band was well separated from the L-β-hydroxy-*n*-caproic acid band. Of the several solvents tried for the separation of L-β-hydroxy-*n*-caproic acid from acetic acid, chloroform proved the most satisfactory. Since the "tail" of the band due to the hydroxyacid overlapped the "head" of the acetic acid band, the continuous addition of weakly basic indicator solution as prescribed by Neish (7) for the detection of acid bands proved less convenient than the collection of 2 ml. samples between 126 and 136 ml. of effluent and testing the central ones for acidity. If the sample tested required less than 0.06 ml. of 0.01 *N* sodium hydroxide, the point of its collection was taken at the point of separation and the remaining samples were combined with either the L-β-hydroxy-*n*-caproic or acetic acid

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bands depending on the side of the test sample on which they were collected. Thus, in the actual analysis of a ustilagic acid sample, the acidity in the first 16 ml. of effluent was attributed to *n*-caproic acid, that in the next 44 ml. to L-β-hydroxy-*n*-caprylic acid, the acidity found from 60 ml. of effluent to the above described test sample was taken as due to L-β-hydroxy-*n*-caproic acid and the remainder of the effluent was titrated for the acetic acid. The discontinuity in the acetic acid band, as shown in Plots B and C of Fig. 1, was usually detected. It was probably brought about by the change from chloroform developer to the 5% butanol in benzene developer.

Transesterification of Ustilagic Acid

A sample of ustilagic acid, 0.496 gm. (0.630 m.e.) which on analysis was found to possess 0.96 acetyl, 0.70 L-β-hydroxy-*n*-caproyl, 0.30 L-β-hydroxy-*n*-caprylyl, and 0.06 *n*-caproyl groups per neutral equivalent, 787, was dissolved in 10 ml. of dry methanol. A solution, 10 ml., of 0.27 *N* sodium methylate in dry methanol was then added and the mixture was left at room temperature for one hour. On the addition of 60 ml. of dry ether a white precipitate formed which was collected by filtration and washed three times with 20 ml. volumes of ether. To the filtrate collected in a pressure bottle, 25 ml. of water was added and the mixture was rapidly made neutral to phenophthalein indicator with *N* hydrochloric acid. After carefully adjusting the pH to the end point of the indicator, 25 ml. of 0.1 *N* sodium hydroxide solution was added and the capped bottle was shaken for 16 hr. at room temperature. Titration of the excess alkali with standard 0.1 *N* hydrochloric acid showed that, as compared to a blank, 1.26 m.e. of the alkali had been consumed. This corresponds to 2.00 equivalents of ester per neutral equivalent of ustilagic acid. The neutral solution was evaporated to dryness and the salts were dissolved in water to yield 5 ml. of solution. The analysis of this solution by the above described chromatographic technique showed it to contain 0.03 m.e. of *n*-caproic acid, 0.17 m.e. of L-β-hydroxy-*n*-caprylic acid, 0.46 m.e. of L-β-hydroxy-*n*-caproic acid, and 0.76 m.e. of acetic acid as their sodium salts. The reason for the slightly high acetic acid content is not known. The above described precipitate was readily soluble in water. On the addition of 5 ml. of *N* hydrochloric acid, glucoustilic acid precipitated and this precipitate was collected on a weighed sintered glass funnel, washed several times with water, and dried *in vacuo* at 65°C. for eight hours. The weight was 0.383 gm. or 99.2% of that expected on the basis that one equivalent of ustilagic acid yields 612 gm. of glucoustilic acid.

The Fractionation of Ustilagic Acid

Ustilagic acid, 5.00 gm., was dissolved in 50 ml. of warm dry methanol. The solution was filtered free of a slight turbidity and left at −14°C. for three hours. The granular precipitate, Fraction 1, which formed was gathered on a Büchner funnel where it was pressed as dry as possible. The filtrate was diluted with 50 ml. of diethyl ether, 25 ml. of benzene, and 50 ml. of Skellysolve C. On

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cooling overnight at 4°C., a granular precipitate, Fraction 2, formed. This material was isolated as above and the filtrate was diluted with 100 ml. of Skellysolve C and left overnight at −15°C. The precipitate which formed was collected to yield Fraction 3. The filtrate was evaporated to dryness *in vacuo* and the semisolid residue was washed three times by trituration with 25 ml. volumes of ether. The powdery white material which remained formed Fraction 4. The ether solution was evaporated to dryness to yield Fraction 5—an amber-colored oil contaminated with some insoluble solid phase. The fractions were dried in air, then *in vacuo* at 65°C. for three hours. The compositions of these materials are shown in Table II. The neutralization and saponification equivalents and the glucose contents were determined as previously described (5).

Acknowledgments

The valuable suggestions pertaining to partition chromatographic technique provided by Dr. A. C. Neish are gratefully acknowledged.

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THE NITROLYSIS OF HEXAMETHYLENETETRAMINE

VII. INTERMEDIATES IN THE NITROLYSIS[1]

By L. Berman, R. H. Meen, and George F. Wright

Abstract

The evidence presented by Vroom and Winkler that 3,5-dinitro-3,5-diazapiperidinium nitrate is an intermediate compound in the conversion of hexamine dinitrate to Cyclonite has been vitiated by the demonstration that it cannot survive the reaction conditions in which it supposedly was formed. Presumably the formation of 3,5-dinitropiperadinium nitrate occurs during dilution by decomposition of 1-dimethylolaminomethyl-3,5-dinitro-1,3,5-triazacyclohexane and/or 1-methylol-3,5-dinitro-1,3,5-triazacyclohexane. Evidence favoring the latter as the stable intermediate is afforded by demonstration that dimethylolnitramide also is present. When the cold nitrolysis mixture is treated with acetic anhydride rather than water the intermediate is esterified and nitrolyzed to 1-acetoxy-7-nitroxy-2,4,6-trinitro-2,4,6-triazaheptane and 1,7-diacetoxy-2, 4, 6- trinitro-2,4,6-triazaheptane.

It is obvious that the nitrolysis of hexamine, which involves at least three particles of nitric acid and one particle of the amine, must proceed to the eventual formation of Cyclonite (V) through intermediate steps. Because of the rapidity of reaction, intermediate compounds representing such steps could not be isolated in this laboratory. However, the isolation of 1,9-diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane by ethanolysis of a small amount of the dinitroxy analogue (III, R = NO_2) produced in the normal nitrolysis of hexamine with 99% nitric acid (5) indicated that 1-dimethylolaminomethyl-3,5-dinitro-1,3,5-diazacyclohexane (I) may have been an intermediate. Furthermore the formation of 1,7-dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane (IV, R = NO_2) by nitrolysis of hexamine with nitric acid containing nitrogen pentoxide (5) indicated that 1-methylol-3, 5-dinitro-1, 3, 5-triazacyclohexane (II) was present in the reaction mixture as a derivative either of hexamine or of (I). The conversion of hexamine to Cyclonite has thus been considered as a series of tertiary amine nitrolyses following the sequence, hexamine $\rightarrow$ I $\rightarrow$ II $\rightarrow$ V.

Recently Vroom and Winkler (10) have presented a different interpretation of Cyclonite formation on the basis of the isolation of 3,5-dinitro-3,5-diazapiperidinium nitrate (VI). They consider VI to be an intermediate compound of appreciable life in the reaction mixture and they interpret the formation of Cyclonite as a combined nitrolysis and nitration following the sequence, hexamine $\rightarrow$ I $\rightarrow$ VI $\rightarrow$ V.

Neither the amount of nitric acid used for preparation of VI nor the yield using 97% nitric acid was reported by Vroom and Winkler. A ratio of 47-49 moles of nitric acid per mole of hexamine was chosen as intermediate in the ratios used in their kinetic work. Under these conditions it was found that a

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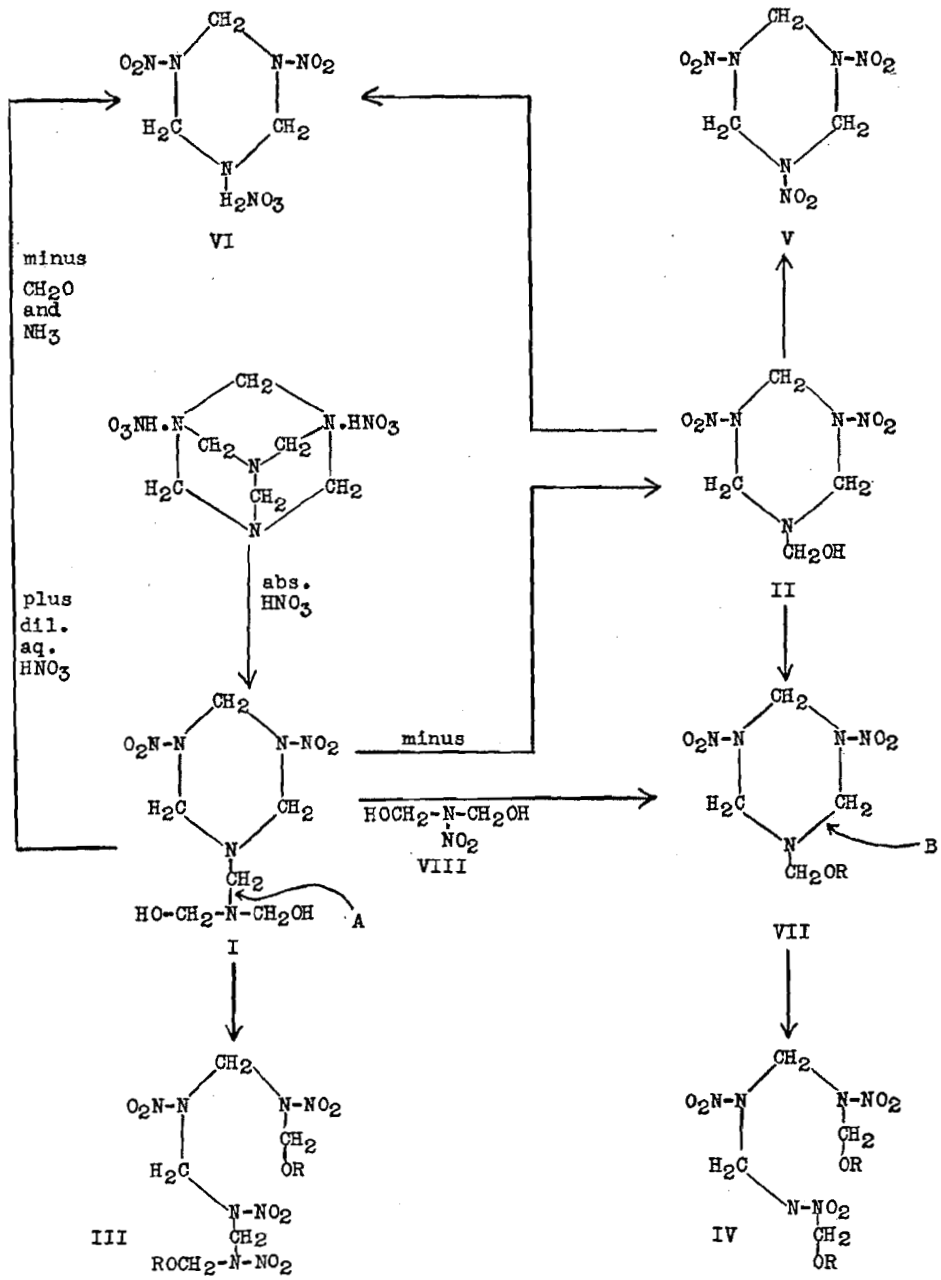

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yield of 0.5-2.5% of Cyclonite (V) always was formed, although it was not isolable unless the drowned reaction mixture was boiled. The yields of V in Table I are based on unboiled reaction liquors and are comparable with those of Vroom and Winkler if they corrected only for the slight solubility of V in water. Presumably they did not boil their reaction liquors since otherwise they would have reported slight yields of V in all preparations.

TABLE I

NITROLYSIS OF 0.01 MOLE HEXAMINE DINITRATE IN 0.47 MOLE OF NITRIC ACID

Reaction time, sec.	Concentration aqueous nitric acid	Temperature, °C.		Yield	
		Initial	Final	VI %	V %
45	99	−38	−20		10
45	99	−35	−18		13
45	98	−50	−50		0
45	100	−40	−35		23
130	97	−40	−20	57	7
60	99	−40	−25		31
60	99	−40	−10		62
130	97	−40	−30	57	0
120	97	−40	−31	62	0
60	98	−40	−22		43*
60	88	−50	0	53	Trace
45	97	−40	−35	40	None
45	97	−40	−30	36	None
45	97	−40	−30	48	None
60	97	−45	−40	51	None
60	97	−45	−40	54	None
60	97	−42	−32	33	None*
60	97	−40	−35	52	None

** Prior to dilution 50 ml. of absolute ether was added and then decanted from the precipitate.*

The conditions of temperature, concentration, and excess of acid must be controlled carefully. Thus with 47 equivalents of 97% nitric acid a temperature rise 5-10 degrees higher than those specified in Table I will produce 5-8% of Cyclonite isolable from the unboiled liquors. Likewise reaction with 92 moles of 97% nitric at −40° to −30°C. causes formation of 4-7% of Cyclonite. The effect of these factors is exemplified by the experiments shown in Table I wherein nitric acid at concentrations of 98-100 were used and the reaction, once started, could not be held within the specified temperature limits.

The recommended preparative method of Vroom and Winkler using 88% nitric acid was repeated and found to yield 10% more of VI than they reported. The remainder of the experiments reported in Table I were carried out in 97% nitric acid. Yields of 33-62% of the theoretical quantity of VI were obtained free from contaminant Cyclonite (V) when the reaction period was varied from 45 to 130 sec.

It was noted that when the 97% acid reaction mixture was diluted with ice the solution was at first clear, but it became increasingly turbid over a period

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of about one minute. It seemed possible from this behavior that the formation of 3,5-dinitro-3,5-diazapiperidinium nitrate (VI) occurred in the aqueous diluate rather than in the original reaction mixture. Under these circumstances the intermediate indicated by the difference found by Vroom and Winkler between hexamine consumption and Cyclonite producibility should be either I or II. Demethylolation of such substances in cold dilute acid might then produce VI.

A test of this hypothesis that VI was not present as an intermediate of appreciable life in the nitrolytic medium but, instead, was formed after aqueous dilution might be afforded by determining the stability of VI in 97% nitric acid. While direct comparison with nitrolysis of hexamine was complicated by the low solubility of VI in the cold strong acid, it was evident by the 5° rise in temperature that a reaction had occurred. The results obtained after subsequent dilution and destruction of recovered VI in hot 70% nitric acid are shown in Table II. In every case the formation of Cyclonite demonstrated that 3,5-dinitro-3,5-diazapiperidinium nitrate was not stable under the controlled nitrolytic conditions presumably employed by Vroom and Winkler.

Despite the fact that the stability of VI in 97% nitric acid was not altered by inclusion of 5% hexamine dinitrate (Expt. 1, Table II) it might be argued by some that VI could survive the actual reaction system comprising degradation fragments dissolved in the acid. We partially simulated such conditions by treating hexamine dinitrate with 97% nitric acid under the controlled conditions previously outlined, and subsequently added 3,5-dinitro-3,5-diazapiperidinium nitrate using the same controlled conditions over the same length of time. The results, shown in Table III, confirm that VI is unstable under the controlled reaction conditions, although (as might be expected) less Cyclonite is formed than in the absence of hexamine dinitrate.

It is thus evident that 3,5-dinitro-3,5-diazapiperidinium nitrate (VI) is not yet formed during the 45-60 sec. reaction period with hexamine dinitrate

TABLE II

NITRATION OF 3, 5-DINITRO-3, 5-DIAZAPIPERIDINIUM NITRATE WITH 0.235 MOLE 97% NITRIC ACID

Moles amine nitrate	Reaction time, sec.	Temperature, °C.		Yield	
		Initial	Final	VI %	V %
.005*	60	−40	−28	42	16
.004	60	−55	−45	68	2
004	60	−40	−45	75	1
.004	60	−45	−40	72	2
.003	60	−40	−32	50	13
.003	60	−38	−35	48	9
.004	120	−40	−38	62	9
.004	45	−43	−38	50	2

* *Contained 5% of hexamine dinitrate.*

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in 97% nitric acid at −40°. since otherwise the isolated product would have contained Cyclonite. The formation of (VI) during dilution attests the extreme instability of the methylolamines (I) and (II) in aqueous acid, and renders doubtful that either will ever be isolated from this medium.

However isolation of derivatives of (I) or (II) wherein hydroxyl groups were blocked should be possible, and this was attempted in two ways with acetic anhydride. In the first instance the nitrolysis system was chilled below −55°C. and acetic anhydride was added slowly so that the temperature did not exceed −25°. As might have been expected this produced Cyclonite since the water content of the nitric acid was reduced below 2%.* In addition to this 50% yield a 25% yield of 1-acetoxy-7-nitroxy-2,4,6-trinitro-2,4,6-triazaheptane (IV, R = CH_3CO, R′ = NO_2) was obtained. A variation of this procedure involved addition of the nitrolyzed system into the cold acetic anhydride. The Cyclonite yield was about the same but the second product was not the mixed ester, but instead, 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (IV, R, R′ = CH_3CO) in 15% yield together with a persistent impurity which could not be isolated as a chemical individual.

TABLE III

NITRATION OF 3, 5-DINITRO-3, 5-DIAZAPIPERIDINIUM NITRATE WITH HEXAMINE DINITRATE TREATED IN 0.47 MOLE 97% NITRIC ACID AT −40° TO −30° OVER ONE MINUTE

Moles HADN	Moles VI	Time, VI → V sec.	Temperature, °C.		Yield, moles	
			Initial	Final	VI	V
0.01	0.01	60	−38	−30	0.0146	0.0002
0.01	0.01	60	−42	−31		0.0002
0.01	0.01	120	−55	−30	0.0142	0.0004
0.01	0.0025	60	−40	−28	0.0084	0.0001
0.005	0.005	60	−40	−29	0.0061	0.0008*
0.005	0.01	60	−38	−30	0.0105	0.0011*

** Under these conditions the hexamine dinitrate alone would account for 0.0004 moles of Cyclonite.*

Neither of these products (containing four carbon atoms) could have been derived from VI (which contains three carbon atoms) unless resynthesis of hexamine fragments occurred (11, 1). The high purity of the Cyclonite which was obtained in the same reaction indicates that resynthesis did not occur. An intermediate must therefore be sought which contains four or more carbon atoms.

Evidence contributing toward specification of this intermediate has recently been presented by Dunning and Dunning (7). They nitrolyzed hexamine dini-

** The sharp transition in nitrolytic effect when the concentration of water is less than 2% has been attributed by some to the consequent stabilization of nitronium or nitracidium salts. While such stabilization has amply been demonstrated it does not necessarily follow that either of these salts per se is directly involved in nitrolysis. Instead in proper environment, an amine nitrate may become an amine–nitronium salt analogous with, but alternate to, the water–nitronium type known as nitracidium salt. Indeed, presence of the latter may be detrimental to formation of the former.*

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trate in 97% nitric acid over nearly six minutes, drowned it in diethyl ether, and obtained a gum which yielded 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane in 17% yield when it was treated with ethanol. This is presumptive for a larger amount of the 1-nitroxy analogue in the gum. Although they isolated no 3,5-dinitro-3,5-diazapiperidinium nitrate (VI) they seemed not to be certain of its absence. This uncertainty probably was due to their isolation of 3-nitramino-2-nitro-2-azapropylammonium nitrate which might have been formed from VI by degradation. Certainly they demonstrated that a cyclic compound comprising more than three carbon atoms survived in the nitrolysis system at $-28.5°$ for more than five minutes.

Both of the linear compounds (IV) which we obtained by treatment of the nitrolysis system at $-40°$ with acetic anhydride were undoubtedly derived either from 1-hydroxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (II) or 1-dimethylolaminomethyl-3,5-dinitro-1,3,5-triazacyclohexane (I). This is evident in the fact that the type of ester linkage obtained was dependent on the mode of addition of acetic anhydride. Since reaction in a side chain is more facile than in the ring (otherwise Cyclonite would not be the principal product under normal conditions of reaction) the first step in the formation of IV will be either esterification of II, or nitrolysis of I at linkage "A". In either case the product will be VII, wherein OR will be nitroxy or acetoxy depending on the relative concentrations of nitrogen pentoxide and acetic anhydride.* The second step, evidently slower than the first, involves nitrolysis of the ring at linkage "B". In consequence OR′ will preponderantly be acetoxy because of the excess of acetic anhydride when this slower reaction occurs. No other explanation can account for the isolation of IV ($R = NO_2$, $R' = CH_3CO$) largely uncontaminated with the two alternative symmetrical esters.

The evidence thus far presented by Dunning, Dunning, and ourselves cannot differentiate between I and II as the stable reaction intermediate from which dinitrodiazapiperidinium nitrate (VI) was derived by hydrolysis with water. A choice ought to be possible, however, if dimethylolnitramide (VIII) could be found in the hydrolyzate. If the intermediate were II then VIII ought to be found as well, whereas only formaldehyde and ammonia would be obtained if 1-dimethylolaminomethyl-3,5-dinitro-1,3,5-triazacyclohexane were the progenitor in the hydrolyzate which produced dinitropiperidinium nitrate (VI). A simple method for detection of VIII involves neutralization of the hydrolyzate with ammonia in presence of formalin, whereby 1, 5-endomethylene-3, 7-dinitro-1,3,5,7-tetracycloöctane (IX) is precipitated if dimethylolnitramide (VIII) is present (4).

* *It is assumed that the equilibrium* $Ac_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2HOAc$ *prevails in the nitric acid–acetic anhydride system and that acetyl nitrate is practically absent. The presence of nitrogen pentoxide has been suggested by Jones and Thorn (8) and the absence of acetyl nitrate by the demonstration (9) that this substance will not cause nitrolysis of hexamine. It was surprising to observe that Dunning and Dunning (7) continually mention acetyl nitrate as a nitrolytic agent. If these authors actually used the nitric acid–acetic anhydride mixture then a correction ought to be issued by them in consideration of the danger in manipulation of true acetyl nitrate.*

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Unfortunately, in the interest of exact correlation, the presence of VIII cannot be demonstrated in a reaction mixture containing more than 20 moles of nitric acid per mole of hexamine (4). For this reason the conditions which Vroom and Winkler probably used could not be simulated for this test. However when we used 20 moles of 97% nitric acid per mole of hexamine at −40° to −20° we were able to isolate IX in quantity representing 8% of the dimethylolnitramide which would have been formed by nitrolysis of 1-dimethylolaminomethyl-3,5-dinitro-1,3,5-triazacyclohexane (I) to give 1-methylol-3, 5-dinitro-1,3,5-triazacyclohexane, II. The other product of the reaction was dinitrodiazapiperidinium nitrate contaminated with hexamine dinitrate but not with Cyclonite. It is therefore evident that at least some of II has an appreciable lifetime under these reaction conditions. The low yield does not, of course, preclude the simultaneous presence of I.

In summary it should be observed that, while the isolation of 3, 5-dinitro-3, 5-diazapiperidinium nitrate does not establish it as a stable intermediate in the nitrolysis of hexamine to Cyclonite, it cannot be excluded as an individual in the reaction sequence which is involved in the complete nitrolysis. Its ease of nitration, characteristic of a weak secondary amine (6) precludes the necessity for nitramine formation by nitrolysis, which has been observed with a less easily nitrated amine (2). No evidence yet at hand excludes the possibility that II may simply demethylolate to give VI which is easily nitrated to V.

Experimental*

3, 5-Dinitro-3, 5-diazapiperidinium Nitrate (VI) and Cyclonite, V

The requisite concentration of nitric acid was prepared from colorless 100% and 70% acids. A 125 ml. flask equipped with thermometer was immersed in a dry-ice bath until it began to freeze, was then transferred to a bath at −40°C., and the amine nitrate added at once. The flask was swirled for the requisite time and then chilled in the dry-ice bath while sufficient ice was added at once to bring the volume to 50 ml. The temperature rose to about −18° during this dilution. When the mixture had warmed to 0° it was filtered and the solid washed with cold 95% ethanol and ethyl ether. The vacuum-dried product melted variously from 98° to 103°C. regardless of the content of Cyclonite.

The amount of Cyclonite was determined by treating 1/10th gm. samples of product with 1.5 ml. of 70% nitric acid. After the mixture was heated to boiling it was let stand without additional heat until strenuous decomposition occurred after several minutes. After dilution with 2.5 ml. of water the Cyclonite was filtered and washed with ethanol and ether. The vacuum-dried product melted variously from 196°-202°C. Recrystallization from 70% nitric acid raised this melting point to 204°-205°.

The yields of Cyclonite obtained in this manner do not include those amounts dissolved in the reaction liquors. If such reaction liquors are boiled until gas evolution is complete and then are cooled and half neutralized with alkali,

* *All melting points have been corrected against reliable standards.*

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additional Cyclonite is precipitated which augments the original yield by 0.5-2.5%. The yields reported in Tables I, II, and III represent Cyclonite isolated from unboiled reaction liquors.

3, 7-Endomethylene-1, 5-dinitro-1, 3, 5, 7-tetrazacycloöctane (IX)

The procedure was identical with that described above except that 2.66 gm. (0.01 mole) of hexamine dinitrate was treated with 8 ml. (0.20 mole) of 97% nitric acid at −45° to −25° over two minutes and then poured into fine ice. After five minutes the diluted reaction mixture was filtered rapidly at −15°. The filtrate was received into 150 gm. of ice containing 2 ml. of formalin. This cold filtrate was rapidly but cautiously and repeatedly neutralized with about 18 ml. of concentrated ammonia to pH 5.6. After three hours at +5° the endomethylenedinitrotetrazacycloöctane was filtered off, wt. 0.83 gm. This 4% yield was identified by mixed melting point. Decomposition with hot 70% nitric acid did not yield any Cyclonite.

1-Acetoxy-7-nitroxy-2, 4, 6-trinitro-2, 4, 6-triazaheptane (IV, R = NO_2; R′ = CH_3CO)

After 20 ml. (0.47) mole) of 97% nitric acid had been chilled to −45°C. and had partially crystallized it was treated at once with 2.66 gm. (0.01 mole) of hexamine dinitrate. The mixture was stirred for one minute while the temperature rose to −35°C. and then was chilled to −55° during one minute. To this stirred mixture was added over seven minutes 48.5 ml. (0.5 mole) of acetic anhydride with cooling so that the temperature was maintained between −35° and −25°.

A precipitate (Cyclonite, V) began to form after about half the anhydride was added. When the addition was complete the suspension was warmed to −20°C. and filtered. The Cyclonite (1.25 gm. or 56% of theoretical) melted at 204.5°-205°. It was evidently free from 1,3,5,7-tetranitro-1,3,5,7-tetrazacycloöctane (3) since 70% could be recovered (m.p. 205°-206°) by destruction of unstable impurities with boiling nitric acid.

The filtrate from which the Cyclonite was removed was diluted into 200 gm. of finely ground ice, and 120 ml. of 40% aqueous potassium hydroxide was added. The vacuum-dry compound which precipitated weighed 1.60 gm. (m.p. 126°-160°C.) after washing with cold ethanol and ether. This product was extracted with 12 ml. of dry acetone at 25°C. to leave 0.6 gm. of potassium nitrate. The extract was diluted with 30 ml. of petroleum ether (b.p. 40°-60°). The precipitate (0.62 gm.) melted at 143°-143.5°. Repeated purification from acetone–petroleum ether increased this melting point to 146°-147°C. (decomp.). Calc. for $C_6H_{11}N_7O_{11}$: C, 20.2; H, 3.11; N, 27.4%. Found: C, 19.8; H, 2.96; N, 27.9%. When this compound was crystallized by three minute reflux in ethanol it was converted to 1-acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, m.p. 107°-108° (IV, R = Et, R′ = CH_3CO) (5). Calc. for $C_8H_{16}N_6O_9$: C, 28.5; N, 24.7%. Found: C, 28.2; N, 24.8%. Further proof was obtained by treatment of IV (R = NO_2, R′ = CH_3CO) with sodium ace-

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tate in acetic acid. It was thus converted to IV (R, R′ = CH_3CO) and identified by melting point, mixed melting point, and comparison of the X-ray diffraction patterns.

The principal lines of the X-ray diffraction patterns are recorded for these substances in Table IV together with that of 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (VII, R = Et) in order to show nonidentity of the latter (7) with the compound specified as IV (R = Et, R′ = CH_3CO).

TABLE IV

X-RAY DIFFRACTION; Cu, Kα RADIATION; *d*, *k*X

Substance	Intensity, I/I_0									
	1	2	3	4	5	6	7	8	9	10
IV (R = NO_2,R′ = Ac)	4.57	3.31	4.76	2.80	12.2	3.03	6.15	4.11	3.73	5.11
	2.92	3.48								
IV (R = Et, R′ = Ac)	2.37	1.89	4.14	4.52	6.13	3.26	2.69	2.97	3.92	5.20
IV (R, R′ = Ac)	8.56	2.10	4.32	3.03	3.28	2.89	3.75	13.1	3.97	5.08
	6.33	4.77	1.97	3.38	2.95	2.77	2.72	3.61	4.06	4.56
VII (R = Et)	2.56	7.31	2.46	4.03	3.13	3.04	3.79	3.62	8.06	5.77
	2.24	2.83	2.33	2.67	2.89	6.69	6.13	3.40	4.56	5.20

1, 7-Diacetoxy-2, 4, 6-trinitro-2, 4, 6-triazaheptane

The nitrolysis was identical with that of the previous experiment. The reaction mixture at −55° was then added over 45 sec. to 0.5 mole of acetic anhydride at −70°C. The temperature of the cooled mixture rose to −35° and then receded to −50° where it was maintained for five minutes. A precipitate appeared after the second minute. The suspension was warmed to −35° during three minutes and then was filtered to remove 0.75 gm. of Cyclonite, m.p. 202°-204°.

The filtrate was diluted into 200 gm. of fine ice to which 130 ml. of 40% aqueous potassium hydroxide was added. The vacuum-dry precipitate weighed 1.40 gm. after filtration and cold ethanol- and ether-washing, m.p. 152°-180° (soft at 142°). Decomposition of an aliquot with hot 70% nitric acid showed that it contained 15% of Cyclonite, augmenting the yield of this substance to 44% of theoretical.

The crude product was extracted with hot chloroform and this evaporated extract crystallized from carbon tetrachloride and then from 1 : 4 water–ethanol to yield 0.52 gm. (15% of theoretical) of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, m.p. 157°. A mixed melting point with an authentic sample was not depressed, and the X-ray powder patterns for the two samples were identical.

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MOLTEN SALTS

ELECTRICAL CONDUCTIVITY IN THE SYSTEM SILVER CHLORIDE – SILVER NITRATE [1]

By R. C. Spooner[2] and F. E. W. Wetmore

Abstract

Conductivity and density data have been obtained for the system silver chloride – silver nitrate. The Arrhenius activation energy for electrical migration in molten silver chloride is constant at 1280 cal. mole^{-1} from 460 to 530°C.; for silver nitrate there is a variation from 3300 cal. mole^{-1} at 220° to 2700 at 320°C., which indicates a diminution of structural forces in molten silver nitrate with increase in temperature. The activation energy for binary melts of the two salts at 320°C. is constant at 2700 cal. mole^{-1} from 0 to 20 mole % silver chloride; Frenkel's simple equation for the dependence of the activation energy on composition is not supported by this work.

Considerable progress has been achieved in the theoretical treatment of the behavior of dilute solutions of electrolytes in both aqueous and non-aqueous media through study of processes of transport, namely diffusion (transport of matter), viscosity (transport of momentum), electrical conductivity (transport of charge), and electrical migration (transport of matter and charge simultaneously). In the assessment of the behavior of molten salt systems it seems probable that similar studies can yield information of value. Moreover, molten salts are in general very concentrated electrolytes; study of these may even help in developing more adequate theories for concentrated aqueous solutions than exist at present.

The determination of diffusion coefficients in salt melts would appear to be quite difficult. The viscosity and electrical conductivity can be determined with precision, but most of the considerable body of data reported lacks the accuracy required for exact interpretation. Transference by electrical migration in molten salts is not wholly analogous to that in aqueous solutions; this matter will be discussed in a later report.

Materials and Procedure

All water used was of conductivity quality. Silver nitrate of reagent grade was recrystallized from water three times, with a final yield of 60%. The crystals were dried first by gentle heating and then by fusion. Silver chloride was prepared by diluting a saturated solution of silver nitrate 30:1 with water and then adding dilute hydrochloric acid in 5% excess. The precipitate was washed 15 times with water and dried, first by suction and then by slow heating well below the melting point. These operations were carried out in semi-darkness to yield a pure-white product. The binary salt melts were made up by heating together weighed amounts of the dry salts. It was found important

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in transferring salt melt from one container to another to avoid crystallization during the transfer, since compositional segregation occurs in the formation of new phases.

Temperatures were maintained in the cell by placing it in a deep hole in a 40-lb. cylindrical copper slug, heated electrically. The amount of thermal insulation outside the heater was such that the slug could be cooled at a rate of about 20° per hour with the heating current off. Temperatures were measured with Chromel–Alumel junctions sheathed in thin Pyrex or silica tubes. The couples were standardized in duplicate (±0.2°) at the melting point of tin (231.8°C.) and that of lead (419.4°C.); for work at higher temperatures some couples were standardized at the melting point of antimony (630.5°C.). Interpolations between the fixed points were made with the aid of the Smithsonian Tables.

The conductivity bridge was essentially similar to that described by Jones and Josephs (7). It was constructed of General Radio components, certified to be exact within 0.1%, and found by calibration to be within 0.05% or better. Lead corrections were made on all measured values. The voltage input to the bridge was kept as low as possible, 0.05 to 0.3 v. A conventional two-stage electronic amplifier was used to raise the output signal from the bridge to audible level. Most of the determinations were made with alternating current of frequency 2200 cycles sec.$^{-1}$, from an electronic oscillator. To ensure the absence of polarization effects, resistances were determined at 400, 800, 1600, and 8200 cycles sec.$^{-1}$ as well; no variation was found.

Several types of conductivity cells in Pyrex and silica were prepared and tested. They were all comprised of vertical capillary tubes joined to tubes of

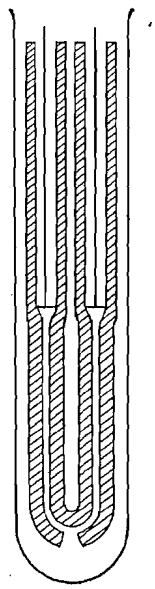

FIG. 1. *Form of the conductivity cell.*

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wider bore to carry the electrodes. The most convenient type was that shown in Fig. 1. It is a "dip" type, which admits of easy filling, draining, and cleaning. Undesirable conductivity can occur horizontally across such cells if the temperature is sufficiently high to increase the conductivity of the cell walls to a significant value. Thickening of the cell walls is of some help, but it is clear that such cells are not suitable for high temperatures. Tests were made to ensure that false conductivity was not present under the conditions used here. The cell was immersed in the salt melt contained in a test tube set in the copper slug; the conductivity was found to be independent of the exact level of the melt in the test tube. The electrodes consisted of circular platinized platinum disks butt-welded to platinum leads; the disks fitted the bore of the larger part of the cell and rested on a narrow shelf formed at the junction of the capillary tube with larger tube. Mica disks on the platinum leads kept the latter centered in the tubes. The electrodes were not fixed in place, for removing and replacing them did not alter the conductivity by more than 1:3000.

Temperature gradients in the melts were determined. There was no horizontal gradient detectable; a total vertical variation of 0.8° over the height of the cell was observed and allowance made for this in placing the thermocouple, so that an average temperature was obtained. The error introduced into the conductivity number by the existence of this gradient is estimated to be not greater than 1:2000.

The shape factors of the conductivity cells (about 500 $cm.^{-1}$) were determined with demal potassium chloride at 25° and calculated through the data of Jones and Prendergast (8), with reproducibility better than 0.05%. Corrections were made for the thermal expansion of the cells at higher temperatures. Determinations made at the beginning of and late in the series of runs with melts showed no variations of the shape factors.

Density determinations were made by the buoyancy method, with bobs of silver and of silver encased in Pyrex. The bob was suspended by a fine platinum wire from a hook on the pan of an analytical balance. The level of the liquid was adjusted so that the same length of suspending wire was immersed in each run. Calibrations were made with deaerated conductivity water; *in vacuo* and thermal volume corrections were made. In some cases a small cylindrical heater was placed about the suspending wire to prevent solidification of the melt on the wire. This was of value for determinations made near the liquidus temperature of the system.

In all conductivity and density determinations on a particular sample the temperature was increased and decreased at least twice over the range studied to show whether the observed quantities were single-valued in the temperature. Melts high in silver nitrate proportion showed inconsistencies after excursions above about 350°C., probably due to slight decomposition. The range of temperature was restricted accordingly.

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Experimental Results

The specific conductivity and density of silver nitrate melts are shown in Table I; interpolations were made on large-scale plots. Fig. 2 shows the consistency of the conductivity data. Table II gives the interpolated data for silver chloride melts, Table III for binary melts of the two silver salts. It is striking that the variation with composition is so small over the range from 0 to 18 mole % silver chloride. Table IV gives the density data for the binary melts in a range of temperature of interest for comparisons.

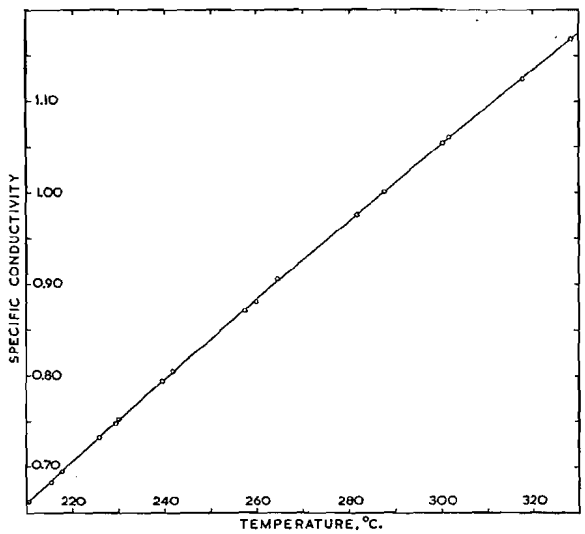

FIG. 2. *Specific conductivity of molten silver nitrate.*

TABLE I

PROPERTIES OF MOLTEN SILVER NITRATE

t, temp. °C.	k, sp. cond.	Λ, equiv. cond.	ΔU, act. energy
210	(0.660)	28.34	
220	0.706	30.39	3250
230	0.751	32.41	3150
240	0.796	34.44	3070
250	0.840	36.44	2950
260	0.883	38.40	2890
270	0.926	40.37	2840
280	0.968	42.31	2800
290	1.010	44.26	2760
300	1.051	46.18	2710
310	1.092	48.10	2710
320	1.133	50.04	2690
330	1.173	51.94	

Note: Density, gm./cc. $= 4.16_1 - 1.00 \times 10^3 t$.

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TABLE II

PROPERTIES OF MOLTEN SILVER CHLORIDE

t, temp. °C.	d, density, gm./cc.	k, sp. cond., mho/cm.	Λ equiv. cond., mho cm.²/eq.
460	4.867	3.836	113.02
470	4.858	3.874	114.35
480	4.850	3.912	115.67
490	4.841	3.949	116.98
500	4.833	3.985	118.24
510	4.824	4.021	119.53
520	4.816	4.057	120.80
530	4.808	4.091	122.02

$$\log \Lambda = 2.4339 - 1278/(4.576\ T).$$

TABLE III

SPECIFIC CONDUCTIVITY OF SILVER CHLORIDE – SILVER NITRATE MELTS

°C.	Mole % silver chloride						
	0.00	10.49	14.48	17.87	22.87	33.70	44.15
210	(0.660)		0.663	0.664			
220	0.706	0.705	0.710	0.712			
230	0.751	0.752	0.755	0.758	0.775		
240	0.796	0.797	0.800	0.803	0.821		
250	0.840	0.841	0.844	0.847	0.865	0.916	
260	0.883	0.884	0.888	0.890	0.908	0.961	
270	0.926	0.926	0.931	0.932	0.950	1.005	1.092
280	0.968	0.968	0.973	0.974	0.992	1.049	1.136
290	1.010	1.009	1.015	1.015	1.035	1.093	1.180
300	1.051	1.050	1.056	1.056	1.077	1.137	1.224
310	1.092	1.091	1.097	1.097	1.119	1.181	1.268
320	1.132	1.132	1.138	1.138	1.161	1.223	1.312
330	1.173	1.173			1.203	1.266	1.356
340					1.244	1.308	
350						1.349	

TABLE IV

SOME PROPERTIES OF SILVER CHLORIDE – SILVER NITRATE MELTS

Mole % silver chloride	Density, d (gm./cc.)			Equiv. cond., Λ			Energy of activ., ΔU
	310°	320°	330°	310°	320°	330°	320°
0.00	0.3857	0.3847	0.3837	48.10	50.04	51.94	2690
10.49	0.3932	0.3922	0.3912	46.37	48.23	50.11	2710
14.48	0.3969	0.3959	0.3949	45.90	47.73	49.58	2690
17.87	0.3987	0.3977	0.3967	45.43	47.25	49.08	2700
22.87	0.4028	0.4018	0.4008	45.50	47.33	49.16	2700
33.70	0.4121	0.4111	0.4101	46.12	47.87	49.68	2600
44.15	0.4218	0.4209	0.4200	47.55	49.31	51.07	2490

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The conductivity data for silver nitrate are in agreement with those of Goodwin and Mailey (5), except at the lower temperatures. The density data agree very well with those of Goodwin and Mailey, and both sets are at variance with those reported by Jaeger (6). Data reported for silver chloride melts have been inconsistent (1, 9, 11).

Discussion

Frenkel (4) has suggested that in a unary melt the smaller ion (usually the cation) bears the electrical charge through the melt, while the larger ion accounts for the viscosity, and he has extended these ideas to binary melts with a common ion. Pauling (12) gives the radius of silver ion as 1.26 Å, that of chloride ion as 1.81 Å, and the N–O distance in nitrate ion as 1.21 Å. These data and Frenkel's assumption lead to the belief that silver ion is the carrier of charge in silver nitrate and silver chloride, and in binary melts of the two.

From the simple electrodynamic theory for the transfer of charge through a unary melt the specific conductivity, k, of the melt is given by the relation $k = 96500\ (u + v)\ c$, in which u and v are the mobilities of the cation and anion, respectively, in cm.^{2} sec.$^{-1}$ v.$^{-1}$, and c is the concentration of the melt in equivalents cm.$^{-3}$ By Frenkel's assumption this expression would be reduced to $k = 96500\ u\ c$ for silver nitrate and silver chloride. In order to dispose of the concentration term, the equivalent conductivity, Λ, can be used and the relation expressed:

$$\Lambda = k/c = 96500\ u. \tag{1}$$

Values of the equivalent conductivity for the pure silver salts and their binary melts are given in Tables I, II, and IV.

From Eq. 1 variations in Λ should be attributed to proportional variations in u. In Frenkel's theory it is assumed that u can be expressed as a function of the temperature in terms of the Arrhenius equation (*v.* Ref. 3)

$$u = A.\ \exp(-\Delta U/RT) \tag{2}$$

in which A is constant and ΔU is the activation energy for the migration process in calories mole^{-1}, $R = 1.987$ cal. mole^{-1} deg.$^{-1}$, and T is the Kelvin temperature. It is assumed that ΔU will depend on the nature of the ions present. For the binary melt with the common ion smallest it is assumed that the activation energy depends in a simple way on the mole fraction composition of the melt:

$$\Delta U = \Delta U_1 N_1 + \Delta U_2 N_2 = \text{constant} + \text{constant}'\ N_2. \tag{3}$$

A plot of log Λ against $1/T$ for silver chloride yields a straight line having the equation given in Table II. Thus there is no variation of the energy of activation from 460 to 530°. On the other hand, the corresponding plot for silver nitrate is a bent curve, such that the activation energy decreases as the temperature of the melt is increased, as shown in Fig. 3. This evidence suggests that the structure of the solid, which lessens the mobility, persists in

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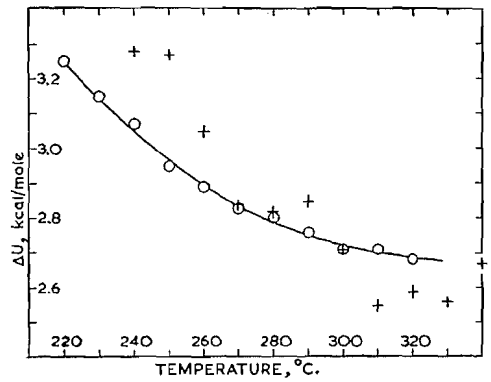

FIG. 3. *Activation energy for conductivity in silver nitrate.*
O *Present work;* + *Calculated from data of Goodwin and Mailey.*

molten silver nitrate above the melting point, but fades rapidly as the temperature is increased; the activation energy appears to be near its steady value at 320°C. Silver chloride conducts quite well in the solid condition (10, 13), whereas silver nitrate does not. A simple interpretation of the foregoing results is that the silver chloride undergoes a much smaller change in structure during the process of liquefaction than does the silver nitrate; this is in agreement with the idea that solid silver chloride has greater lattice defects than solid silver nitrate.

Values of the equivalent conductivity for various concentrations of the binary melt are given in Table IV, along with energies of activation calculated for 320°C. This temperature was chosen as high as permitted by the data in order to avoid complications due to variations of the energy of activation with the temperature. The change of the energy of activation with change in composition of the melt is shown in Fig. 4. It must be realized that a variation of 0.001 in the specific conductivity over a range of 20° will cause a variation of about 70 cal. mole^{-1} in the energy of activation calculated. Nevertheless, Fig. 4 makes it clear that Eq. 3 is not sustained by the findings for this system. Barzakovsky (2) found agreement for the system silver chloride – silver bromide; these two salts would, of course, be expected to be more similar in behavior than the chloride and nitrate.

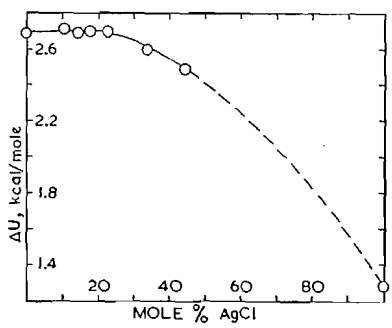

FIG. 4. *Activation energy in binary melts at 320°C. (for pure silver chloride from 460 to 530°C.)*

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Acknowledgment

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THE REACTION OF DIOXANE WITH HYDROGEN BROMIDE[1]

By A. B. Van Cleave and R. I. Blake[2]

Abstract

Dioxane reacted slowly at room temperature with anhydrous, bromine free hydrogen bromide to form 2, 2′-dibromodiethyl ether as a principal product. The 2, 2′-dibromodiethyl ether was characterized by comparison with a known sample, analysis, molecular weight determination, and by conversion to divinyl ether which was subsequently brominated to yield 1, 1′, 2, 2′-tetrabromodiethyl ether. When refluxed with constant boiling hydrobromic acid 2, 2′-dibromodiethyl ether was partially converted to ethylene dibromide. An intermediate compound in the formation of 2, 2′-dibromodiethyl ether from dioxane and hydrogen bromide was isolated by solvent extraction using petroleum ether. Its properties indicated that it was probably an oxonium salt.

Introduction

In studying the kinetics of the hydrolysis of cyanogen halides in dioxane solution (7), it was found that solutions of anhydrous hydrogen bromide in dioxane showed a steady disappearance of hydrogen bromide with time. A survey of the literature revealed that no work on the reaction of dioxane with hydrogen bromide had been reported; consequently, the present work was undertaken to establish the nature of the products formed.

Paterno and Spallino (6) reacted bromine and iodine with dioxane and obtained addition products $(C_2H_4O)_2Br_2$ and $(C_2H_4O)_2I_2$. They also studied the reaction between dioxane and hydrogen iodide in sealed tubes at 140°C., and identified iodine, acetic acid, and ethyl iodide among the products. They concluded that dioxane behaved in a manner similar to compounds containing a double bond, and that it conforms in some ways to the character of compounds containing basic oxygen.

The present investigation has shown that 1,4-dioxane reacts slowly with anhydrous hydrogen bromide at 25°C. and that the principal product isolated on fractional distillation was a high boiling point liquid with characteristics resembling those reported for 2, 2′-dibromodiethyl ether by McCusker and Kroeger (5). A sample of this ether was prepared by treating diethylene glycol dissolved in pyridine with phosphorus tribromide as described by Ali-Zade and Arbuzov (4). The product isolated from the dioxane–hydrogen bromide reaction was characterized as 2, 2′-dibromodiethyl ether by analysis, molecular weight determination, and by conversion to divinyl ether which was subsequently brominated to yield symmetrical tetrabromoethyl ether.

One might expect to obtain some ethylene dibromide when dioxane is treated with hydrogen bromide. Starting with anhydrous hydrogen bromide no evi-

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dence for the formation of ethylene dibromide was obtained. However, when a sample of 2, 2′-dibromodiethyl ether was refluxed with constant boiling hydrobromic acid it was partially converted to ethylene dibromide.

What appeared to be an intermediate compound in the formation of 2, 2′-dibromodiethyl ether from dioxane and hydrogen bromide was isolated by solvent extraction with petroleum ether. This product was a brown colored liquid freezing below −79°C. It was water soluble and possessed acidic properties. On neutralization with alkali it yielded a light colored precipitate which was not identified. The brown colored liquid was unstable and when an attempt was made to purify it by fractional crystallization it appeared to decompose into dioxane and hydrogen bromide. When some of it was refluxed for a time it was possible to isolate some 2, 2′-dibromodiethyl ether from the mixture. It was presumed that the intermediate compound was an oxonium salt similar to that known to be formed between dioxane and sulphuric acid (6). The yield of the supposed oxonium compound was found to be considerably greater when anhydrous, bromine free hydrogen bromide was bubbled into refluxing dioxane at 101°C. than was obtained on prolonged contact of hydrogen bromide with dioxane at room temperature.

Experimental

Materials

1,4-Dioxane, Eastman Kodak, practical grade, stabilized with *p*-benzylaminophenol was purified by the method of Fieser (2).

Anhydrous, bromine free hydrogen bromide was prepared by admitting liquid bromine to a reaction flask containing red phosphorus and water. The gas was passed through a solution of phenol in carbon tetrachloride, a cold trap at −55°C., a tube filled with glass beads coated with red phosphorus, and finally through drying tubes containing calcium chloride and calcium bromide.

Solutions of hydrogen bromide in dioxane were prepared by bubbling the hydrogen bromide into 400 ml. of dioxane through a sintered glass disk until the mixture was approximately 1 *N*.

The Rate of Disappearance of Hydrogen Bromide in Dioxane Solution

The progress of the reaction between dioxane and hydrogen bromide at 25°C. was followed for one month by daily removal of 1.0 ml. samples which were diluted with 10 ml. of water and titrated with standard potassium hydroxide using methyl red as an indicator. A solution with an initial normality of 0.821 showed a decrease in normality to 0.301 in 30 days. Packing the reaction vessel with Pyrex glass wool did not affect the reaction rate. Another solution with an initial normality of 0.875 showed a decrease to 0.209 in seven months on standing at room temperature. The rate of the reaction was not linear but was greater in the initial stages, that is, during the first few days at 25°C.

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Isolation and Identification of 2, 2′-Dibromodiethyl Ether

2, 2′-Dibromodiethyl ether was first isolated from a dioxane–hydrogen bromide mixture that had been maintained at 25°C. for one month. This mixture was fractionally distilled at atmospheric pressure into fractions boiling above and below 105°C. After repeated distillations to remove dioxane these fractions boiled above 110°C. and below 92°C., respectively. Further investigation showed the lower boiling fraction to be largely a mixture of dioxane and water.

The portion boiling above 110°C. was distilled under reduced pressure and a fraction boiling between 94° and 101°C. at 13 mm. was taken, washed with water, dried over anhydrous sodium sulphate, and redistilled to give a fraction boiling from 90°-94°C. at 9 mm. This material was fractionated in a packed column at 1 mm. pressure, the middle fraction being retained for subsequent work.

It was later found that the same material could be isolated by solvent extraction from a dioxane–hydrogen bromine mixture that had been allowed to stand for several months at room temperature. The reaction mixture was neutralized with sodium bicarbonate, then petroleum ether and water were added to form a double layer. The solvent layer was separated and distilled yielding a residue boiling above 110°C. (atm. press.). This residue was washed with water and dried over sodium sulphate. The maximum yield of 2, 2′-dibromodiethyl ether obtained in this way was 38.7% based on the amount of hydrogen bromide that was no longer titratable in the original mixture. The low yield was probably mainly due to inefficient recovery but it is possible that some other bromine containing compounds were formed and not isolated.

2, 2′-Dibromodiethyl ether was first characterized as a reaction product by analysis. Carbon and hydrogen were determined by standard micro procedure* and bromine by a modified micro Carius method. Considerable difficulty was experienced with the latter as the sealed tubes invariably exploded unless the amount of nitric acid used was reduced to somewhat less than 0.30 ml. for 10 mgm. samples. The results of the analyses are shown in Table I.

TABLE I

ANALYSES OF REACTION PRODUCT

	% Carbon	% Hydrogen	% Bromine
Sample 1	22.37	4.01	69.55
Sample 2	22.26	4.00	65.65
Sample 3	.....	.....	66.25
Mean	22.31	4.00	67.15
Theoretical for 2, 2′-dibromodiethyl ether	20.72	3.48	68.93

* *The authors are indebted to Dr. R. U. Lemieux and Miss Carol Brice of the Prairie Regional Laboratory of the National Research Council for carbon–hydrogen analyses.*

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The molecular weights of the reaction product and of 2, 2′-dibromodiethyl ether prepared by the method of Ali-Zade and Arbuzov (1) were determined by the Beckman cryoscopic method using benzene as the solvent. The cyroscopic constant for benzene was determined using twice recrystallized naphthalene at several concentrations and extrapolating to infinite dilution. A similar procedure was employed in obtaining corrected freezing point depressions for the unknowns. The known sample of 2, 2′-dibromodiethyl ether was found to have a molecular weight of 231.5 (theoretical 232) whereas the product isolated from the dioxane–hydrogen bromide reaction had a molecular weight of 225. This result was taken to indicate that there was still a small percentage of lower molecular weight material contaminating the product; probably some β-bromoethyl ether of ethylene glycol ($BrCH_2$-CH_2-O-CH_2-CH_2-OH, mol. wt. 169) the boiling point of which is very close to that of 2, 2′-dibromodiethyl ether.

Derivatives of 2, 2′-Dibromodiethyl Ether

Divinyl ether was prepared from the reaction product by the method used by Hibbert *et al.* (4) for dichlorodiethyl ether. Thirty-five grams of 2, 2′-dibromodiethyl ether, isolated from the reaction, were slowly dropped into molten potassium hydroxide in a copper pot over the course of two hours. The copper pot was provided with a reflux condenser at 40°C. to permit the escape of divinyl ether but not of intermediate or unreacted products. A second condenser connected to the first was maintained at 6°C. The refluxing was continued for three hours yielding 2.6 gm. (24%) of a product boiling at 34.5° to 35.5°C. The reported boiling point for divinyl ether is 34°-35°C. (4).

The same experiment was repeated using alcoholic potassium hydroxide but no divinyl ether was obtained.

One gram of divinyl ether prepared as indicated above was dissolved in chloroform and a bromine–chloroform solution was slowly added, the reaction flask being immersed in ice. On evaporation of the solvent a crystalline product was obtained. After recrystallization from ether this product melted at 63°C. and analysis showed it to contain 12.36% carbon and 1.64% hydrogen. The reported melting point for 1, 1′, 2, 2′-tetrabromodiethyl ether is 63°-64°C. (4) and the theoretical carbon is 12.33% and hydrogen 1.55%.

From the above evidence it was concluded that the product which had been isolated from the dioxane–hydrogen bromide mixture was fairly pure 2, 2′-dibromodiethyl ether.

Cleavage of 2, 2′-Dibromodiethyl Ether

2, 2′-Dibromodiethyl ether (4.58 gm.) isolated from the dioxane–hydrogen bromide reaction was refluxed with constant boiling hydrobromic acid (50 ml.) for several hours. The excess acid was neutralized with sodium bicarbonate and the mixture extracted with ether. The ether layer was washed with water, dilute sulphuric acid, 10% sodium bicarbonate solution, and then with water again. The extract was dried over sodium sulphate and on fractional distil-

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lation yielded 4.1 gm. of a product b.p. 130°-131°C., m.p. 10.0°C. The reported values for ethylene dibromide are b.p. 131.6°C., m.p. 9.97°C. (3). The product was therefore identified as ethylene dibromide.

Evidence for the Formation of an Oxonium Compound

Anhydrous, bromine free hydrogen bromide was bubbled into 200 ml. of refluxing dioxane at 101°C. The solution changed from colorless to dark brown and its normality was observed to be 0.214 on titration against standard alkali. Petroleum ether was added to the mixture to bring about separation into two layers. The lower dark brown colored layer (13.6 ml.) was separated off for further tests. This material had an odor resembling that of hydrogen bromide, was practically all soluble in water, and had a normality of 2.39 as an acid. When a similar procedure to that outlined above was applied to 200 ml. of dioxane – hydrogen bromide solution that had been standing for several months at room temperature (normality decrease 0.875 to 0.209), only 1.6 ml. of the dark brown colored lower layer having a normality of 2.89 was obtained.

In all cases when portions of the brown colored material were neutralized with sodium hydroxide a light colored precipitate formed. Unfortunately, time did not permit the identification of this solid.

An attempt was made to purify the brown colored liquid by fractional freezing. The material which crystallized out appeared to be mainly dioxane, and eventually a fraction which would not freeze in a dry ice – acetone bath was obtained; 2.4 gm. of this partially purified material was refluxed for three hours in an atmosphere of nitrogen, then washed with water, dried over sodium sulphate, and fractionally distilled to yield about 0.7 gm. of 2, 2′-dibromodiethyl ether.

It was concluded that in all probability the brown colored liquid was an oxonium salt of dioxane and hydrogen bromide of limited stability. It may decompose to dioxane and hydrogen bromide, or it may undergo cleavage and subsequent reaction to give 2, 2′-dibromodiethyl ether. It appeared almost certain to be an intermediate compound in the formation of the latter from dioxane and hydrogen bromide.

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SOLVENT EFFECT ON IODIDE EXCHANGE[1]

By R. D. Heyding and C. A. Winkler

Abstract

The exchange of iodine between hydrogen iodide and *n*-butyl iodide has been studied in several organic solvents. In solvents of high dielectric constant (methanol, ethanol, *n*-butanol), exchange occurred by reaction of iodide ions with butyl iodide. In solvents of low dielectric constant (*n*-hexanol, *n*-dodecanol, acetic acid), it appeared that exchange also occurred between butyl iodide and the associated IHI^- triple ion. Orders of magnitude of the individual specific rate constants have been calculated, using approximate values for the dissociation constants of hydrogen iodide. The rate constant – dielectric constant relation developed by Laidler and Eyring for ion – neutral molecule reactions appears to hold for exchange in homologous solvents, but does not seem to represent the effect of nonhomologous solvents. This discrepancy and the small differences observed in activation energies for the various exchanges may be due to solvation effects.

Introduction

It has been found that thermal exchange of halogens between alkyl halides and uni-univalent inorganic halides occurs only in the presence of polar solvents (6, 7, 11, 12, 13). The variations in reaction velocity with concentration in the exchange of lithium bromide with alkyl bromides in acetone, and of sodium iodide with alkyl iodides in methanol, have been quantitatively related to the degree of dissociation of these inorganic halides (2). Recently, it has been shown that lithium, sodium, and caesium iodides, which are highly ionized in acetonitrile, have essentially the same rates and activation energies for exchange with *n*-butyl iodide in this solvent (5). There seems little doubt, therefore, that exchange reactions of this type occur between the neutral organic halide and an ion supplied by the inorganic halide.

For reactions between ions and neutral molecules, Laidler and Eyring have proposed that an increase in the dielectric constant of the solvent should decrease the reaction velocity (8). In the present study, the validity of this theoretical conclusion was investigated by comparison of the rates of exchange of iodine between hydrogen iodide and *n*-butyl iodide in several pure organic solvents.

Experimental and Results

Preparation and Dielectric Constants of the Solvents

Since hydrogen iodide is a strong reducing agent and reacts with many common organic solvents, the investigation was limited to hydrocarbons, aliphatic alcohols, and carboxylic acids. The solvents used were toluene, methanol, ethanol, *n*-butanol, *n*-hexanol, *n*-dodecanol, and glacial acetic acid. The specifications and preparation of these solvents are given below.

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Toluene: Reagent grade; dried by distillation from sodium. Boiling point 110.5°–110.8°C.

Methanol: Reagent grade, acetone free; dried with magnesium methylate. Boiling point 64.5°–64.7°C.

Ethanol: Industrial absolute; impurities reduced with zinc and potassium hydroxide; dried with magnesium ethylate. Boiling point 78.3°C.

n-Butanol: Boiling point 117.2°–117.5°C.

n-Hexanol: Boiling point 156°–157°C.

n-Dodecanol: Technical grade; distilled under vacuum discarding first 25% and last 15%. Redistilled under nitrogen, fraction boiling between 160°–162°C. at 30 mm. retained. Melting point 21°C.

Acetic acid: Reagent grade; boiling point 116.5°–116.7°C., melting point 16.2°C. No attempt was made to remove the trace of moisture.

The solvents were refluxed with nitrogen and subsequently stored and handled under this inert gas to prevent oxidation of hydrogen iodide by dissolved oxygen.

The dielectric constants at 100 kilocycles and 25°C. for ethanol, butanol, hexanol, dodecanol, and acetic acid were determined by the substitution method using a General Radio Co. T-716*c* capacitance bridge. These values, together with the dielectric constants reported in the literature for acetonitrile, methanol, and ethanol, are given in Table I.

TABLE I

DIELECTRIC CONSTANTS AT 100 KILOCYCLES AND 25°C.

Solvent	*D* (exp.)	*D* (lit.)	Ref.
Acetonitrile		36.7	(9)
Methanol		32.66	(1)
Ethanol	24.2	24.26	(9)
n-Butanol	17.3		
n-Hexanol	12.8		
n-Dodecanol	6.15		
Acetic acid	6.27		

Conductance Measurements

Conductance experiments were made on solutions of hydrogen iodide in the various solvents, using a conductivity cell designed for solutions of high resistance, and an Industrial Instruments Inc., Model RC-1, conductivity bridge. All measurements were made at 25°C. Fig. 1 shows that while the equivalent conductance in the lower alcohols decreased with increasing electrolyte concentration in the normal manner, the equivalent conductance in hexanol, dodecanol, and acetic acid passed through a minimum value. Minima in conductance curves have been explained by Fuoss and Kraus on the basis of triple ion formation (3). Hence it would appear that the HIH^+ and IHI^- ions were formed to an appreciable extent in these solvents.

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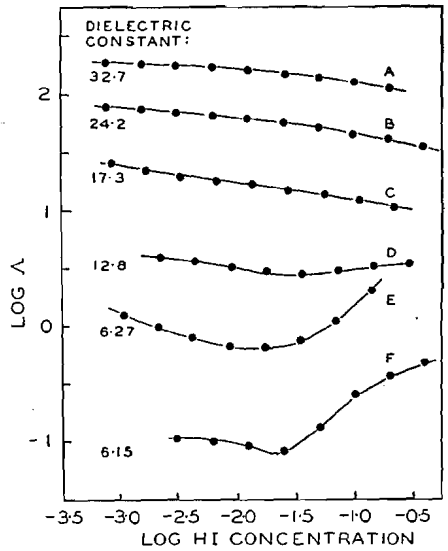

FIG. 1. *Equivalent conductance of hydrogen iodide as a function of the concentration in solvents of various dielectric constants.*

A. Methanol
B. Ethanol
C. n-Butanol
D. n-Hexanol
E. Acetic acid
F. n-Dodecanol

Exchange Experiments

Radioactive iodine, I^{131}, was obtained as carrier-free sodium iodide from the National Research Council Atomic Energy Project, Chalk River.

n-Butyl iodide was shaken with mercury to remove traces of free iodine, and freshly distilled as required to avoid the recurrence of iodine due to decomposition. A fraction boiling at 129.8°–130°C. was taken for the kinetic studies.

Hydrogen iodide was prepared by dropwise addition of water to 20 parts of iodine and one of red phosphorus (14). The gas evolved was purified by passing it through red phosphorus and two cold traps, the first at 0°C. and the second at −35°C., slightly above the boiling point of hydrogen iodide. The product was recovered in a storage trap cooled by a mixture of dry ice and acetone. The product was pure white and had a melting point of −51°C.

To prepare active hydrogen iodide, a suitable quantity of aqueous NaI^{131} was evaporated to dryness in the storage trap prior to the generation of hydrogen iodide. The hydrogen iodide subsequently collected was liquefied and exchanged with the sodium iodide. It was found that the exchange was essentially complete in one to two hours at −45°C.

Stock solutions were prepared by distillation of hydrogen iodide from the storage trap into the various solvents, discarding the first and last 15% of the product in the trap. The concentration of the stock solution was determined by titration with standard silver nitrate solution, using eosin as an indicator. Although these stock solutions were stored in the dark under nitrogen, their slow decomposition was made evident by the pink color of free iodine, formed

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by the reaction of hydrogen iodide with traces of dissolved oxygen and other oxidizing impurities in the solvents. The degree of decomposition was estimated by colorimetric comparison with solutions of iodine in the same solvent. Decomposition of 0.5% of the hydrogen iodide was tolerated.[1]

The exchange reactions were initiated by mixing solutions of active hydrogen iodide and inactive butyl iodide, each of appropriate concentration and previously brought to the temperature in the thermostat. The reactions were conducted in Erlenmeyer flasks in an atmosphere of nitrogen, with the exception of the experiments in toluene and acetic acid for which sealed tubes were employed. Light was excluded from the reaction flasks to preclude the possibility of exchange by a photochemical mechanism. Because of the appreciable loss of hydrogen iodide by oxidation in dilute solutions, the experiments were limited to hydrogen iodide concentrations greater than 0.01 *M*.

At suitable intervals, samples were withdrawn with a rapid-delivery pipette, and the reaction quenched by separation of the reactants by benzene–water extraction. The exchange was followed by determining the decrease in activity of the hydrogen iodide with time. The halide was precipitated with silver nitrate solution and the silver iodide prepared for counting by the procedure outlined by Hodgson, Evans, and Winkler (5). Specific activities were determined with end-window Geiger tubes, using an Atomic Instrument Co. scaler, Model 101A.

In addition to the zero time sample removed when the reactants were mixed, the activity of the stock hydrogen iodide solutions was determined. Wherever possible, duplicate counting slides were prepared for all samples. The precision of duplicate counting analysis was normally better than one per cent and invariably better than two per cent.

Attempts were made to follow the exchange of hydrogen iodide with sodium iodide in hexanol. To separate the reactants, hydrogen peroxide was added to the water–benzene mixture to oxidize the hydrogen iodide to iodine and permit its removal in the benzene layer. As a control to this separation, the exchange of iodine with sodium iodide in hexanol was also investigated. These exchange reactions were essentially complete in the time required to separate the reactants.

The kinetics of exchange of hydrogen iodide with butyl iodide in the various solvents were most accurately expressed by the second order rate equation (5, 13)

$$k_e = \frac{1}{(a_0 + b)t} \ln \frac{1}{1 - \sigma},$$

where k_e is the experimental rate constant in liters per mole per hour,
a_0 is the total hydrogen iodide concentration,
b is the butyl iodide concentration, and
σ is the degree of exchange.

[1]*Stock solutions were discarded when three to four days old. In this time interval, the conductance and rates of exchange were independent of the age of the solution, showing the reaction of hydrogen iodide with the solvent to be insignificant.*

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In these experiments, the degree of exchange was determined by the relation

$$\sigma = \frac{A_0 - A_t}{A_0 - A_\infty},$$

where A_0 and A_t are the specific activities at zero time and at time t respectively, and A_∞, the specific activity of the hydrogen iodide at theoretically complete exchange, was given by

$$A_\infty = \frac{a_0}{(a_0 + b)} A_0 .$$

In toluene, σ had the value of 4.0 after 163 hr. at 48.6°C., corresponding to $k_e < 4 \times 10^{-4}$ l. mole^{-1} hr.$^{-1}$. Table II summarizes the data obtained for exchange in the alcohols and in acetic acid. The value of k_e recorded for given experimental conditions is the average of the individual values calculated for different reaction times. The mean deviation of the individual values of k_e from the average was generally less than ±3%. The uncertainty in the experimental rate constant for exchange in acetic acid supercooled to 0°C. was ±10% owing to the small degree of exchange observed in this experiment.

TABLE II

EXCHANGE OF HYDROGEN IODIDE WITH *n*-BUTYL IODIDE IN VARIOUS SOLVENTS

Temp., °C.	Concentration of hydrogen iodide, moles liters^{-1}	Concentration of *n*-butyl iodide, moles liters^{-1}	k_e, l. mole^{-1}-hr.$^{-1}$
Methanol			
0.0	0.0751	0.500	0.00874
25.0	0.0563	0.625	0.162
36.2	0.0409	0.455	0.525
	0.107	0.286	0.480
48.6	0.0751	0.200	1.49
Ethanol			
0.0	0.0539	0.500	0.0215
25.0	0.0098	0.600	0.519
	0.0290	0.334	0.473
	0.0342	0.600	0.469
	0.0866	0.200	0.382
	0.103	0.600	0.413
	0.168	0.600	0.379
	0.244	0.600	0.362
	0.335	0.600	0.333
34.7	0.0268	0.100	1.43
	0.0356	0.267	1.27
48.6	0.0356	0.133	5.56
n-Butanol			
0.0	0.102	0.625	0.0260
25.0	0.102	0.625	0.561
36.2	0.0387	0.143	1.87
	0.170	0.375	1.86
48.6	0.0387	0.143	6.15

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TABLE II—*Concluded*

Temp., °C.	Concentration of hydrogen iodide, moles liters^{-1}	Concentration of *n*-butyl iodide, moles liters^{-1}	k_e l. mole^{-1}-hr.$^{-1}$
n-Hexanol			
0.0	0.0993	0.625	0.0276
25.0	0.0247	0.800	0.364
	0.0617	0.800	0.465
	0.0993	0.625	0.484
	0.123	0.800	0.486
	0.339	0.800	0.540
	0.678	0.800	0.550
36.2	0.0442	0.250	1.55
	0.118	0.556	1.65
48.6	0.0756	0.214	4.63
n-Dodecanol			
25.0	0.0119	1.00	0.174
	0.0228	1.00	0.197
	0.0603	1.00	0.248
	0.125	1.00	0.319
	0.159	0.333	0.330
	0.159	1.00	0.342
	0.251	1.00	0.349
	0.318	1.00	0.385
Acetic Acid			
0.0	0.0819	1.00	0.0043
25.0	0.0148	1.00	0.0352
	0.0520	1.00	0.0521
	0.0615	0.625	0.0611
	0.104	1.00	0.0765
	0.208	1.00	0.101
	0.312	1.00	0.0980
36.2	0.0819	1.00	0.200
48.6	0.0467	0.715	0.594
	0.117	0.286	0.726

Discussion

Since hydrogen iodide may be regarded as essentially undissociated in toluene, the exchange of molecular hydrogen iodide with molecular *n*-butyl iodide is apparently at least a thousand times slower than the rate of iodide ion exchange in the more polar solvents. Hence the contribution of the molecular mechanism to exchange in the polar solvents may be regarded as insignificant. The experimental rate constants for exchange in methanol, ethanol, and butanol were found to decrease with increasing hydrogen iodide concentration, while in hexanol, dodecanol, and acetic acid, the opposite concentration effect was observed. The reaction mechanism in the latter solvents will be considered separately.

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Exchange in Methanol, Ethanol, and n-Butanol

The exchange of hydrogen iodide with butyl iodide via the iodide ion may be represented by the equations

$$HI^* + I^- \rightleftharpoons I^{*-} + HI, \qquad (1)$$
$$BuI + I^{*-} \rightleftharpoons I^- + BuI^*. \qquad (2)$$

Since the exchange of hydrogen iodide with sodium iodide in hexanol was too rapid to be followed experimentally, it may be assumed that the inorganic exchange (Reaction 1) is comparatively rapid and essentially complete at all times. The exchange of iodide ion with the organic halide is then the rate controlling step.

If a is the concentration of hydrogen iodide, i.e. the associated ion pairs,
b the concentration of butyl iodide,
i the concentration of iodide ion,
c the initial concentration of active hydrogen iodide,
y the concentration of active iodide ion at time t, and
x the concentration of active butyl iodide at time t,
then the rate of formation of active butyl iodide is given by

$$\frac{dx}{dt} = k_1(by - ix),$$

where k_1 is the specific rate constant for this reaction. Since Reaction (1) is assumed to be complete at all times,

$$\frac{c - x}{a_0} = \frac{y}{i},$$

where a_0 is the total hydrogen iodide concentration.
Substituting for y and rearranging

$$\frac{dx}{b(c - x) - a_0x} = \frac{i}{a_0} k_1dt.$$

The experimental second order rate constant, k_e, represents the over-all reaction between hydrogen iodide and butyl iodide and is given by the differential equation

$$\frac{dx}{b(c - x) - a_0x} = k_edt.$$

It is immediately evident that the true rate constant, k_1, and the experimental rate constants are related by the expression

$$k_e = \frac{i}{a_0} k_1.$$

The factor i/a_0, the degree of dissociation of the electrolyte, may be expected to decrease with increasing hydrogen iodide concentration and result in a decrease in the observed specific rate constant. This is consistent with the experimental evidence.

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Exchange in n-Hexanol, n-Dodecanol, and Acetic Acid

The experimental rate constants for exchange in these solvents were observed to increase with increasing hydrogen iodide concentration. It is significant that the conductance experiments indicated the presence of triple ions as well as simple ions in these solvents. Accordingly, the possibility of exchange by the reaction of the triple ions with the organic halide must be considered.

Since the exchange of butyl iodide with the associated ion pair, H^+I^-, was found to be negligibly slow, it seems reasonable to suppose that exchange with the positive triple ion, HIH^+, is also insignificant. Exchange via the negative triple ion may be represented by

$$HI^* + IHI^- \rightleftharpoons IHI^{*-} + HI, \qquad (3)$$
$$BuI + IHI^{*-} \rightleftharpoons IHI^- + BuI^*. \qquad (4)$$

Again it can be assumed that the inorganic exchange (Reaction 3) is comparatively rapid. The rate of formation of active butyl iodide will be given by

$$\frac{dx}{dt} = k_3(zb - 2xj),$$

where j is the concentration of hydrogen diiodide, z is the concentration of active triple ion at time t, and k_3 is the specific rate constant for triple ion exchange. The factor 2 in this equation represents the fact that while every exchange of active butyl iodide with inactive triple ion will result in a transfer of active iodine, there is only a 50% probability that such a transfer will occur when an active triple ion exchanges with inactive butyl iodide.

Since Reaction (3) is regarded as complete at all times,

$$\frac{c - x}{a_0} = \frac{z}{2j},$$

and

$$\frac{dx}{b(c - x) - a_0x} = \frac{2j}{a_0} k_3.$$

When simple ions as well as triple ions are present, exchange will proceed by Reactions (2) and (4) simultaneously, and the experimental rate constant will be the sum of the terms in the individual rate constants for these reactions:

$$k_e = (i/a_0)k_1 + (2j/a_0)k_3.$$

For the equilibria existing between inorganic species in these solvents,

$$HI = H^+ + I^-$$
$$HIH^+ = HI + H^+$$
$$IHI^- = HI + I^-$$

let a be the concentration of undissociated HI; h and i, the simple hydrogen and iodide ions; and j and l, the IHI^- and HIH^+ triple ions. The dissociation constants for these equilibria are

$$K = hi/a, \qquad K_2 = ha/l, \qquad K_3 = ia/j.$$

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Hydrogen and iodine balances yield the equation

$$i = h + l - j,$$

in which the concentrations h, l, and j may be replaced by terms in a, i, and the equilibrium constants, and rearranged to give

$$i = \left[Ka\,\frac{(1 + a/K_2)}{(1 + a/K_3)}\right]^{\frac{1}{2}}.$$

Similarly, since $j = ai/K_3$,

$$j = \frac{a}{K_3}\left[Ka\,\frac{(1 + a/K_2)}{(1 + a/K_3)}\right]^{\frac{1}{2}}.$$

If it is assumed that the dissociation of hydrogen iodide is small, the term a may be replaced by a_0, the total hydrogen iodide concentration, and substitution for i and j in the experimental rate constant expression yields

$$k_e = \left[\left(\frac{K}{a_0}\right)^{\frac{1}{2}} k_1 + \frac{2(a_0K)^{\frac{1}{2}}}{K_3}\,k_3\right]\left[\frac{(1 + a_0/K_2)}{(1 + a_0/K_3)}\right]^{\frac{1}{2}}.$$

Finally, if it is assumed that the triple ions are formed to the same extent, i.e. if K_2 and K_3 are equal, the last term vanishes and this equation reduces to one of the form

$$k_e = A/a_0^{\frac{1}{2}} + Ba_0^{\frac{1}{2}},$$

where $A = K^{\frac{1}{2}}k_1$, and $B = 2K^{\frac{1}{2}}k_3/K_3$.

This equation implies that above some concentration, depending on the relative magnitudes of A and B, the second term on the right hand side will become greater than the first, and the experimental rate constant may be expected to increase with increasing hydrogen iodide concentration. By multiplying this expression by $a_0^{\frac{1}{2}}$,

$$a_0^{\frac{1}{2}}k_e = A + Ba_0,$$

it is evident that if this mechanism is correct, a plot of $a_0^{\frac{1}{2}}k_e$ versus a_0 should result in a straight line of slope equal to B and an intercept on the ordinate equal to A. The plots representing exchange in hexanol and dodecanol are given in Fig. 2, and for exchange in acetic acid, in Fig. 3.

Linear relations are obtained for exchange in dodecanol and acetic acid at low hydrogen concentrations, but at higher concentrations a decrease in slope is apparent. In deriving this expression, it was assumed that K_2 and K_3 are equal. If, however, contrary to this assumption, negative triple ions have a greater tendency to form than positive triple ions, the omission of the term in these dissociation constants is not valid. Accordingly, if K_2 is slightly greater than K_3, a decrease in slope at higher concentrations is to be expected.

The assumption that the concentration of associated ion pairs is equal to the total hydrogen iodide concentration will become less valid as the concentration decreases. Moreover, the larger the dissociation constant, K, the greater will be this error. Failure of the experimental points for exchange in hexanol to obey the linear relation at low concentrations may be attributed to the error introduced by this assumption.

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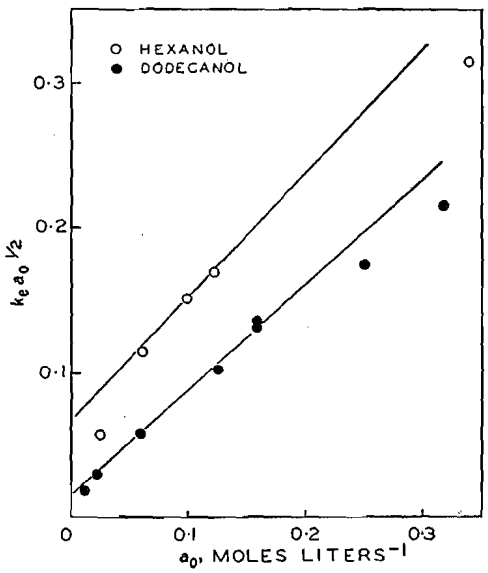

FIG. 2. *Application of triple ion mechanism to exchange in n-hexanol and n-dodecanol at 25°C.*

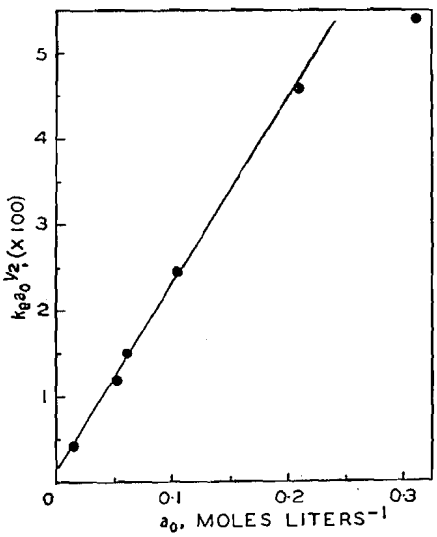

FIG. 3. *Application of triple ion mechanism to exchange in acetic acid at 25°C.*

Estimation of Individual Rate Constants

While it is not possible to separate the dissociation and rate constants for exchange in hexanol, dodecanol, and acetic acid by kinetic data alone, the true rate constant (k_1) for exchange in the lower alcohols could theoretically be obtained by extrapolation to infinite dilution. Since these experiments were limited to concentrations greater than 0.01 M, extrapolation could not be

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justified. However, the order of magnitude of the rate constants may be obtained using estimated dissociation constants.

The conductance data reported by Goldschmidt and Dahl (4) have been used in obtaining dissociation constants of 0.015, 0.022, and 0.020 for HCl, HBr, and HI in ethanol (10). Ogston recorded a value of 0.118 for the dissociation constant of HCl in methanol (15). In view of the similarity in the dissociation constants for the halogen acids in ethanol, it seems reasonable to assign a value of 0.1 to the dissociation constant of HI in methanol.

When triple ions are formed, the conditions for minimum conductance are governed by the equations (3)

$$K^{\frac{1}{2}} = \frac{\Lambda_m a_m^{\frac{1}{2}}}{2},$$

$$K_3 = \Lambda_3^0 a_m/\Lambda^0,$$

where Λ^0 and Λ_3^0 represent the limiting conductance of the simple and triple ions respectively, and Λ_m and a_m are the conductance and concentration at the minimum point. These equations have been used to estimate the dissociation constants of HI in hexanol, dodecanol, and acetic acid using the minimum values observed in the conductance experiments, and limiting conductances obtained with the aid of Walden's rule.

The best values of the ionic conductance of hydrogen and iodide ion in the Landolt–Bornstein tables yield conductance–viscosity products of 119 and 103 mho-poise per equivalent in methanol and ethanol. A constant of 100 mho-poise per equivalent was assumed for the higher alcohols and acetic acid. In estimating K_3, it was assumed that the limiting conductance of the triple ions was half that of the simple ions. The results of these calculations are given in Table III. In view of the regular decrease in K in the alcohol series, a value of 1×10^{-3} may be assigned to the dissociation constant in butanol.

Degrees of dissociation have been applied to the experimental rate constants to estimate the true rate constants (k_1) for exchange in methanol,

TABLE III

DISSOCIATION CONSTANTS OF HYDROGEN IODIDE IN VARIOUS SOLVENTS
($\Lambda_3^0/\Lambda^0 = 0.5$)

Solvent	Λ_m	$a_m^{\frac{1}{2}}$	Λ^0	K	K_3
Methanol			207	1×10^{-1}	
Ethanol			89.7	2×10^{-2}	
n-Butanol				(1×10^{-3})	
n-Hexanol	2.9	0.19	23	1×10^{-4}	2×10^{-2}
n-Dodecanol	0.080	0.14	5.3	4×10^{-6}	1×10^{-2}
Acetic acid	0.66	0.11	85	7×10^{-7}	6×10^{-3}

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ethanol, and butanol. The values of the dissociation constants together with the slopes (B) and the intercepts (A) (Figs. 2 and 3) were used to obtain orders of magnitude of the rate constants for simple and triple ion exchange in hexanol, dodecanol, and acetic acid. These values, and the specific rate constant for exchange of iodide ion with *n*-butyl iodide in acetonitrile recorded by Hodgson, Evans, and Winkler (5), are given in Table IV.

TABLE IV

SPECIFIC RATE CONSTANTS FOR THE EXCHANGE OF IODIDE ION AND HYDROGEN DIIODIDE ION WITH *n*-BUTYL IODIDE IN VARIOUS SOLVENTS AT 25°C.

Solvent	Dielectric constant	k_1, l. mole^{-1}-hr.$^{-1}$	k_3, l. mole^{-1}-hr.$^{-1}$
Acetonitrile	36.7	10.9*	
Methanol	32.7	0.23	
Ethanol	24.2	1.17	
n-Butanol	17.3	6.0	
n-Hexanol	12.8	6.7	0.85
n-Dodecanol	6.15	8.0	1.8
Acetic acid	6.27	1.7	0.8

*Reference (5).

Effect of Solvent on Rate Constant

For the reaction of an ion with a neutral molecule, Laidler and Eyring have shown that the change in specific rate constant at infinite dilution with the dielectric constant of the medium is given by the equation (8)

$$\frac{d(\ln k_0)}{d(1/D)} = \frac{(z\epsilon)^2}{2kT}\left[\frac{1}{r} - \frac{1}{r^\ddagger}\right],$$

where r and $r^\ddagger$ are the radii of the ion and the reaction complex respectively. Since $r^\ddagger$ will normally be greater than r, an increase in rate constant with decreasing dielectric constant is to be expected.

Since it has not been possible to calculate the rates of exchange at infinite dilution, a rigorous test of this relation cannot be made. Nevertheless, qualitative agreement is shown by the increase in k_1 with decreasing dielectric constant for the alcohol series (Table IV). Fig. 4 shows that a plot of the logarithm of the estimated specific rate constants in methanol, ethanol, and butanol versus the inverse of the dielectric constants results in an essentially linear relation. However, the rate constant for exchange in acetonitrile is considerably greater than would be expected in an alcohol of comparable dielectric constant. Similarly, the rate of exchange in acetic acid appears to be slower than the rate in dodecanol, although these solvents have essentially the same dielectric constant. Hence it would appear that the relation does not hold for exchange in nonhomologous solvents. The reason for this discrepancy is not clear, although it may be due, at least in part, to solvation effects.

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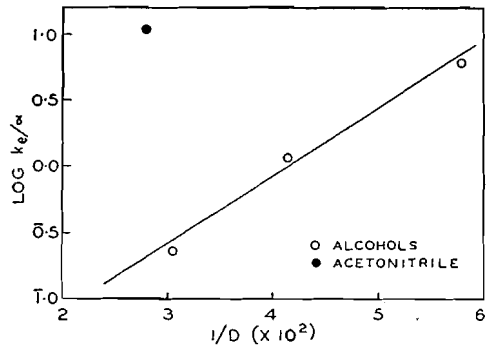

FIG. 4. *Variation in specific rate constant with dielectric constant of the solvent.*

Effect of Temperature

Table V summarizes the experimental activation energies (E_e) and the non-exponential parameters of the Arrhenius equation for these exchange reactions. Although the activation energies have been determined at finite concentrations (0.05-0.1 *M* HI), and therefore contain small energy terms associated with the dissociation constants, they may be assumed to be essentially equal to the true activation energies. Since exchange in acetic acid at concentrations greater than 0.1 *M* is almost completely due to the triple ion reaction, it would appear that the activation energies for simple and triple ion exchange are of the same order of magnitude. The small energy differences for simple ion exchange in acetonitrile, methanol, ethanol, and butanol are probably due to variation in the height of the solvation barrier.

TABLE V

ARRHENIUS PARAMETERS FOR THE EXCHANGE REACTIONS

Solvent	log A	E_e kcal. mole^{-1}
Acetonitrile		18.1*
Methanol	12.8	18.6
Ethanol	14.0	19.5
n-Butanol	14.0	19.4
n-Hexanol	13.2	18.4
Acetic acid	12.1	18.2

*Reference (5).

Acknowledgments

One of us (R.D.H.) gratefully acknowledges the award of a Fellowship for two years by Imperial Oil Limited. The authors wish to express their appreciation to the Committee on Research, McGill University, for financial assistance in the preparation of this manuscript.

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I. MESYL ESTERS OF GLYCEROL[1,2]

BY ERICH BAER AND ALAN G. NEWCOMBE[3]

Abstract

The syntheses of L-α-monomesylin[4,5], D-α,β- and DL-α,β-dimesylin, and trimesylin are described and some of their physical properties are reported. It was observed that the optical rotations of L-α-monomesylin and D-α,β-dimesylin in pyridine solutions change with time, whereas the rotations of the same compounds in the sterically hindered base, 2,6-lutidine, remain constant. Of the two previously reported values for the refraction of the $-O-SO_2-$ group the value of Tasker and Purves was confirmed. The mono- and dimesylins form the starting materials for the syntheses of the diacyl L-α-monomesylins and the acyl D-α,β-dimesylins.

Introduction

During the past 14 years methods have been developed in this Laboratory which permit the syntheses of the pure enantiomeric forms of asymmetrically substituted glycerol derivatives of predetermined constitution and configuration. These methods have been applied mainly to the preparation of lipids and phospholipids. It was felt that it would be of interest to extend our studies to the field of the sulphonic acid esters of glycerol as well. It was decided to prepare the following four mesyl esters, namely, L-α-monomesylin, DL- and D-α,β-dimesylin, and trimesylin. The syntheses are illustrated by reaction schemes A, B, and C.

The optical purity of the L-α-monomesylin was established by converting it into dipalmitoyl L-α-monomesylin and distearoyl L-α-monomesylin and preparing these compounds also by an independent method. The rotations of the corresponding mixed acid triglycerides were, within experimental error, identical. The optical purity of the D-α,β-dimesylin was established in a similar manner. The syntheses of these mixed acid triglycerides will be described in a subsequent paper.

[1] *Manuscript received June 25, 1951.*

Contribution from the Banting and Best Department of Medical Research, Banting Institute, Toronto, Ont. This paper forms part of a thesis submitted by A. G. Newcombe to the Department of Chemistry of the University of Toronto, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1950.

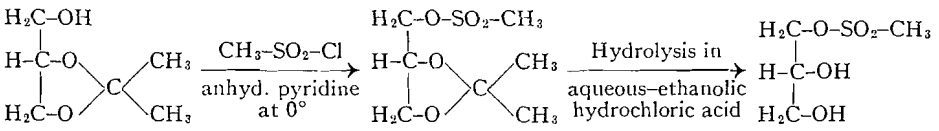
[2] *The use of "mesyl", instead of "methanesulfonyl-", was suggested by Helferich and Gnüchtel (9) and is followed here.*

[3] *Recipient of a scholarship from the Research Council of Ontario, 1948-1949, and from the National Research Council of Canada, summer, 1949.*

[4] *In conformity with the nomenclature applied to the glycerol esters of fatty acids, monomesyl glycerol, dimesyl glycerol, and trimesyl glycerol will be called monomesylin, dimesylin, and trimesylin, respectively.*

[5] *With regard to the optical classification of asymmetrically substituted glycerol derivatives see Fischer, H. O. L. and Baer, E. Chem. Revs. 29: 295, 299. 1941.*

(*A*) *Synthesis of* L-α-*monomesylin**

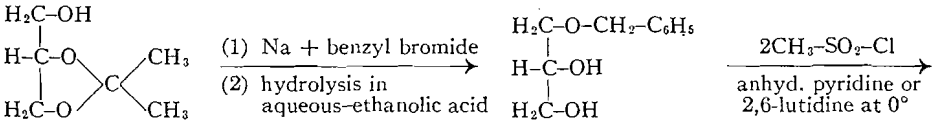


D-Acetone glycerol — I

II

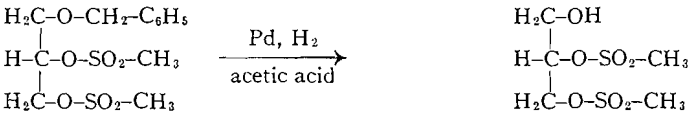
L-α-Monomesylin — III

(*B*) *Synthesis of* D-α,β-*dimesylin**



D-Acetone glycerol — IV

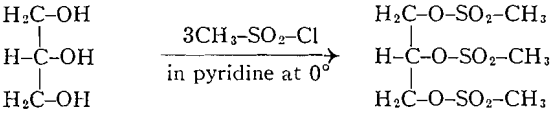
L-α-glycerol benzyl ether — V



D-α,β-Dimesylin benzyl ether — VI

D-α,β-Dimesylin — VII

(*C*) *Synthesis of trimesylin*



VIII

Trimesylin — IX

REACTION SCHEMES

* *The use of* L- *or* DL-*acetone glycerol as starting material yields* D-α- *or* DL-α-*monomesylin and* L-α,β- *or* DL-α,β-*dimesylin, respectively.*

It was observed that the optical rotations of pyridine solutions of L-α-monomesylin and D-α,β-dimesylin changed with time (see Table 1). The fact that the optical rotation of a solution of D-α,β-dimesylin in 2,6-lutidine, a sterically hindered base (5), was constant over a period of nine days suggests that the change of rotation in pyridine solution is caused by the formation of the glyceryl pyridinium mesylates of both the dimesylin and the monomesylin. This type of reaction has been observed by Ferns and Lapworth (6) to occur rapidly with ethyl tosylate and pyridine. The possibility that the change of rotation in pyridine was caused by the elimination of methanesulphonic acid, resulting in the formation of an epoxy-ring, was considered, but seems to be unlikely since the strongly basic 2,6-lutidine could be expected to act like pyridine in removing the methanesulphonic acid.

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The possession of four new liquid mesyl esters was a challenge to re-determine the molecular refraction of the $-O-SO_2-$ group for which two values have been reported. The average value of 10.44 ± 0.27 found by us is in good agreement with that found by Tasker and Purves (11) 10.53 ± 0.35, but varies slightly from that reported by Whitmore and Landau (12), 9.7 ± 0.2.

Experimental

D-*Acetone Glycerol* L-α-MONOMESYLIN

This substance was prepared according to the method of Baer and Fischer (2) by the catalytic reduction of acetone D-glyceraldehyde at atmospheric pressure (4) and was obtained in an average yield of 70%. $[\alpha]_D^{24°} = +13.7°$ in substance. $n_D^{22°} = 1.4360$.

Monomesyl D-*Acetone Glycerol*

To an ice-cold solution of 17.7 gm. (0.134 mole) of D-acetone glycerol in 75 ml. of anhydrous pyridine, protected against the intrusion of moisture, was added slowly and with agitation 15.3 gm. (0.134 mole) of mesyl chloride. The solution was allowed to stand at 0° for a period of 17 hr. At the end of this time crushed ice and a slurry of 11.3 gm. (0.134 mole) of sodium bicarbonate in 40 ml. of water was added to the reaction mixture. After concentrating the solution under reduced pressure, the residue, consisting of solid sodium chloride and a pale yellow oil, was treated with 100 ml. of anhydrous ether and the ether extract was cleared by centrifugation (ether extract I). The sodium chloride and undissolved oil was then treated with a mixture of 125 ml. of anhydrous ether and 125 ml. of 99% ethanol, and the extract, after freeing from sodium chloride, was concentrated *in vacuo* to a thick oil. The oil was dissolved in anhydrous ether, freed from traces of sodium chloride, and combined with ether extract I. The extracts were decolorized with activated charcoal and concentrated under reduced pressure. The residual oil was then fractionally distilled *in vacuo*, using a flask with sealed-on receiver (1). The fraction boiling from 91 to 93° (0.07 mm.) weighed 23.9 gm. (84.9% of theory) and was pure monomesyl D-acetone glycerol. $[\alpha]_D^{24°} = -8.0°$ in substance; $[\alpha]_D^{28°} = -7.4° \pm 0.1°$ in 95% ethanol (c, 7); $n_D^{15.5°} = 1.4555$, $n_D^{21°} = 1.4535$, $n_D^{25°} = 1.4520$, $d^{15.5°} = 1.2470$, $d^{21°} = 1.2409$, $d^{25°} = 1.2370$. Calc. for $C_7H_{14}O_5S$ (210.24): C, 39.98; H, 6.71; S, 15.25; acetone, 27.6%. Found: C, 39.88; H, 6.70; S, 14.96; acetone, 27.5%.

L-α-*Monomesylin*

A solution of 5.1 gm. (0.0243 mole) of monomesyl D-acetone glycerol in 150 ml. of 95% ethanol and 30 ml. of 0.5 *N* hydrochloric acid was allowed to stand at room temperature. The rotation of the solution was determined from time to time and was found to become constant at the end of 12 hr. After standing for a total of 18 hr. the mixture was made neutral to litmus by the addition of an aqueous solution of sodium bicarbonate and concentrated

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under reduced pressure. The mixture of oil and solid sodium chloride was treated with several portions of 99% ethanol, and the combined extracts were concentrated *in vacuo*. The residue, which still contained sodium chloride, was treated with five 80 ml. portions of anhydrous ether, and the combined extracts were again concentrated under reduced pressure. The residual oil was freed of solvent and moisture in a high vacuum over phosphorus pentoxide. In this manner 3.45 gm. (83.4% of theory) of L-α-monomesylin was obtained. Attempts to distill the monomesylin *in vacuo* resulted in the decomposition of the material. $n_D^{15°} = 1.4580$, $n_D^{25°} = 1.4553$, $d^{15°} = 1.370$, $d^{25°} = 1.358$. Calc. for $C_4H_{10}O_5S$ (170.18): C, 28.23; H, 5.92%. Found: C, 28.13; H, 6.19%. $[\alpha]_D^{29°} = -14.1°$ in anhydrous pyridine (*c*, 10). $[\alpha]_D^{30°} = -12.7° \pm 0.3°$ in 0.001 *N* sulphuric acid (*c*, 11). $[\alpha]_D^{30°} = -8.6° \pm 0.3°$ in glacial acetic acid (*c*, 10). $[\alpha]_D^{29°} = -9.3° \pm 0.2°$ in 90% acetic acid (*c*, 11). $[\alpha]_D^{32°} = -15.7° \pm 0.5°$ in a solvent consisting of 8.3 ml. of 95% ethanol and 1.7 ml. of 0.5 *N* hydrochloric acid (*c*, 12). The reported specific rotations are those observed shortly after preparing the solutions. The rotation of the L-α-monomesylin in 90% acetic acid, the de-acetonation mixture, or 0.001 *N* sulphuric acid remained constant for at least two, three, or six days, respectively. However, in pyridine the rotation increased, becoming more and more negative (Table I), while in glacial acetic acid the rotation decreased, becoming zero in the course of one week.

TABLE I

Days	L-α-Monomesylin in pyridine (*c*, 10) $[\alpha]_D^{23-27°}$	D-Dimesylin in pyridine (*c*, 9) $[\alpha]_D^{23-27°}$	D-Dimesylin in 2,6-lutidine (*c*, 10) $[\alpha]_D^{23-27°}$
0	−14.0° ±0.2°	+2.1° ± 0.2°	+6.1° ±0.2°
1	15.0 0.5		
2	16.0 0.2		
3			5.8 0.2
5			5.7 0.1
6	18.9 0.4	3.0 0.2	
9	21.3 0.3	3.5 0.1	+6.2 0.1
10	22.0 0.2		
11	22.7 0.6		
12	23.5 0.6		
13	24.2 0.2		
14		3.6 0.1	
16	26.6 0.4		
19	28.7 0.6		
23	31.4 0.6		
27		+4.1 0.2	
30	35.0 0.6		
40	41.3 0.1		
49	42.4 0.1		
143	−75.0 0.2		

Vicinal-Glycol Titration with Lead Tetraacetate in Aqueous Acetic Acid

Five milliliter aliquots of a 0.0348 *M* solution of L-α-monomesylin in 50% acetic acid were mixed each with a 20 ml. portion of an approximately 0.015 *M* solution of lead tetraacetate in glacial acetic acid and the consumption of lead

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tetraacetate was determined at stated intervals. At the end of 2.5, 6.33, 6.66, 21.0, 21.5, 41.0, and 44.5 hr., 0.562, 0.764, 0.764, 0.992, 0.983, 0.996, and 1.03 moles, respectively, of lead tetraacetate per one mole of monomesylin had been consumed. According to the final consumption of lead tetraacetate the monomesylin was the pure α-isomer.

The periodate oxidation of the L-α-monomesylin in dilute (8×10^{-2} or 8×10^{-4} N) sulphuric acid proceeded in an anomalous fashion consuming 1.95 moles of periodate in the course of two hours.

D- AND DL-α,β-DIMESYLIN

The L-α- and DL-α-benzyl glycerol ethers were prepared by the slightly modified (4) procedure of Sowden and Fischer (10).

D-α,β-*Dimesylin Benzyl Ether*

To a solution of 4.53 gm. (0.0248 moles) of L-α-benzyl glycerol ether in 30 ml. of anhydrous pyridine was added dropwise and with cooling 5.69 gm. (0.0497 moles) of mesyl chloride. After standing overnight at 0°C. the solution was poured into 500 ml. of ice water and the D-dimesylin benzyl ether was extracted with three 175 ml. portions of ether. The combined ether extracts were washed twice with 200 ml. of ice-cold 0.5 N sulphuric acid, twice with 200 ml. of saturated aqueous sodium bicarbonate solution, and twice with water. The ether solution was then dried over anhydrous sodium sulphate, filtered, and concentrated under diminished pressure. The residual oil after being completely freed from solvent *in vacuo* (0.1 mm.) weighed 7.05 gm. (84% of theory) and was pure D-dimesylin benzyl ether. $n_D^{20°} = 1.5156$; $d^{20°} = 1.338$; $d^{25°} = 1.328$; $[\alpha]_D^{26°} = +8.72° \pm 0.23°$ in anhydrous chloroform (c, 8.6), $[M]_D = +29.5° \pm 0.9$. Calc. for $C_{12}H_{18}O_7S_2$ (338.38): C, 42.59; H, 5.36%. Found: C, 42.63; H, 5.32%.

In an experiment which was identical with the foregoing except that anhydrous 2,6-lutidine (30 ml.) was used in place of pyridine, 92% of the theoretical amount of the α-benzyl ether of D-dimesylin was obtained. $[\alpha]_D^{26°} = +8.72° \pm 0.12°$ (c, 8.8 in anhydrous chloroform).

DL-α,β-*Dimesylin Benzyl Ether*

Prepared as described for the D-isomer. Yield 85% of theory. $n_D^{20°} = 1.5161$; $n_D^{25°} = 1.5142$; $n_D^{30°} = 1.5128$. Calc. for $C_{12}H_{18}O_7S_2$ (338.38): C, 42.59; H, 5.36%. Found: C, 42.71; H, 5.36%.

D-α,β-*Dimesylin*

A freshly prepared solution of 5.0 gm. (0.0148 mole) of D-dimesylin benzyl ether in 35 ml. of glacial acetic acid together with 1.0 gm. of palladium catalyst was vigorously shaken at room temperature in an atmosphere of hydrogen at an initial pressure of approximately 50 cm. of water, until the consumption of hydrogen ceased (30 min.). After displacing the hydrogen with nitrogen,

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the mixture was centrifuged and the catalyst was washed first with 99% ethanol and then with anhydrous ether. The combined solutions were concentrated under reduced pressure and the residue freed *in vacuo* (0.01 mm. Hg) from organic solvents and moisture. The D-dimesylin weighed 3.29 gm. (89.6% of theory) and was analytically pure. $[\alpha]_D^{26°} = +3.36° \pm 0.1°$ in anhydrous pyridine (*c*, 9). $n_D^{20°} = 1.4698$, $n_D^{25°} = 1.4681$, $d^{20°} = 1.438$, $d^{25°} = 1.440$. Calc. for $C_5H_{12}O_7S_2$ (248.27): C, 24.19; H, 4.87%. Found: C, 24.11; H, 4.82%.

Columns 2 and 3 of Table I report the specific rotations exhibited by the pyridine and 2,6-lutidine solutions of D-α,β-dimesylin on standing at room temperature. It is of interest to note that the rotation of the lutidine solution remains constant whereas that of the pyridine solution changes considerably with time.

DL-α,β-*Dimesylin*

This compound was prepared by the catalytic hydrogenolysis of DL-α,β-dimesylin benzyl ether according to the procedure described above. The DL-α,β-dimesylin was obtained in almost theoretical yield. Calc. for $C_5H_{12}O_7S_2$ (248.27): C, 24.19; H, 4.87%. Found: C, 24.31; H, 4.86%.

Trimesylin

To the ice-cold solution of 1.01 gm. (0.011 mole) of glycerol dissolved in 10 ml. of anhydrous pyridine was added dropwise 4.4 gm. (0.038 mole) of mesyl chloride. After standing 22 hr. at 0°, approximately 40 gm. of crushed ice was added to the bright red solution and the mixture was placed overnight in an ice box (+ 6°). The almost colorless precipitate was filtered off and washed thoroughly with water. The crude material was recrystallized from warm acetone by the addition of ether and yielded 3.04 gm. (86% of theory) of pure trimesylin, m.p. 79–81°. The trimesylin is soluble in water at 25° to the extent of 0.21 gm. in 100 ml. of solution. Calc. for $C_6H_{14}O_9S_3$ (326.35): C, 22.08; H, 4.32; S, 29.47%. Found: C, 22.09; H, 4.24; S, 29.46%.

Molecular Refraction of the –O–SO_2– Group

The molecular refraction of the –O–SO_2– group was obtained by deducting from the experimentally found molecular refractions of mesyl D-acetone glycerol, L-α-monomesylin, D-α,β-dimesylin benzyl ether, and DL-α,β-dimesylin the calculated molecular refractions of their –O–SO_2– free moieties (Table II). The Lorentz–Lorenz equation and Eisenlohr's (8) atomic refractions were used in these calculations. The atomic refraction of the two oxygen atoms in the five-membered heterocyclic ring of mesyl D-acetone glycerol was assumed to have the same value as hydroxyl-oxygen (1.525). This value agrees fairly well with that (1.515) calculated by us, from the molecular refraction reported by E. Fischer and Pfähler (7) for acetone glycerol.

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TABLE II

MOLECULAR REFRACTION OF THE $-O-SO_2-$ GROUP

Compound	n	d	M.R. found	M.R. calculated for the $-O-SO_2-$free moieties	$-O-SO_2-$ group refraction
Mesyl D-acetone glycerol	15° 1.4555	15° 1.247	45.79	35.38	10.41
	21° 1.4535	21° 1.241	45.84		10.46
	25° 1.4521	25° 1.237	45.86		10.48
L-α-monomesylin	15° 1.4580	15° 1.370	33.90	23.72	10.17
	25° 1.4553	25° 1.358	34.02		10.30
D-dimesylin benzyl ether	20° 1.5161	20° 1.338	76.41	55.66	10.37
	25° 1.5142	25° 1.328	76.51		10.54
DL-α,β-dimesylin	20° 1.4698	20° 1.438	48.16	26.82	10.67
	25° 1.4681	25° 1.440	47.93		10.56
					Aver. value = 10.44 ± 0.27

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ASYMMETRICALLY SUBSTITUTED MIXED ACID TRIGLYCERIDES

ACYL DERIVATIVES OF L-α-MONOMESYLIN AND D-α,β-DIMESYLIN[1]

BY ERICH BAER AND ALAN G. NEWCOMBE

Abstract

As part of a general program concerning the synthesis of the enantiomeric forms of asymmetrically substituted glycerol derivatives, dipalmitoyl and distearoyl L-α-monomesylin, and palmitoyl and stearoyl D-α,β-dimesylin were prepared. With the exception of stearoyl D-α,β-dimesylin, each of the mixed acid triglycerides was synthesized by two independent procedures. The individual triglyceride, regardless of the method of synthesis, was obtained with the same rotation, thus assuring the optical purity not only of the mixed acid triglycerides but also of L-α-monomesylin and D-α,β-dimesylin.

Introduction

The monoacyl D-α,β-dimesylins and diacyl L-α-monomesylins were prepared by two independent methods, (*a*) the mesylation of L-α-monopalmitin, L-α-monostearin, D-α,β-dipalmitin, and D-α,β-distearin, respectively, as shown by Equations *A* and *C*, and (*b*) by the acylation of D-α,β-dimesylin and L-α-monomesylin according to Equations *B* and *D*, using stearoyl and palmitoyl chloride.

The desired products were obtained by both methods with identical rotations thus assuring the optical purity not only of the monoacyl dimesylins and diacyl monomesylins but also of monomesylin and dimesylin. Of the two methods of synthesis the first (*a*) is preferable to the second (*b*) since it offers less preparative difficulties and the yields were found to be considerably higher.

During previous work in this laboratory (2,7) it was observed that with increasing substitution of glycerol by long chain, normal, fatty acids (monoglycerides → diglycerides → triglycerides) the optical activity of the asymmetric glycerides decreases and becomes unobservable in the triglycerides but reappears and increases considerably in magnitude (7,8,9) with the stepwise introduction of aromatic acids. Similar, although not as striking, increases in optical activity have now been observed with the introduction of mesyl substituents in the mixed acid triglycerides.

In making the stereochemical assignments for the mixed acid triglycerides the mesyl glyceride moieties were chosen as compounds of reference, since the mesyl group is common to all of them. This follows the precedent set by this laboratory in choosing the stereochemical moiety of reference for the α-lecithins (4), α-cephalins (5), and α-phosphatidic acids (1). Thus the mixed acid

[1] *Manuscript received June 25, 1951.*
Contribution from the Banting and Best Department of Medical Research, Banting Institute, Toronto, Ont. This paper forms part of a thesis submitted by A. G. Newcombe to the Department of Chemistry of the University of Toronto, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1950.

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triglycerides containing the D-forms of the mesyl glycerides are considered to be members of the D-series and vice versa. The steric classification of the mono- and dimesylins is established unambiguously by relating these compounds to the glyceraldehydes,[2] the compounds of stereochemical reference, *via* acetone glycerol and acetone glyceraldehyde.

Experimental

Stearoyl D-α,β-*Dimesylin* (By Mesylation of Monostearin)

To an ice-cold solution of 3.58 gm. (0.01 mole) of L-α-monostearin (2,3) in 40 ml. of anhydrous pyridine was added slowly and with exclusion of moisture 3.44 gm. (0.03 mole) of mesyl chloride, and the mixture was kept at 0° for 18 hr. At the end of this time 70 gm. of crushed ice was added and the precipitate was collected with suction on a Büchner funnel, washed thoroughly with water, and dried *in vacuo* over phosphorus pentoxide. For purification the crude material was reprecipitated from hot acetone by the addition of 95% ethanol and by cooling to + 6°. The stearoyl D-α,β-dimesylin was obtained in the form of colorless needles and in a yield of 98% (5.05 gm.). This material sintered to a viscous and translucent liquid from 72.5° to 75.0° and formed a meniscus at 89°. For further purification the substance was recrystallized from benzene by the addition of 95% ethanol and by cooling to + 6°. The resultant stearoyl D-α,β-dimesylin (4.25 gm., 83%) started to sinter at 71.5°, formed a viscous, translucent liquid from 75.5–76.5°, and developed a meniscus at 91°. $[\alpha]_D^{26°} = -3.3° \pm 0.2°$ in anhydrous chloroform (*c*, 10). $[\alpha]_D^{26°} = -4.4° \pm 0.1°$ in anhydrous pyridine (*c*, 10). Calc. for $C_{23}H_{46}O_8S_2$ (514.7): C, 53.66; H, 9.01; S, 12.46%. Found: C, 53.22; H, 8.93; S, 12.19%.

Stearoyl DL-α,β-*Dimesylin*

Prepared as described for the optically active compound, starting, however, with DL-α-monostearin (6). The stearoyl DL-α,β-dimesylin, which was obtained in a yield of 98%, sintered to a viscous, translucent liquid at 67–70° and formed a meniscus at 88°. It was insoluble in cold water, ethanol, or cyclohexane, and fairly soluble in cold benzene, or dioxane. It was also fairly soluble in boiling ether, acetone, dioxane, or cyclohexane and readily soluble at room temperature in chloroform, benzene, or pyridine. Calc. for $C_{23}H_{46}O_8S_2$ (514.7): C, 53.66; H, 9.01; S, 12.46%. Found: C, 53.33; H, 8.86; S, 12.37%.

Palmitoyl D-α,β-*Dimesylin* (By Mesylation of Monopalmitin)

Prepared as described for the corresponding stearoyl compound, starting with L-α-monopalmitin (2,3). The crude reaction product sintered at 65.0°, formed a viscous, translucent liquid at 70° and developed a meniscus at 77°. It was recrystallized by dissolving in boiling acetone, diluting the solution

[2] *With regard to the steric classification and nomenclature of glycerides see Fischer, H. O. L. and Baer, E. Chem. Revs. 29 : 287, 299. 1941.*

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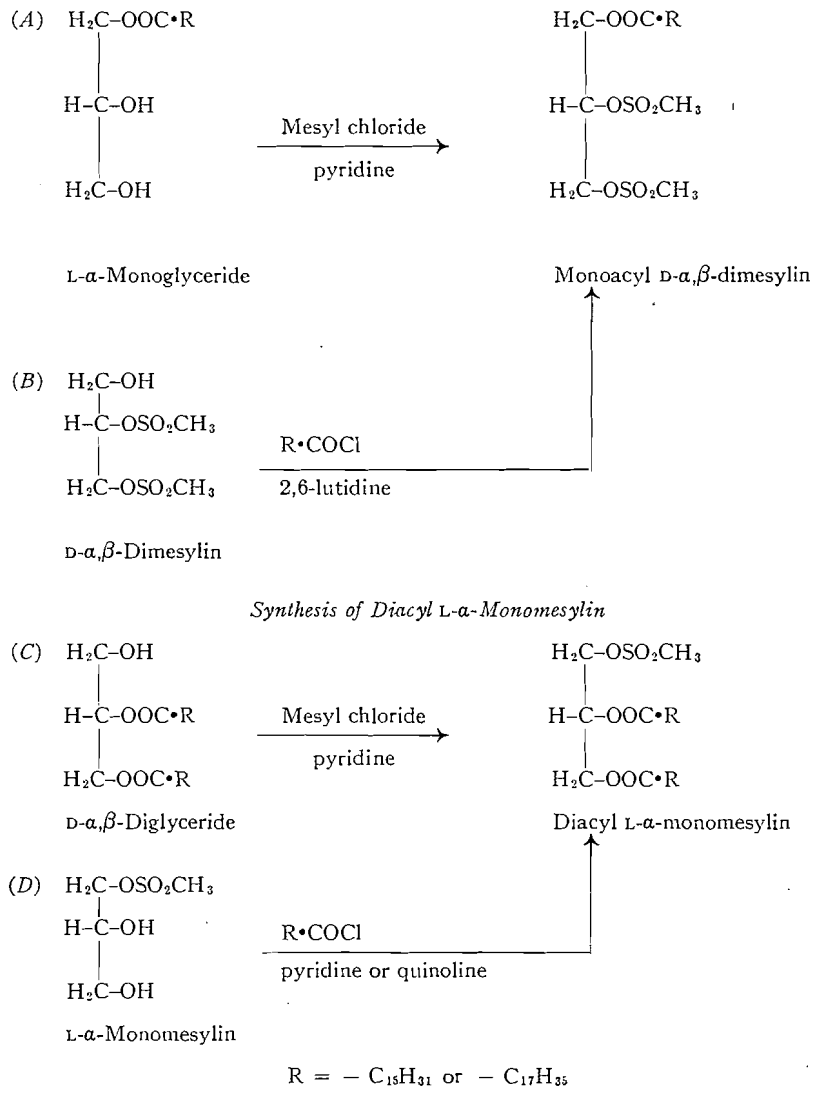
Synthesis of Acyl D-α,β-*Dimesylin*



Synthesis of Diacyl L-α-*Monomesylin*

R = $-C_{15}H_{31}$ or $-C_{17}H_{35}$

with 95% ethanol, and by cooling to + 6°. The pure palmitoyl D-α,β-dimesylin which was obtained in a yield of 88.5%, sintered at 69.5°, formed a viscous, translucent liquid at 71.5 to 72.5° and developed a meniscus at 78.5°. Further recrystallizations did not change the melting point. $[\alpha]_D^{26°} = -4.8° \pm 0.1°$ in anhydrous pyridine[3] (*c*, 10); $[\alpha]_D^{25°} = -3.5° \pm 0.1°$ in anhydrous chloroform (*c*, 10). Calc. for $C_{21}H_{42}O_8S_2$ (486.7): C, 51.83; H, 8.69; S, 13.18%. Found: C, 51.41; H, 8.65; S, 13.15%.

[3] *Unchanged after nine days.*

Palmitoyl DL-α,β-*Dimesylin*

Prepared and purified as described for the optically active compound above, starting, however, with DL-α-monopalmitin (6). The palmitoyl DL-α,β-dimesylin, which was obtained in a yield of 78%, sintered to a viscous, translucent liquid from 60.5 to 62.5° and formed a meniscus at 77.5°. Calc. for $C_{21}H_{42}O_8S_2$ (486.7): C, 51.83; H, 8.69; S, 13.18%. Found: C, 51.56; H, 8.71; S, 13.08%.

Palmitoyl D-α,β-*Dimesylin* (By Acylation of Dimesylin)

To a suspension of 2.48 gm. (0.01 mole) of D-dimesylin[4] in 12 ml. of anhydrous carbon tetrachloride and 2.3 ml. (0.02 mole) of 2,6-lutidine, was added a solution of 2.75 gm. (0.01 mole) of palmitoyl chloride in 8 ml. of anhydrous carbon tetrachloride and the mixture, protected against moisture, was kept at 40°. At the end of 40 hr. the reaction mixture was poured with stirring into a mixture of 100 ml. of ether and 100 ml. of water. The precipitate was centrifuged down, washed thoroughly with water, and, after drying *in vacuo*, recrystallized twice from small volumes of hot acetone by the addition of 95% ethanol and cooling to + 6°. The colorless palmitoyl D-α,β-dimesylin, which was obtained in a yield of 21.4% (1.04 gm.), sintered at 68.0°, formed a viscous, translucent liquid at 70.0°, and developed a meniscus at 76.0°. $[\alpha]_D^{25°} = -4.8° \pm 0.2°$ in anhydrous pyridine (*c*, 10). Calc. for $C_{21}H_{42}O_8S_2$ (486.7): C, 51.83; H, 8.69%. Found: C, 51.76; H, 8.68%.

Distearoyl L-α-*Monomesylin* (By Mesylation of Distearin)

To a solution of 1.25 gm. (0.002 mole) of D-distearin (4,9) in a mixture of 20 ml. of anhydrous ether and 12 ml. of anhydrous pyridine was added at room temperature and under anhydrous conditions 0.46 gm. (0.004 mole) of mesyl chloride. The reaction mixture was allowed to stand at room temperature for 17 hr. At the end of this period crushed ice was added, the mixture was filtered, and the white precipitate, after drying thoroughly, was recrystallized from 50 ml. of acetone. The substance was obtained in the form of fine, colorless needles which melted from 71.2 to 74.0°. Subsequent recrystallizations, first from 50 ml. of a mixture of chloroform and petroleum ether (1:7; v/v) and then from 55 ml. of acetone, yielded a product which melted from 73.5–75.4°. The pure distearoyl L-α-monomesylin was obtained in a yield of 66% (0.93 gm.). $[\alpha]_D^{23°} = +1.6° \pm 0.1°$ in anhydrous chloroform (*c*, 7). Calc. for $C_{40}H_{78}O_7S$ (703.1): C, 68.33; H, 11.18; S, 4.56%. Found: C, 68.45; H, 11.31; S, 4.72%.

Distearoyl DL-α-*Monomesylin*

Prepared as described for the optically active compound, starting, however, with DL-α,β-distearin (4). The distearoyl DL-α-monomesylin, which was obtained in a yield of 63%, melted at 75.0–76.0°. Calc. for $C_{40}H_{78}O_7S$ (703.1): C, 68.33; H, 11.18; S, 4.56%. Found: C, 68.10; H, 11.00; S, 4.63%.

[4] *See preceding paper in this issue.*

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Distearoyl L-*α-Monomesylin* (By Acylation of Monomesylin)

To a solution of 0.85 gm. (0.005 mole) of L-α-monomesylin[4] in 7.5 ml. of anhydrous quinoline was added with cooling and under anhydrous conditions a solution of 3.03 gm. (0.01 mole) of stearoyl chloride in 5.0 ml. of anhydrous quinoline, and the mixture was allowed to stand for four days at room temperature. At the end of this time the reaction mixture was taken up in 100 ml. of ether and 150 ml. of 0.5 *N* hydrochloric acid. After separating the two phases, the ether layer was washed in rapid succession with 150 ml. of 0.5 *N* hydrochloric acid, 100 ml. of water, 100 ml. of a saturated sodium bicarbonate solution, and again with 50 ml. of water. All operations were carried out in the cold. The ether extract was dried over anhydrous sodium sulphate and evaporated to dryness *in vacuo*. The hot acetone solution (55 ml.) of the residue, after treating with activated charcoal, yielded, on cooling to + 6°, colorless distearoyl L-α-monomesylin which, after further recrystallizations from, (*a*) chloroform – petroleum ether, (*b*) acetone, (*c*) chloroform – petroleum ether, melted from 72.5 to 74.2°. Yield 15% of theory (0.54 gm.). $[\alpha]_D^{32°}$ = + 1.7° ± 0.2° in anhydrous chloroform (*c*, 10). Calc. for $C_{40}H_{78}O_7S$ (703.1): C, 68.33; H, 11.18%. Found: C, 68.45; H, 11.05%.

Dipalmitoyl L-*α-Monomesylin* (By Mesylation of Dipalmitin)

The substance was prepared as described for the corresponding stearoyl compound. The mesylation of D-α,β-dipalmitin (4,9) (2.84 gm., 0.005 mole) by means of mesyl chloride (1.15 gm., 0.01 mole) in pyridine (25 ml.) and recrystallization of the crude reaction product from acetone (60–80 ml.), then from 120 ml. of a mixture of chloroform and petroleum ether (1:7; v/v), yielded 2.56 gm. (79%) of pure dipalmitoyl L-α-monomesylin, melting from 68.5–70.0°. $[\alpha]_D^{24°}$ = + 1.7° ± 0.2° in anhydrous chloroform (*c*, 8); $[\alpha]_D^{25°}$ = + 2.4° ± 0.1° in anhydrous pyridine[3] (*c*, 10). Calc. for $C_{36}H_{70}O_7S$ (647.0): C, 66.83; H, 10.91; S, 4.95%. Found: C, 66.83; H, 10.58; S, 5.13%.

Dipalmitoyl DL-*α-Monomesylin*

This substance was prepared in the same manner as the L-isomer. The mesylation of 2.84 gm. (0.005 mole) of DL-α,β-dipalmitin (4) yielded 3.04 gm. (94%) of pure, crystalline dipalmitoyl DL-α-monomesylin, melting at 67.0–68.5°. Calc. for $C_{36}H_{70}O_7S$ (647.0): C, 66.83; H, 10.91; S, 4.95%. Found: C, 66.92; H, 10.85; S, 4.92%.

Dipalmitoyl L-*α-Monomesylin* (By Acylation of Monomesylin)

To a solution of 0.85 gm. (0.005 mole) of L-α-monomesylin[4] in 12 ml. of anhydrous pyridine was added with cooling and exclusion of moisture 2.75 gm. (0.01 mole) of palmitoyl chloride. After standing at room temperature for one day, the solid mass was triturated with 12 ml. of anhydrous carbon tetrachloride and allowed to stand for a further five days. At the end of this period the dark red reaction mixture was poured onto a mixture of crushed ice, water, and chloroform. The chloroform solution was washed consecutively with

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two portions of 180 ml. each of ice-cold 0.5 *N* sulphuric acid, water, saturated sodium bicarbonate solution, and again with water, and after drying with anhydrous sodium sulphate, was evaporated to dryness under reduced pressure. The dark brown solution of the residue in 100 ml. of warm acetone was decolorized with activated charcoal and cooled in ice. The crude product (0.49 gm., 15%), after recrystallization from 20 ml. of a mixture of chloroform and petroleum ether (v/v; 1:7) followed by recrystallization from 35 ml. of acetone, yielded 0.32 gm. (10%) of pure dipalmitoyl L-α-monomesylin, m.p. 66.5–68.5°. $[\alpha]_D^{32°} = +1.8° \pm 0.3°$ in anhydrous chloroform (*c*, 6). Calc. for $C_{36}H_{70}O_7S$ (647.0); C, 66.83; H, 10.91%. Found: C, 66.44; H, 11.10%.

Acknowledgments

One of the authors (A.G.N.) wishes to express his sincerest appreciation to the Research Council of Ontario and the National Research Council of Canada for Scholarships received during the year 1948-49 and 1949 respectively.

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IONIC SPECIES IN CERIC PERCHLORATE SOLUTIONS[1]

By T. J. Hardwick and E. Robertson

Abstract

Ceric ion has been shown to exist in perchloric acid solution as a mixture of Ce^{4+}, $CeOH^{3+}$, and a dimer, probably $(Ce\text{-}O\text{-}Ce)^{6+}$. From a spectral study between 395 and 430 mμ, the values of the equilibrium ratios have been determined, along with the molar extinction coefficients of each ion over this region of wave length. The thermodynamic quantities ΔH, $\Delta F°$, and $\Delta S°$ have been determined for each reaction.

Introduction

Recently Heidt and Smith (2) postulated the existence of a stable dimer of cerium in ceric perchlorate solution. This assumption enabled them to explain some unusual effects observed in the photochemical reduction of ceric ion in perchloric acid. Kolp and Thomas (3) believed that the thermal reduction of ceric perchlorate in aqueous solution could best be explained by the existence of a stable dimer of cerium.

On the other hand, Smith (7) maintained that tetravalent cerium exists as $Ce(ClO_4)_6^-$ in perchloric acid solution. Moore and Anderson (5) in their spectral study of the ceric sulphate complexes, omitted consideration of the possibility of dimerization of ceric ion.

A number of papers have been published on the potential of the ceric–cerous couple in perchloric acid solutions (6, 7) but the data therein shed no light on the question of dimer existence.

It appeared that the most promising way to investigate the existence of dimer was to make a detailed spectral study of ceric perchlorate – perchloric acid solutions. If a dimer is formed, Beer's law will not be followed. At high ceric ion concentrations the apparent molar extinction coefficient should decrease, as the total number of absorbing species actually present is decreased. A change in absorption with changing acid concentration indicates the presence of one or more hydrolysis products of the ceric ion.

Experimental

Materials

Ceric perchlorate solution: This was prepared essentially by the method used by Sherrill (6). C.P. ammonium ceric sulphate (G. Frederick Smith Co.) was dissolved in dilute nitric acid and reduced to the cerous state by hydrogen peroxide. Cerous oxalate was precipitated and washed free from sulphate. The precipitate was dissolved in nitric acid and fumed down successively in hydrochloric and perchloric acids. The resulting syrup was diluted to give a cerium

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concentration of 0.56 *M* and an acid concentration of 2.7 *M*. Negative tests were obtained for nitrate, chloride, and sulphate. Portions of this solution were oxidized electrolytically, about 95% conversion being achieved. This was the stock solution from which all dilutions were made.

Perchloric acid: 4.00 *M* solutions were prepared from Merck's Reagent 70% acid.

Sodium hydroxide: 4.00 *M* solutions were made from Nichol's Reagent sodium hydroxide.

Preparation of Solutions

The stock solutions were kept in a room maintained at 25± 1°C. Appropriate dilutions were made using the stock ceric solution, the acid, and the alkali to give solutions of the required ceric ion concentration, acidity, and ionic strength. The volume of solution made was 25 ml.

Analysis of Solutions

Perchloric acid solutions were standardized against dilute sodium hydroxide; sodium hydroxide solutions against standard hydrochloric acid prepared by the constant boiling method. Cerium analysis was carried out as follows: an aliquot of ceric solution was added to a slight excess of standard ferrous ion in dilute sulphuric acid solution. The excess ferrous ion was determined colorimetrically by the *o*-phenanthroline method. Duplicate analyses were made on a ceric solution before and after a series of spectral measurements. No change was ever noticed in the time interval. Analytical error was in all cases less than 0.4%.

Optical Measurements

The instrument used was a Beckman Photoelectric Quartz Spectrophotometer. A special cell holder housing was made which allowed water at 25.00 ± 0.05°C. to circulate through the walls of the cell compartment.

The solutions to be investigated were immersed in a bath at 25.00 ±.01°C. for at least one hour before use. In making measurements three "corex" cells of 1 cm. path length were used—one containing a blank of perchloric acid – sodium perchlorate solution appropriate to the ceric solution, and the other two the test solution. The cells were placed in the instrument and the per cent transmission measured from 395 mμ to 430 mμ in steps of 5 mμ.

Results

A small amount of cerous ion was invariably present in all samples, arising from incomplete oxidation of stock cerium solution and/or autoreduction of ceric ion during dilution. However, under the conditions used in these experiments, cerous ion does not absorb light and can therefore be omitted from consideration.

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The transmission of ceric perchlorate solutions was measured under the following conditions:

Series	Range of ceric ion concentration	$[H^+]$	Γ
A	$1.3 - 13.0 \times 10^{-3}$ M	0.20	2.00
B	$0.7 - 12.5 \times 10^{-3}$ M	1.00	2.00
C	$1.3 - 13.6 \times 10^{-3}$ M	2.00	2.10
D	6.5 and 9.2×10^{-3} M	1.00	1.10—4.00

where Γ is the molar ionic strength. The results of A, B, and C appear in Fig. 1, those of D in Fig. 3.

Discussion

The apparent molar extinction coefficients will be defined by:

$$\bar{\epsilon} = \frac{1}{C} \log \frac{I_0}{I} \text{ (for unit path length)} \tag{1}$$

$$= \frac{D}{C} \tag{1a}$$

where C is the total concentration of tetravalent cerium, I_0 and I are the intensities of light passing through the blank and test solutions respectively, and D is the optical density of the solution. Fig. 1 shows a plot of $\bar{\epsilon}$ vs. C for various hydrogen ion concentrations at different wave lengths.

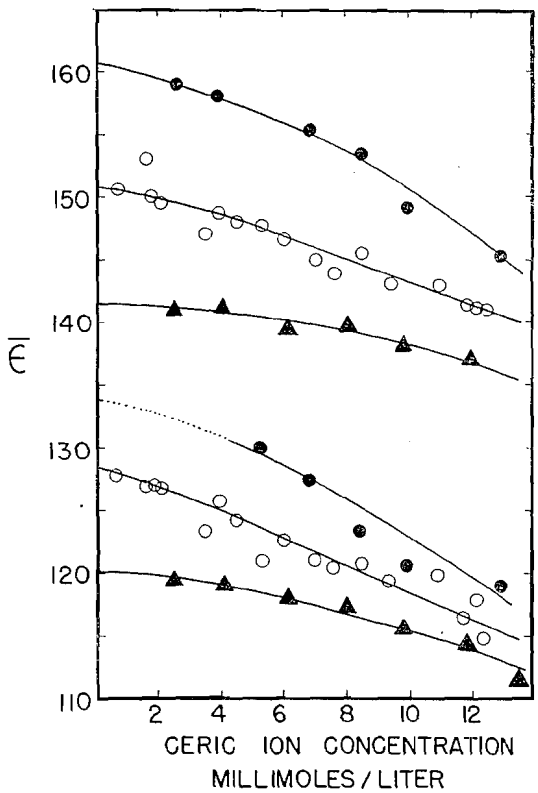

FIG. 1. *Apparent molar extinction coefficients as a function of ceric ion concentration. Upper set:* $\lambda = 400$ *mμ. Lower set:* $\lambda = 405$ *mμ.*
● $[H^+] = 0.20$ *N*, o $[H^+] = 1.00$ *N*, ▲ $[H^+] = 2.00$ *N*

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Two features of these data are noteworthy. First, an increase in acid concentration results in a decreased value of $\bar{\epsilon}$. This shows that an equilibrium involving H^+ or OH^- must be present. Heidt (2) has postulated the equilibrium,

$$Ce^{4+} + H_2O \overset{K_1}{\rightleftharpoons} CeOH^{3+} + H^+ \tag{2}$$

$$K_1 = \frac{[CeOH^{3+}][H^+]}{[Ce^{4+}]} \tag{3}$$

Let M = the concentration of $CeOH^{3+}$ at equilibrium,
X = the concentration of Ce^{4+} at equilibrium,
C = the total concentration of tetravalent cerium in solution, then

$$K_1 = \frac{M[H^+]}{X} \tag{3a}$$

$$= \frac{(C - X)[H^+]}{X} \tag{3b}$$

$$X = \frac{C[H^+]}{K_1 + [H^+]} \tag{4}$$

$$D = \epsilon_x X + \epsilon_m (C - X) \tag{5}$$

$$= \epsilon_x \frac{C[H^+]}{K_1 + [H^+]} + \epsilon_m \frac{CK_1}{K_1 + [H^+]} \tag{5a}$$

where ϵ_x and ϵ_m are the molar extinction coefficients for Ce^{4+} and $CeOH^{3+}$ respectively.

For every value of C, the data allow three equations in the unknowns, ϵ_x, ϵ_m, and K_1 to be set up—one for each acid concentration. These equations may be reduced to the form

$$K_1 D_{1,2,3} - C(K_1\epsilon_m) - C[H^+]_{1,2,3} = -D_{1,2,3}[H^+]_{1,2,3} \tag{5b}$$

By considering $K_1\epsilon_m$ an unknown constant instead of ϵ_m, a solution to these equations may be obtained. The values of $\bar{\epsilon}$ at $C = 1.0 \times 10^{-3} M$ and $\lambda = 400$ mμ were used in calculating K_1. This result ($K_1 = 5.2$) was used to calculate ϵ_m and ϵ_x values at all wave lengths. Calculations of K_1 from data at longer wave lengths gives rise to a large probable error, as the differences between the $\bar{\epsilon}$ values are very small.

Two assumptions have been made in these calculations. First, only one hydrolysis form of ceric ion is considered present, i.e., $CeOH^{3+}$. The formation of $Ce(OH)_2^{2+}$ is not excluded, but such an ion, if present, would either exist in small amounts or possess a spectrum very much similar to that of $CeOH^{3+}$. Second, the pair of ions related by hydrolysis is considered to be $Ce^{4+} - CeOH^{3+}$. This could equally well be $CeOH^{3+} - Ce(OH)_2^{2+}$ as far as mathematical interpretation of the work is concerned. However, with zirconium in 2 M perchloric acid, the average number of hydroxyl ions associated with zirconium is between zero and one (1); with uranous ion in 2 M perchloric acid, *ca.* 98% is found to

be in the U^{4+} state (4). From this work one calculates only 28% present as unassociated Ce^{4+} ions in 2 M perchloric acid. It is therefore quite likely that the hydrolysis couple $Ce^{4+} - CeOH^{3+}$ is the one involved.

The value of $\bar{\epsilon}$ for a particular acid concentration varies when C varies. As will be demonstrated later, this is caused by the formation of a dimer of $CeOH^{3+}$. The true values for K_1, ϵ_x and ϵ_m should be calculated at $C \rightarrow 0$. However, as extrapolation to zero would lead to significant inaccuracies, the calculations were made at $C = 1.0 \times 10^{-3}$ M, at which concentration the proportion of dimer is rather small. Small corrections (amounting to about 1%) were subsequently made to ϵ_x and ϵ_m for dimer; K_1 was found not to change. The corrected values are recorded in Table I and are plotted against wave length in Fig. 2.

TABLE I

MOLAR EXTINCTION COEFFICIENTS

λ mμ	Ce^{4+} ϵ_x	$CeOH^{3+}$ ϵ_m	Dimer ϵ_p
395	100	192	
400	85.5	163	210
405	72	138.5	137
410	61.5	117.5	100
415	53	99.5	70
420	48	83	47.5
425	43.5	69.5	33.5
430	40.5	58	5.7

The second feature of the curves in Fig. 1 is the decrease in $\bar{\epsilon}$ as C increases at constant acidity and ionic strength. This can be explained only by assuming some kind of polymerization of ceric ion. Heidt (2) has suggested that $CeOH^{3+}$ dimerizes.

$$2\ CeOH^{3+} \overset{K_2}{\rightleftharpoons} (Ce-O-Ce)^{6+} + H_2O \tag{6}$$

$$K_2 = \frac{[(Ce-O-Ce)^{6+}]}{[CeOH^{3+}]^2} \tag{7}$$

For convenience let P = the concentration of $(Ce-O-Ce)^{6+}$ at equilibrium with all other symbols as before. The concentration of dimer will be

$$P = \frac{1}{2}\{C - (M + X)\} \tag{8}$$

$$\text{also} \quad D = \epsilon_x X + \epsilon_m M + \epsilon_p P \tag{9}$$

Substituting Equations (3a) and (8) in Equation (9) one obtains

$$M = \frac{D - \frac{1}{2}\epsilon_p C}{\epsilon_x \frac{[H^+]}{K_1} + \epsilon_m - \frac{1}{2}\epsilon_p \left(\frac{[H^+]}{K_1} + 1\right)} \tag{10}$$

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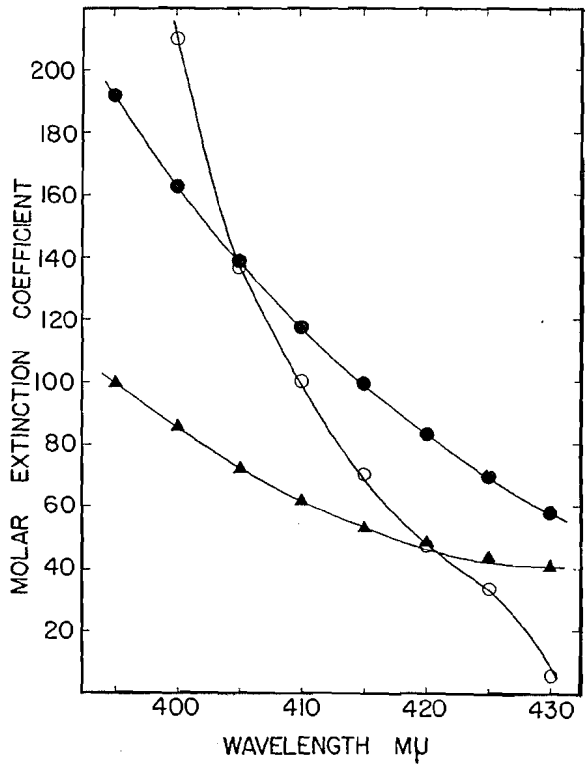

FIG. 2. *Spectra of the species present in ceric perchlorate solution.* ▲ Ce^{4+}, ● $CeOH^{3+}$, o *dimer*

Once M is known, X is obtained from Equation (3*a*), P from Equation (8) and K_2 from Equation (7). Equation (10) contains two unknowns, M and ϵ_p. However, by choosing low acid concentrations and high cerium concentrations, X becomes relatively negligible and P a significant fraction of the total cerium. Equation (10) then reduces to

$$M = \frac{D - \frac{1}{2}\epsilon_p C}{\epsilon_m - \frac{1}{2}\epsilon_p} \qquad (10a)$$

The fraction of the total cerium remaining as $CeOH^{3+}$ is

$$\frac{M}{C} = \frac{\bar{\epsilon} - \frac{1}{2}\epsilon_p}{\epsilon_m - \frac{1}{2}\epsilon_p} \qquad (10b)$$

By successive approximations one can calculate values of ϵ_p at different wave lengths which give a constant value of M/C. One can now substitute these ϵ_p values in Equation (10) to determine M using data from the smoothed curve

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values of $\bar{\epsilon}$ for $[H^+] = 1$. By successive approximations one obtains good values for K_2 and ϵ_p; ϵ_p values are recorded in Table I and are plotted against wave length in Fig. 2. K_2 was found to be 16.5. These extinction coefficients and equilibrium ratios were used to calculate $\bar{\epsilon}$ values. A comparison with the measured ones at 0.2 and 2.0 *M* acid showed an agreement better than $\pm$ 0.5% in most cases.

We have been able to interpret the decrease in $\bar{\epsilon}$ with increasing ceric ion concentration only by assuming that an equilibrium exists between ceric ion and a dimer of ceric ion. The evidence for the existence of this dimer seems quite conclusive, as the calculation of the optical density of a solution (using the constants found in this work) agrees with measured values within 1%. We do not agree with the conclusions of Moore and Anderson that ceric perchlorate solutions obey Beer's law up to concentrations of 0.01 *M*. Reactions of this type have been demonstrated to occur in uranous and zirconium salt solutions (1). It appears that the higher the valence of the ion, the greater the tendency to polymerize.

The chemical form of the dimer may be $(Ce-O-Ce)^{6+}$ or some hydrolyzed form such as $(HO\text{-}Ce\text{-}O\text{-}Ce)^{5+}$ or $(HO\text{-}Ce\text{-}O\text{-}Ce\text{-}OH)^{4+}$. As the apparent extinction coefficient of the dimer is the same for all the acid concentrations studied, we can conclude only that the form of the dimer is the same between 0.2 *M* and 2.0 *M* acid, or that the absorption spectra of the various forms are quite similar.

Effect of Ionic Strength on the Equilibria

K_1 and K_2, like all equilibrium ratios involving ions, depend upon ionic strength. In the preceding work, Γ has been kept constant at 2.00 or 2.10. Fig. 3 shows the effect of changing ionic strength on $\bar{\epsilon}$ for two ceric ion concentrations. The acid was maintained at 1.0 *M* and the ionic strength changed by the addition of sodium perchlorate.

The invariance of $\bar{\epsilon}$ with ionic strength is interpreted to mean that the values of the equilibrium ratios do not change with changes in ionic strength. This may be explained by assuming that the changes in activity coefficients of the ions in Equations (3) and (7) cancel numerically. This will hold true more for K_1 than K_2, as small changes in K_2 would not be noticeable under the conditions used.

The perchlorate ion concentration is increased fourfold with no resultant increase in $\bar{\epsilon}$. It is therefore quite unlikely that any equilibrium involving perchlorate ions is set up.

Effect of Temperature on the Equilibria

In order to investigate the effect of temperature on the $Ce^{4+} - CeOH^{3+}$ equilibrium, conditions were chosen such that dimer concentration would be low and have little effect on the optical density of the system. A solution where

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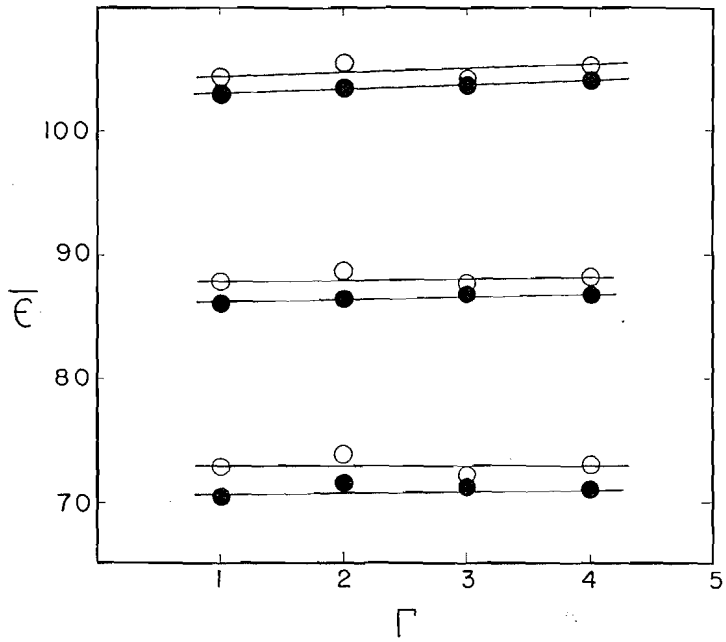

FIG. 3. *Effect of molar ionic strength on the apparent molar extinction coefficient for* $\lambda = 410$, *415, and 420 mμ.*

o $[Ce^{IV}] = 9.2 \times 10^{-3}$ *moles/liter*
● $[Ce^{IV}] = 6.3 \times 10^{-3}$ *moles/liter*

$[H^+] = 2.0\ M$, $\Gamma = 2.1$, total ceric ion $= 2.0 \times 10^{-3}\ M$ was used. The optical densities of this solution were measured between 430 and 395 mμ at 5, 15, 25, and 35°C. The values of X and subsequently K_1 at the different temperatures were found using a modified form of Equation (5).

$$\frac{X}{C} = \frac{\epsilon_m - \bar{\epsilon}}{\epsilon_m - \epsilon_x} \qquad (5c)$$

The mean values of K_1 at each temperature are recorded in Table II and are plotted against $1/T$ in Fig. 4. From the slope of this curve one calculates $\Delta H = 15.5 \pm 1$ kcal. for the first hydrolysis of Ce^{4+}.

TABLE II

EFFECT OF TEMPERATURE ON ASSOCIATION CONSTANTS

Temp., °C.	K_1	K_2
5	0.87	110
15	2.1	41.5
25	5.2	16.5
35	15.0	3.1

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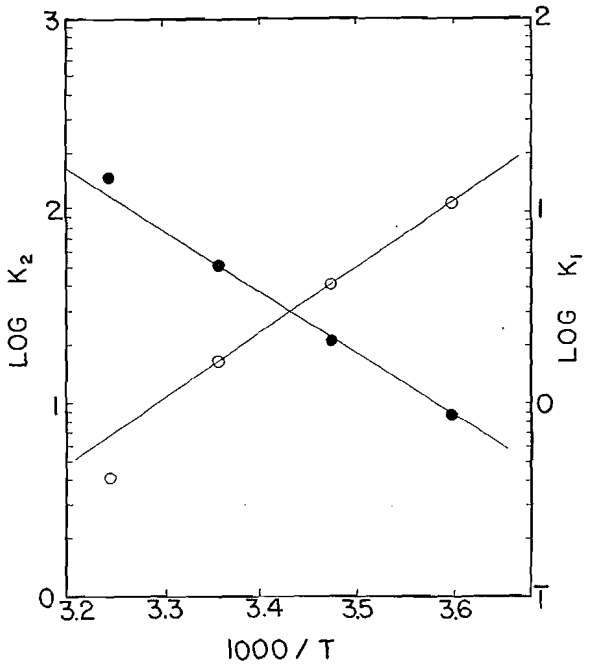

FIG. 4. *Equilibrium ratios as a function of temperature.*
o K_2 *values.* • K_1 *values.*

By choosing the following conditions: $[H^+] = 0.2\ M$, $\Gamma = 2.0$, $[Ce^{IV}]_0 = 1.10 \times 10^{-2}\ M$, only small amounts of Ce^{4+} are present, while dimer is in as large a concentration as is feasible under the conditions of the work. The optical densities of the above solutions were measured over the previous wave length range at temperatures of 5, 15, 25, and 35°C. From Equations (10), (3*a*), (8), and (7) one obtains the value of K_2. The mean values of K_2 at each temperature are recorded in Table II and are plotted against $1/T$ in Fig. 4. From the slope of this curve one calculates $\Delta H = -16 \pm 1$ kcal. for the formation of dimer from $CeOH^{3+}$.

Thermodynamic Constants

Using the Equation $\Delta S = R \ln K + \frac{\Delta H}{T}$ the entropy change may be found for the reactions. The free energy and entropy changes are for

	Hydrolysis	Dimerization
$\Delta F°$ kcal.	− 3.1	− 1.7
$\Delta S°$ e.s.u.	55.4	− 48.3

By adding the corresponding values for the neutralization reaction, one obtains the thermodynamic constants for the association reaction proper.

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	ΔH kcal.	$\Delta F°$ kcal.	$\Delta S°$ e.s.u.
$Ce^{4+} + H_2O \rightarrow CeOH^{3+} + H^+$	15.5	− 3.1	55.4
$H^+ + OH^- \rightarrow H_2O$	− 13.5	−19.1	19
$Ce^{4+} + OH^- \rightarrow CeOH^{3+}$	2.0	− 22.2	74.4

Migration Experiments

A qualitative migration experiment was made to determine the nature of the charge on the ions in solution. A three compartment cell with fine sintered glass partitions was used (Fig. 5). In the center compartment a ceric perchlorate solution was placed ($[Ce^{IV}] = 10^{-2}$ *M*, $[H^+] = 1.0$ *N*, $\Gamma = 2.0$) and in the outer compartments an appropriate perchloric acid – sodium perchlorate solution, all liquid levels being made equal. Migration was determined by the appearance of color in the outer compartments.

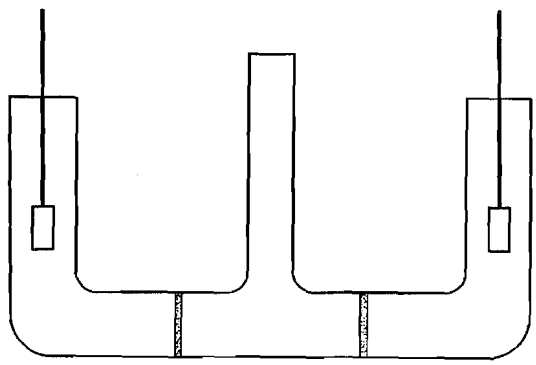

FIG. 5. *Three compartment diffusion cell.*

No natural migration occurred in 24 hr. Application of 67 1/2 v. at the electrode caused migration of color to the cathode, none to the anode. Reversal of electrode polarity reversed the direction of migration. Thus ceric perchlorate solutions contain positive and no negative ceric ions or complexes. Neutral species are not detectable.

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ASSOCIATION OF CERIC IONS WITH SULPHATE (A SPECTRAL STUDY)[1]

By T. J. Hardwick and E. Robertson

Abstract

Ceric ion has been shown to associate with sulphate ion to form successively $Ce(SO_4)^{++}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^=$. The association constants relating these species have been determined at 25°C. The molar extinction coefficients of each associated complex have been found between 395 and 430 mμ. Migration experiments bear out the results qualitatively.

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There is considerable evidence of complex formation between ceric ions and sulphate ions in aqueous solution. Jones and Soper (2) have measured transference in solutions of high sulphuric concentration and found migration of color to the anode. Electromotive force measurements by Kunz (3), Noyes and Garner (6), Smith and Getz (7) indicate that a complex is certainly formed, but its nature could not be explicitly determined. Moore and Anderson (4) found evidence for complexing from kinetic studies on the reaction of ceric ions with arsenite ions. Smith and Getz infer the existence of ceric sulphate complexes from the formation of double salts such as $(NH_4)_2Ce(SO_4)_3$.

Moore and Anderson (5) made a spectral study on the first complex of ceric ion and sulphate in perchloric acid solutions. They analyzed their data by the limiting logarithmic method and the method of continuous variations. They determined the instability constant of the first complex and found it to vary with total ceric ion plus sulphate concentration. Evidence for higher complexes was obtained.

In view of the lack of accurate information on the complexes formed, it seemed advisable to investigate the ceric ion – sulphate ion system thoroughly. The most promising method appeared to be a spectral study supplemented by qualitative migration experiments.

Experimental

Materials

Ceric perchlorate solutions: These were prepared by the method described in the previous paper (1). The solutions contained no detectable chloride, sulphate, or nitrate.

Perchloric acid solutions were prepared from Merck's 70% perchloric acid. Sodium hydroxide solutions (carbonate-free) were prepared from Nichol's Reagent grade sodium hydroxide. Sodium sulphate solutions were prepared gravimetrically from Baker and Adams Reagent grade sodium sulphate. Test

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solutions were made by mixing appropriate amounts of these solutions to give the desired ceric ion concentration, sulphate concentration, acidity, and ionic strength.

Optical measurements were made using a Beckmann Quartz Photoelectric Spectrophotometer. The temperature of the test solutions was kept at 25.0 ±.1°C. The procedure in making measurements was identical with that outlined in the previous paper (1).

In order to characterize the system ceric ion – sulphate ion, the various complexes present must be known, together with their extinction coefficients for particular wave lengths and the association constants which relate the various complexes.

It has been indicated that the complex $Ce(SO_4)_3^{=}$ is present in high sulphate concentrations. As will be shown later, the sulphate complexes contain no hydrogen, or hydroxyl ion; hence it will be assumed that the species Ce^{4+} (unassociated), $CeSO_4^{++}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{=}$ are present under the proper conditions.

In a previous paper it was shown that in perchloric acid solutions, ceric ion is most probably present as a mixture of Ce^{4+}, $CeOH^{3+}$, and $(Ce\text{-}O\text{-}Ce)^{6+}$. The association constants relating these ions have been determined, together with the molar extinction coefficients of each ion. Thus the relative amounts of the ions, and the optical density of the solution can be determined for any ceric ion concentration in perchloric acid solution. In the remainder of this report Ce^{4+} will be taken to mean ceric ion unassociated with sulphate, regardless of its state of hydrolysis or dimerization. The term ϵ_0, the extinction coefficient of unassociated ceric ion, will be defined by

$$\epsilon_0 = \frac{\epsilon_{Ce^{4+}} C_{Ce^{4+}} + \epsilon_{CeOH^{3+}} C_{CeOH^{3+}} + \epsilon_{(Ce\text{-}O\text{-}Ce)^{6+}} C_{(Ce\text{-}O\text{-}Ce)^{6+}}}{C_{Ce^{4+}} + C_{CeOH^{3+}} + 2\, C_{(Ce\text{-}O\text{-}Ce)^{6+}}} \qquad (1)$$

A small amount of cerous ion was invariably present in all samples, arising from incomplete oxidation of stock cerium solution and/or reduction of ceric ion during dilution. However, under the conditions used in these experiments, cerous ion does not absorb light. There is a possibility that sulphate concentration might be significantly reduced by the formation of a cerous – sulphate complex, but this has been neglected as no correction to equilibrium sulphate concentration from this source seems indicated in the calculation of association constants.

It was not certain whether the ceric sulphate complexes contained hydrogen ion or hydroxyl ion. This was resolved by determining the optical density of ceric ion solutions which had a fixed hydrogen ion to bisulphate ion ratio over a range of acid concentrations. Under these conditions, as bisulphate ion is a weak acid, the sulphate ion concentration remains constant but the bisulphate ion concentration varies. A change in optical density indicates either a change in the relative concentrations of the complexes, i.e. that bisulphate ion entered

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the complex as a unit or that hydroxyl ion is present in the complex. It was found experimentally that negligible change occurred; hence it was concluded that associated ceric sulphate does not contain hydrogen or hydroxyl ions.

The data obtained are required to establish the thermodynamic constants of the following association equilibria:

$$Ce^{4+} + HSO_4^- \rightleftarrows CeSO_4^{++} + H^+$$

$$K_1 = \frac{[CeSO_4^{++}][H^+]}{[Ce^{4+}]\,[HSO_4^-]} \tag{2}$$

$$CeSO_4^{++} + HSO_4^- \rightleftarrows Ce(SO_4)_2 + H^+$$

$$K_2 = \frac{[Ce(SO_4)_2]\,[H^+]}{[CeSO_4^{++}]\,[HSO_4^-]} \tag{3}$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftarrows Ce(SO_4)_3^= + H^+$$

$$K_3 = \frac{[Ce(SO_4)_3^=]\,[H^+]}{[Ce(SO_4)_2]\,[HSO_4^-]} \tag{4}$$

For convenience, the following symbols have been adopted:

C_0, C_1, C_2, and C_3 are the equilibrium concentrations of Ce^{4+}, $CeSO_4^{++}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^=$ respectively and ϵ_0, ϵ_1, ϵ_2, and ϵ_3 are the corresponding molar extinction coefficients. At a particular wave length, the subscript of the wave length in millimicrons will be used, e.g. $\epsilon_{1_{395}}$.

C_T is the total concentration of tetravalent cerium in solution.

S and S_T are the equilibrium and total concentrations of HSO_4^- respectively in solution. At concentrations above 0.1 M HSO_4^- the difference in values between these two quantities is negligible under the conditions of this study.

The equilibrium equations now become

$$K_1 = \frac{C_1[H^+]}{C_0 S} \tag{2a}$$

$$K_2 = \frac{C_2[H^+]}{C_1 S} \tag{3a}$$

$$K_3 = \frac{C_3[H^+]}{C_2 S} \tag{4a}$$

First Complex $Ce(SO_4)^{++}$

A series of solutions was made up in which the total sulphate concentration was maintained at 1.00×10^{-3} M and the total ceric ion concentration varied from 0.16×10^{-3} to 5.2×10^{-3} M. The molar ionic strength Γ was 2.00, and the acidity 1.00 N in all cases. The optical density of these solutions was measured from 395 mμ to 430 mμ in steps of 5 mμ. The optical density of the solutions at 400 mμ is plotted against total ceric ion concentration in Fig. 1.

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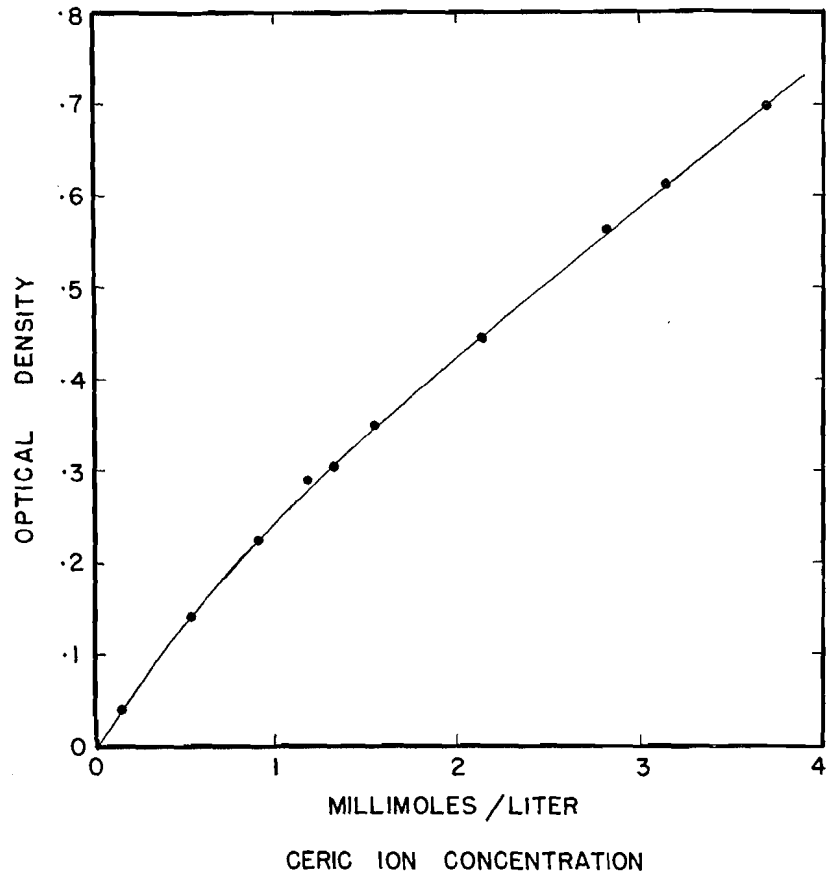

FIG. 1. *Optical density as a function of ceric ion concentration. Total sulphate concentration* $= 1.00 \times 10^{-3}$ *moles/liter.* $[H^+] = 1.00$ *N.* $\lambda = 400$ *mμ.*

From Equation (2*a*)

$$K_1 = \frac{C_1[\mathrm{H}^+]}{(C_T - C_1)(S_T - C_1)} \tag{2b}$$

$$C_1 = \frac{1}{2}\left[\left\{C_T + S_T + \frac{[\mathrm{H}^+]}{K_1}\right\} - \sqrt{\left(C_T + S_T + \frac{[\mathrm{H}^+]}{K_1}\right)^2 - 4C_T S_T}\right] \tag{5}$$

$$D = \Sigma \epsilon_i C_i$$

$$= \epsilon_0 C_T + \frac{1}{2}(\epsilon_1 - \epsilon_0)\left[\left\{C_T + S_T + \frac{[\mathrm{H}^+]}{K_1}\right\} - \sqrt{\left(C + S + \frac{[\mathrm{H}^+]}{K_1}\right)^2 - 4C_T S_T}\right] \tag{6}$$

Direct solution of this equation is not simple. However, by successive approximations values of K_1 and ϵ_1 are obtained which will fit the curve in Fig. 1. This value of K_1 is used to find ϵ_1 values at other wave lengths. Optical den-

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sities calculated from these ϵ_1 values fitted the curves well throughout the whole range of ceric ion concentrations, which demonstrates that K_1 was reasonably well chosen. The values of ϵ_1 are recorded in Table I. The value of K_1 obtained was 3500.

TABLE I

MOLAR EXTINCTION COEFFICIENTS

Wave length mμ	ϵ_0*	$\epsilon CeSO_4^{++}$	$\epsilon Ce(SO_4)_2$	$\epsilon Ce(SO_4)_3^{=}$
430	56	109	246	286
425	67	138	296	358
420	79.3	160	351	441
415	93.5	192	426	546
410	110	228	506	666
405	130	270	608	812
400	153	320	730	982
395	176	383	890	1190

* *Taken from $\bar{\epsilon}$ values for ceric perchlorate solutions at $10^{-3}M$ Ce^{IV}. This includes Ce^{4+}, $CeOH^{3+}$, and $(Ce-O-Ce)^{6+}$ as reported in the previous paper (1).*

In order to check these values, solutions containing sulphate ion ($5\times10^{-4}M$) and excess ceric ion were made up. The measured optical densities were compared with those calculated from the molar extinction coefficients in Table I. The agreement was within 0.6%.

The Higher Complexes $Ce(SO_4)_2$ and $Ce(SO_4)_3^{=}$

The extinction coefficients of the highest complex ϵ_3, may be found by measuring the light absorption of solutions which are low in ceric ion and high in sulphate ion. A series of solutions where $C_T = 1.00 \times 10^{-3}$ M, $[H^+] = 1.00$ M, $\Gamma = 2.00$, and sulphate concentration varied from 0.12 to 0.7 M, were tested in this manner. A plot of optical density against total sulphate ion (Fig. 2) shows that the optical density approaches an asymptote, the value of which is $\epsilon_3 C_T$. The ϵ_3 values are recorded in Table I.

The values for ϵ_2 and K_2 may be determined by assuming that from about 0.12 M sulphate to 0.7 M sulphate the only complexes present are $Ce(SO_4)_2$ and $Ce(SO_4)_3^{=}$. Deviations of the optical density from the value $\epsilon_3 C$ indicate the presence of the second complex. In this region one can assume that $S \cong S_T$. From Equation (4*a*)

$$K_3 = \frac{C_3[H^+]}{(C_T - C_3)S} \tag{7}$$

$$C_3 = \frac{K_3 C_T S}{[H^+] + K_3 S} \tag{8}$$

$$C_2 = C_T - C_3 = \frac{[H^+]\, C_T}{[H^+] + K_3 S} \tag{9}$$

$$D = \epsilon_2 C_2 + \epsilon_3 C_3$$

$$= \epsilon_3 C_T - \frac{[H^+]\, C_T\, (\epsilon_3 - \epsilon_2)}{[H^+] + K_3 S} \tag{10}$$

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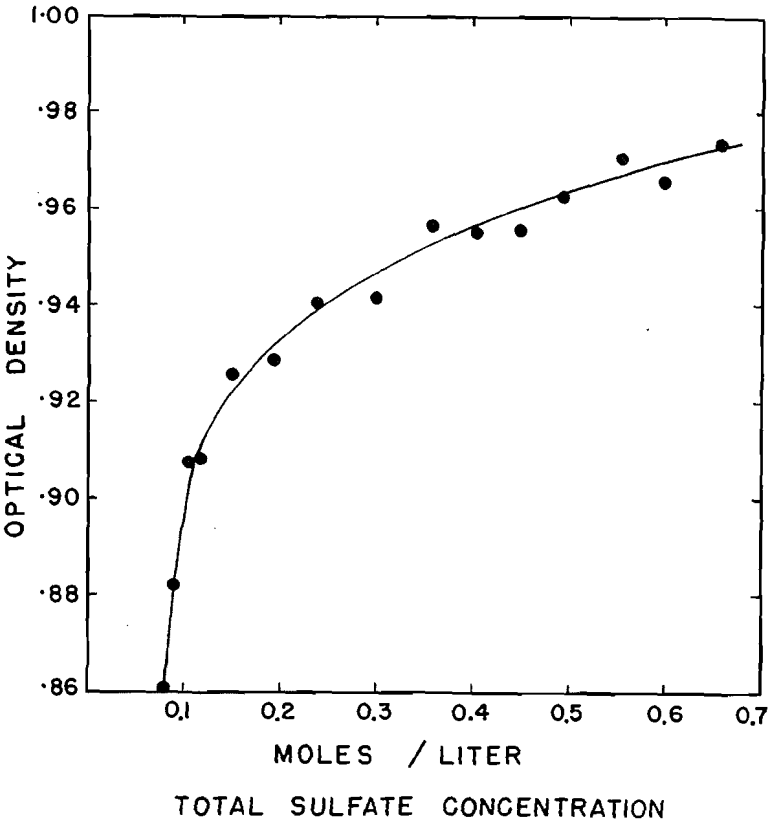

FIG. 2. *Optical density as a function of sulphate ion concentration. Total ceric ion concentration* $= 1.00 \times 10^{-3}$ *moles/liter.* $[H^+] = 1.00$ *N.* $\lambda = 400$ *mμ.*

By successive approximations, values of K_3 and ϵ_2 may be found which will satisfy Equation (10). The value of K_3 is 20; ϵ_2 values are recorded in Table I.

To determine K_2, the optical densities of solutions of the following composition were measured: $C_T = 1.00 \times 10^{-3} M$ $[H^+] = 1.00$ M $\Gamma = 2.00$, and total sulphate was varied from .004 M to 0.12 M. The results are plotted in Fig. 3.

From equation

$$\frac{C_3}{C_2} = \frac{K_3 S}{[H^+]} \tag{4b}$$

and

$$\frac{C_2}{C_1} = \frac{K_2 S}{[H^+]} \tag{3b}$$

one obtains

$$\frac{C_3}{C_1} = \frac{K_2 K_3 S^2}{[H^+]^2} \tag{11}$$

Substituting in $C_T = C_1 + C_2 + C_3$
one obtains

$$C_T = C_1\left(1 + \frac{K_2 S}{[H^+]} + \frac{K_2 K_3 S^2}{[H^+]^2}\right) \tag{12}$$

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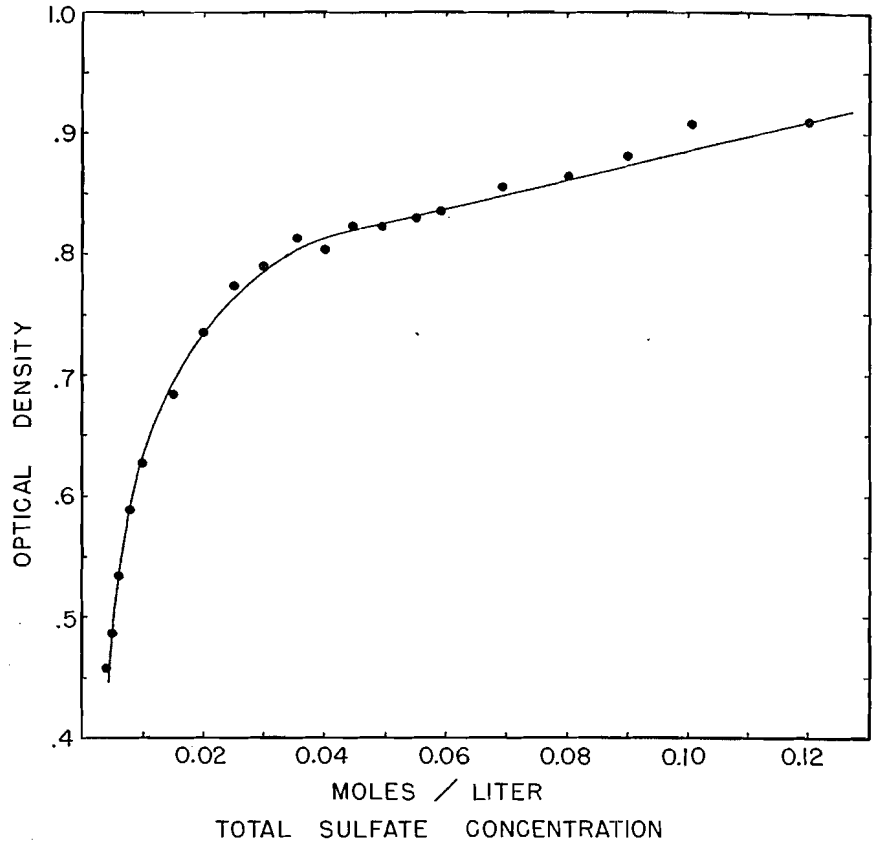

FIG. 3. *Optical density as a function of sulphate ion concentration. Total ceric ion concentration* $= 1.00 \times 10^{-3}$ *moles/liter.* $[H^+] = 1.00$ *N.* $\lambda = 400$ *mμ.*

If a value of K_2 is assumed, then one can calculate C_1, C_2, and C_3, and hence the optical density of the solution. A comparison with the measured optical density indicates the accuracy of the K_2 value chosen. By successive approximation one can obtain a value of K_2 which will give good agreement between measured and calculated optical densities. The value of K_2 determined in this way was 200.

At the sulphate concentrations used for the evaluation of K_2, the amount of sulphate associated with the ceric ion is an appreciable fraction of the total. In Fig. 3 the total sulphate is plotted against optical density. To find the correct optical density, an approximate value of K_2 must be known in order to determine the equilibrium concentration of sulphate. This correction, however, is simply applied as part of the method of successive approximations.

The association constants were calculated from data obtained at 400 and 395 mμ. Fig. 4 shows a comparison of the measured with calculated optical densities as a function of total sulphate concentration. The agreement is good over the whole range. The values of the association constants and extinction coefficients are therefore quite satisfactory.

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In Fig. 5 the fraction of the cerium in each stage of association is plotted as a function of total sulphate concentration. It is not possible to obtain one type of association complex free from the others, except at high sulphate concentrations.

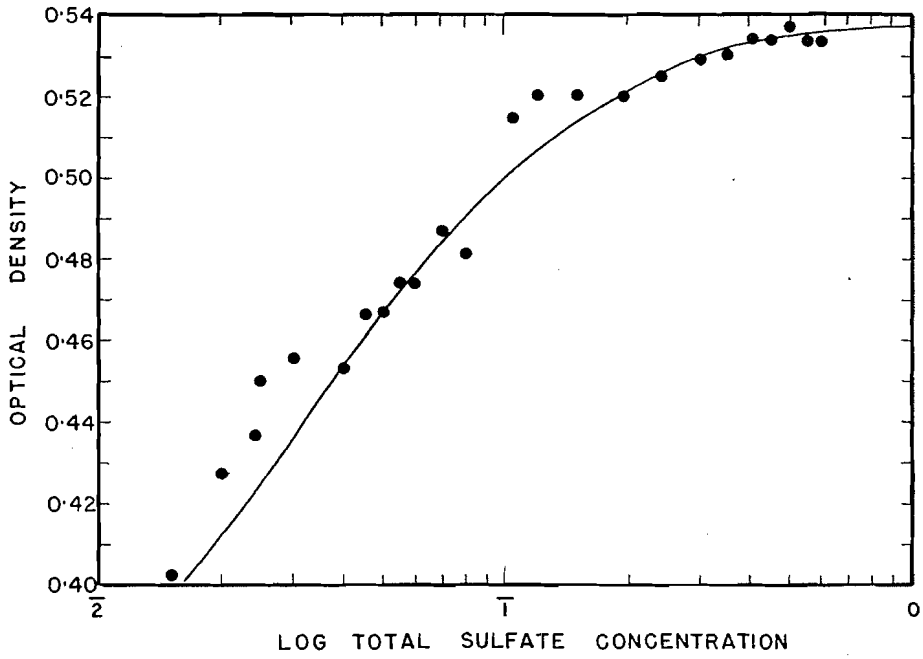

FIG. 4. *Comparison of calculated and measured optical density as a function of total sulphate concentration. Total ceric ion concentration = 1.00 × 10^{-3} moles/liter. $[H^+]$ = 1.00 N. λ = 415 mμ. Straight line represents calculated values; circles, experimental points.*

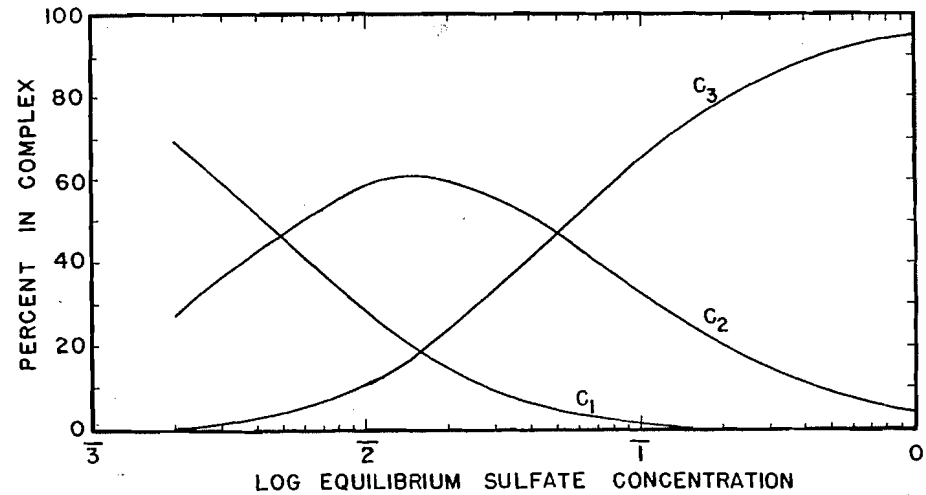

FIG. 5. *Per cent of ceric ion present in each complex as a function of sulphate concentration. Total ceric ion concentration = 1.00 × 10^{-3} moles/liter.*

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Migration Experiments

Qualitative migration experiments were made in order to obtain the charge on the ions at various sulphate concentrations. A three compartment cell with fine sintered glass partitions was used (Fig. 6). In the center compartment a ceric solution was placed $[H^+] = 1.00M$, $\Gamma = 2.00$, $[Ce^{IV}] = 1.00 \times 10^{-3}M$ and containing various amounts of sulphate. In the outer compartments an identical solution was placed, but containing no ceric ion. All liquid levels were equal. Migration was determined by the appearance of color in the outer compartments. A potential of 67 1/2 volts was applied at electrodes placed in the outer cells. The results are found in Table II.

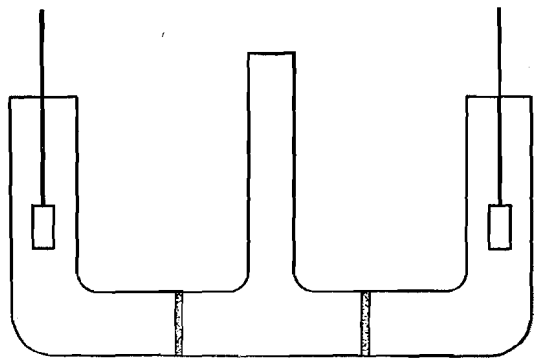

FIG. 6. *Three compartment migration cell.*

TABLE II

RESULTS OF MIGRATION EXPERIMENTS

All solutions $[H^+] = 1.00M$, $\Gamma = 2.00$;			$[Ce^{IV}] = 1.00 \times 10^{-3}M$ (center compartment only)
Soln.	Total conc. of sulphate moles/liter	Natural migration 24 hr.	Induced migration of color, direction
A	.01	None	Mostly towards cathode, small trace towards anode
B	.05	None	Migration both directions
C	.5	None	Towards anode only

These migration experiments are in complete agreement with the spectral results as recorded in Fig. 5. Solution *A* contains mostly $Ce(SO_4)^{++}$ and $Ce(SO_4)_2$ but with a small amount of $Ce(SO_4)_3^{=}$. Solution *B* contains similar amounts of all three forms. Solution *C* contains mostly $Ce(SO_4)_3^{=}$, a little $Ce(SO_4)_2$, but practically no $Ce(SO_4)^{++}$.

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Discussion

It has been shown that ceric ion associates successively with one, two, and three sulphate ions to form complexes. As might be expected, the tendency to associate becomes smaller as the number of sulphate ions in the complex increases. There is no indication that more than three sulphates are ever associated with a ceric ion.

In concentrated ceric sulphate solution, practically all the cerium will be present as $Ce(SO_4)_3^=$. This corresponds to the tendency for ceric ion to form double sulphate salts such as ammonium ceric sulphate $(NH_4)_2Ce(SO_4)_3$.

The data presented in this paper do not agree with that reported by Moore and Anderson (5). We can offer no explanation for this. However, it can be pointed out that those workers used limiting logarithmic and continuous variations methods of analyzing their data, which we find cannot be used with our data, as the associated species overlap one another to such an extent. Furthermore, Moore and Anderson found that solutions of ceric perchlorate obeyed Beer's Law up to 0.01 *M*, whereas the deviations from Beer's Law formed the basis of a complete study in a previous paper (1). It is therefore difficult to reconcile the results from the two studies.

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THE PREPARATION OF ANHYDROUS SODIUM STEARATE[1]

By G. Stainsby,[2] R. Farnand, and I. E. Puddington

Abstract

A method for preparing sodium stearate by the action of sodium amalgam with stearic acid under moisture free conditions is described. From the similar density–temperature behavior of these samples and those prepared by titration of stearic acid followed by melting *in vacuo*, it is concluded that melting under low pressure completely removes the water associated with the sodium ion in soaps.

Previous publications have described dilatometric studies on anhydrous sodium soaps from room temperature to the isotropic liquid state (1, 2, 4, 5). Since these soaps apparently do not melt suddenly but pass through several phases before liquefaction, the studies are of considerable interest. However, the published results have been justifiably criticized on the grounds that the soaps used were not unambiguously anhydrous (3). In most cases the samples were prepared by titration followed by melting *in vacuo* (about 300°C.) to remove the water. It has been considered by Ralston that this treatment is not sufficiently drastic to remove the last traces of water associated with the sodium ion and the same opinion is expressed by Lawrence (2). In view of this it is implied that the peculiar dilatometric behavior of these compounds may be partially due to incomplete dehydration of the samples. The present communication describes a method of preparation which appears to overcome this objection and dilatometric measurements have been made on samples prepared by both methods.

The soap was prepared by the action of sodium on stearic acid in a moisture free atmosphere. The apparatus is shown in Fig. 1 and the preparation was carried out as follows: Prior to assembly, a weighed quantity (5 gm.) of Eastman's white label stearic acid was placed in Flask C (capacity 10 cc.) and mercury in Flasks E and D (capacity 25 and 50 cc. respectively). Clean sodium in large excess of the amount required to neutralize the fatty acid was then placed in A. Tube A was immediately sealed off above the sodium and the pressure inside the apparatus reduced to 10^{-6} mm. The stearic acid was melted and boiled, the sodium melted, the mercury in Flasks E and D boiled, and the remainder of the apparatus strongly flamed.

The sodium was then freed from oxide. This was accomplished by filtering it through the 0.5 mm. capillaries in the column between A and B. Since the assembly could rotate freely about the ground glass joint at F, it was easy to control the flow of the molten sodium from bulb to bulb. Each bulb was sealed off as the sodium passed into the succeeding one. Bulb B was suffi-

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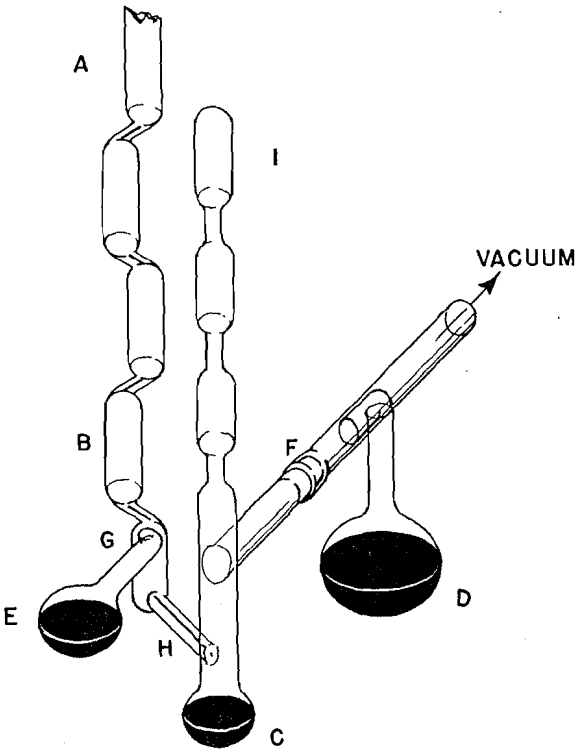

FIG. 1. *Apparatus.*

ciently large to hold about 50% more sodium than required for the neutralization of the acid and it was used as a meter, the excess being sealed off in the previous bulb. Early experiments demonstrated that pure sodium was not suitable for neutralizing the acid. The reaction tended to be too vigorous initially and sodium became trapped in the soap. Further, if the mix were heated too strongly the fatty acid decomposed with considerable blackening. This occurred at temperatures in the vicinity of 300°C.

In order to modify the rate of reaction the sodium was amalgamated in G by distillation in an appropriate volume of mercury from E. The amalgam was then transferred to C and the capillary sealed off at H. Preliminary experiments showed that a good deal of foaming occurred if the reaction were allowed to proceed under the low pressure and to prevent this, an inert gas, dried by passage through a liquid nitrogen trap, was added until the pressure was approximately atmospheric. It has been demonstrated frequently that sodium does not readily react with some acids when the system is completely anhydrous. The reaction between sodium and stearic acid proceeded smoothly under the conditions described above, however, and the temperature was gradually increased, by placing an air bath about Bulb C, until a temperature of about 300°C. was reached and no further hydrogen was evolved. The pressure in the system was then reduced to a hard vacuum and cooled until

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the soap solidified and pulled away from the walls. By rotating the apparatus through 180° and gently tapping it, virtually all of the residual amalgam flowed into I. This bulb was then sealed off and the assembly again rotated through 180° for further washing with fresh mercury.

In some cases if the amalgam were allowed to cool for an extended period either in G or C it formed a solid that was quite difficult to remelt. No difficulty was encountered when the procedure was carried out continuously. Any residue of the amalgam was removed by washing the soap twice with mercury. The mercury was distilled in from D, the inert gas added, and the soap melted as before, followed by the cooling and decanting of the mercury washings into the bulbs below I.

The soap was finally melted and degassed under a hard vacuum. After cooling, mercury was distilled into Flask C until the neck was partially filled. The neck was constricted and cut off, after air was admitted to the system. The remainder of the dilatometer was then sealed on, evacuated, and completely filled with mercury.

Some experiments that were of considerable interest were carried out to obtain information on the thermal stability of the sodium stearate. Soap containing free fatty acid produced water and stearone when highly heated, until the excess acidity was removed. This reaction is easily detected when carried out at low pressure as the water and ketone deposit in separate bands on the cool part of the apparatus. The neutral soap appears to be very stable and, if oxygen is excluded, may be heated for at least 16 hr. at 350°C. with no apparent decomposition. The above decomposition was first noted when an attempt was made to prepare soap with insufficient sodium. No difficulty was encountered when an excess of sodium was used and the reaction kept at 200°–250°C. until substantially complete.

After completing the dilatometric measurements the soap samples were removed, weighed, and analyzed. The results are shown in Table I. The sample prepared using insufficient sodium to react with the stearic acid was neutral but was low in ash and also low in stearic acid when titrated with standard hydrochloric acid. The samples prepared using excess sodium, however, showed no significant departure from the theoretical. These samples were white solids and melted to give liquids with a faint yellow color.

TABLE I

ANALYSIS OF SODIUM STEARATE SAMPLES

Sample	Sodium used	% Ash	M.p. recovered stearic acid	Free acidity or alkalinity
1	Insufficient	15.4	—	Neutral
2	Excess	17.3	68.6	Neutral
4	Excess	17.2	—	Neutral
Theoretical	—	17.3	68.8	

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The volume changes were determined using a weight dilatometer and an air thermostat that could be controlled to better than ± 0.05°C. over the range 25° to 350°C. Calibrated complete immersion thermometers were used to avoid stem corrections. Some difficulty was experienced in obtaining reproducibility in the weight of mercury expelled by the dilatometers at temperatures below 130°C. when the samples were taken to about 300° and then cooled. This seemed to be due to cavitation within the sample, on cooling. To reduce this effect the arms of the dilatometers were extended with 0.5 mm. capillary to give a pressure of about 4 atm. on the samples. Using this device, it was possible to go through the cycle of melting to isotropic liquid and cooling to room temperature several times with no substantial change in the low temperature volume.

For comparison, the density–temperature relations of a sample of sodium stearate prepared by neutralizing an alcoholic solution of stearic acid with alcoholic sodium hydroxide were determined concurrently. The behavior of the samples is shown in Fig. 2, where the weight of mercury (in grams) expelled from the dilatometers is plotted as a function of temperature. Samples 2 and 4 were prepared as described above. Sample 3 was obtained by neutralizing the stearic acid with alcoholic sodium hydroxide. As the same sample weights

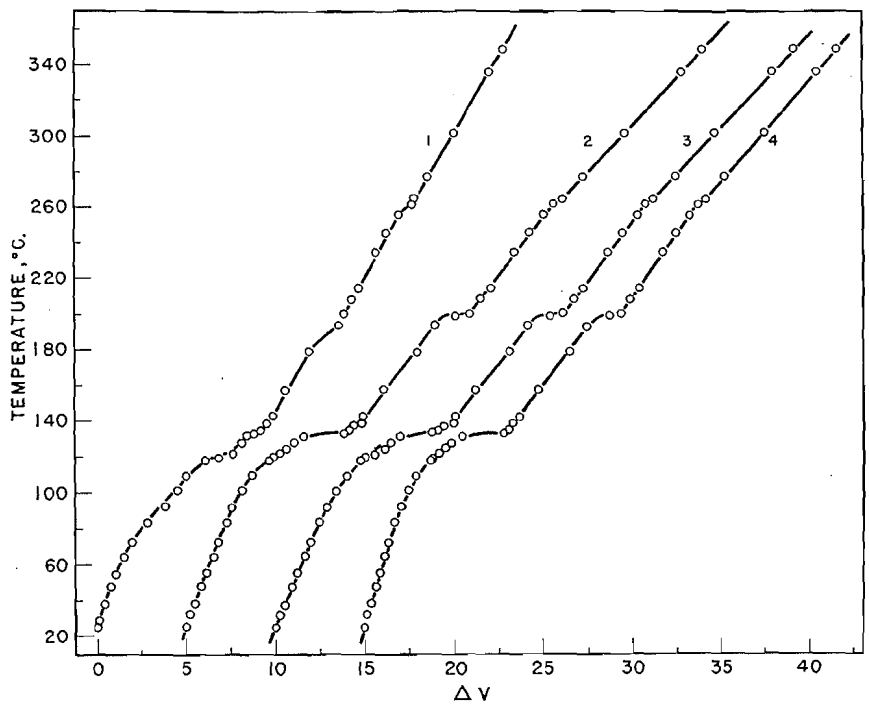

FIG. 2. *Dilatometric behavior of anhydrous sodium stearate. Graphs from left to right represent respectively the behavior of samples prepared (1) from sodium and stearic acid using an excess of stearic acid, (2) from sodium and stearic acid using an excess of sodium, (3) from sodium hydroxide and stearic acid by titration, and (4) from sodium and stearic acid using an excess of sodium.*

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and similar dilatometers were used, the slopes should be comparable. Sample 1 indicates the behavior when insufficient sodium was used in the preparation. The sample weight here is also less than with the other preparations, which accounts for the difference in slope. It would seem probable that the extra points of discontinuity that occur in the graph representing the behavior of this sample are due to the presence of the decomposition products of the excess fatty acid that it contains.

Since the dilatometric behavior of the other three samples appears to be identical, it would seem that melting the soap under low pressure is sufficient to render it anhydrous.

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SYNTHESIS AND ULTRAVIOLET ABSORPTION OF SOME PYRAZOLONES[1]

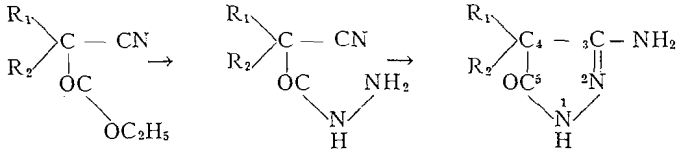
By P. E. Gagnon, B. Nolin,[2] and R. N. Jones

Abstract

Thirteen 3-amino-5-pyrazolones substituted only in position 4 have been synthesized from the corresponding mono- or disubstituted cyanoacethydrazides or cyanoacetic esters in alkaline medium. Their ultraviolet light absorption spectra have been determined in neutral and acid solutions.

Introduction

In 1947, the preparation of 3-amino-5-pyrazolones substituted only in position 4 was reported for the first time (6). The authors prepared substituted cyanoacetic esters (I) and found that the corresponding crude acethydrazides (II) could undergo transformation into 4-substituted-3-amino-5-pyrazolones (III).



I II III

R_1, R_2 = H, alkyl or aryl group

This reaction was recently reinvestigated (1, 2, 3, 4).

In the present work, eight 4-monosubstituted and five 4,4-disubstituted-3-amino-5-pyrazolones were synthesized and their ultraviolet absorption spectra determined.

Experimental

Pyrazolones of both types were soluble in water, acids, and alkalies, and insoluble in ether and sodium bicarbonate solution. The 4 monosubstituted compounds, however, were more soluble in water than the 4,4-disubstituted ones.

They all gave a positive color test with ferric chloride, which is indicative of the presence of an actual or potential hydroxyl group. The nitrous acid test was also positive, indicating the presence of an amino group.

The individual properties are summarized in Table I. Melting points are uncorrected.

[1] *Manuscript received May 21, 1951.*
Contribution from the Department of Chemistry, Laval University, Quebec, and the Division of Chemistry, National Research Council, Ottawa. Published as N.R.C. 2519.
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4-Monosubstituted-3-amino-5-pyrazolones

With the exception of 4-acethydrazide-3-amino-5-pyrazolone, these compounds were prepared by treatment of the corresponding hydrazides (5) with strong alkalies as described in (3).

4-Acethydrazide-3-amino-5-pyrazolone was obtained directly from α-cyanodiethyl succinic ester and hydrazine hydrate. When two equivalents of hydrazine were slowly added to the ester, dissolved in cold ethanol or not, the intermediate dihydrazide could not be isolated but was cyclized into the corresponding pyrazolone.

4, 4-Disubstituted-3-amino-5-pyrazolones

These compounds were prepared by heating disubstituted cyanoacetic esters with hydrazine hydrate in the presence of sodium ethylate. The detailed preparation was reported previously (3).

4,4-Diethyl-3-amino-5-pyrazolone was also obtained by mixing the corresponding ester with hydrazine hydrate at room temperature. The melting points of the sample prepared in both ways were the same and a mixed melting point was not depressed.

The other disubstituted pyrazolones could not be obtained in the latter way.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were determined on a Beckman spectrophotometer Model DU in neutral (95% ethanol) and acid ($N/10$ aqueous hydrochloric acid in 95% ethanol) solutions. The experimental details have been reported previously (6).

TABLE I

PROPERTIES OF INDIVIDUAL PYRAZOLONES

Compound	Formula	M.p., °C.	Analysis		Absorption maxima			
			Nitrogen, %		Neutral solvent		Acid solvent	
			Calc.	Found	Wave length, Å.	Intensity, log E_m	Wave length, Å.	Intensity, log E_m
4-Monosubstituted-3-amino-5-pyrazolones								
4-*n*-Hexyl-	$C_9H_{17}ON_3$	133–135	22.9	22.8	2880	3.58	2820	3.60
4-*n*-Heptyl-	$C_{10}H_{19}ON_3$	136–138	21.3	21.0	2870	3.58	2810	3.60
4-*n*-Decyl-	$C_{13}H_{25}ON_3$	234–235	17.6	17.9	2840	3.59	2770	3.61
4-(2-Ethyl-*n*-butyl)-	$C_9H_{17}ON_3$	190–196	22.9	22.8	2880	3.56	2820	3.57
4-(2-Ethyl-*n*-hexyl)-	$C_{11}H_{21}ON_3$	131–132	19.9	20.2	2890	3.54	2820	3.57
4-Cyclohexyl-	$C_9H_{15}ON_3$	239–241	23.2	23.3	2870	3.57	2820	3.58
4-(α-Naphthylmethyl)-	$C_{14}H_{13}ON_3$	Dec.	17.6	17.8	2950	3.89	2950	3.85*
					2830	4.00	2830	3.99
					2730	3.92	2730	3.92
					2240	4.91	2240	4.89
4-Acethydrazide-	$C_5H_9O_2N_5$	212–213	40.9	41.0	2410	4.16	2320	4.05
4, 4-Disubstituted-3-amino-5-pyrazolones								
4, 4-Dimethyl	$C_5H_9ON_3$	249–251	33.0	33.2	2690	3.69	2610	3.74
4, 4-Diethyl	$C_7H_{13}ON_3$	208–209	27.1	27.2	2710	3.67	2630	3.75
4, 4-Di-*n*-propyl-	$C_9H_{17}ON_3$	236–239	22.9	22.9	2710	3.69	2640	3.71
4, 4-Di-*n*-butyl-	$C_{11}H_{21}ON_3$	223–225	19.9	20.1	2710	3.67	2630	3.71
4, 4-Di-*n*-amyl-	$C_{13}H_{25}ON_3$	200–201	17.6	17.7	2710	3.66	2630	3.66

* *Inflection point.*

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The intensities of the absorption maxima are listed in Table I and representative spectra are plotted in Figs. 1-4.

4-Monosubstituted-3-amino-5-pyrazolones

The spectrum of 4-*n*-hexyl-3-amino-5-pyrazolone (Fig. 1) is representative of those given by the compounds containing alkyl or cyclohexyl substituents at position 4.

The spectrum of 4-(α-naphthylmethyl)-3-amino-5-pyrazolone is dominated by the absorption of the naphthalene chromophore. This is illustrated in Fig. 2

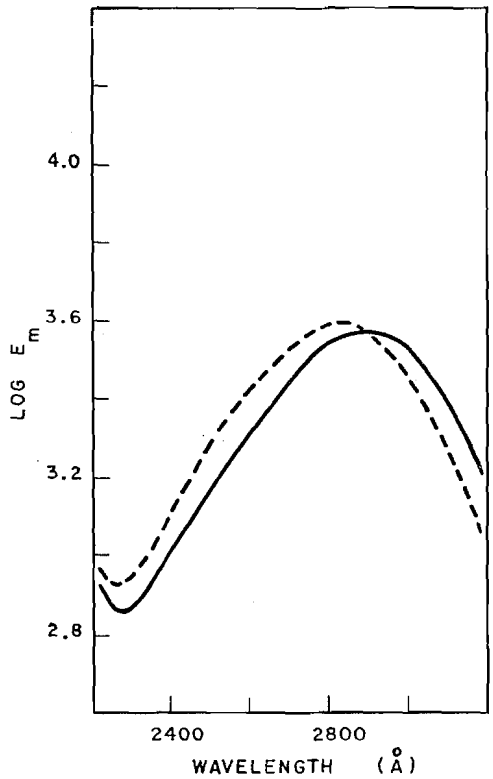

FIG. 1. *Ultraviolet absorption spectra.*
—— *4-n-Hexyl-3-amino-5-pyrazolone (neutral).*
- - - *4-n-Hexyl-3-amino-5-pyrazolone (acid).*

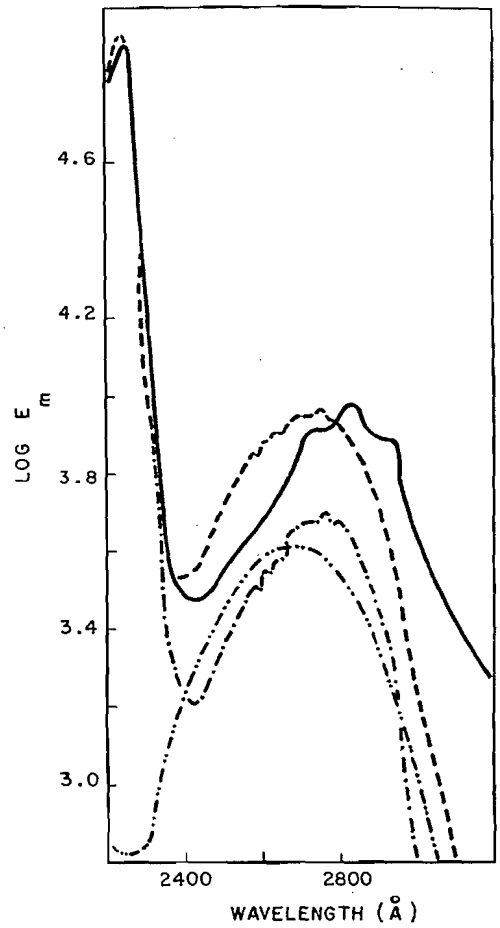

FIG. 2. *Ultraviolet absorption spectra.*
A –·–·– *α-Methylnaphthalene (neutral).*
B ——·—— *4-Methyl-3-amino-5-pyrazolone (neutral). Taken from Ref. 3.*
C - - - - *Calculated curve obtained by addition of Curve A and Curve B.*
D ——— *4-(α-Naphthylmethyl)-3-amino-5-pyrazolone (neutral).*

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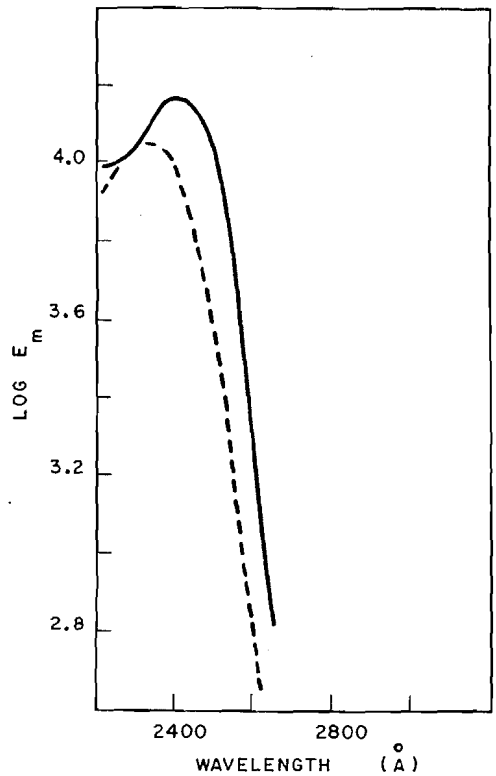

FIG. 3. *Ultraviolet absorption spectra.*
—— *4-Acethydrazide-3-amino-5-pyrazolone (neutral).*
- - - - *4-Acethydrazide-3-amino-5-pyrazolone (acid).*

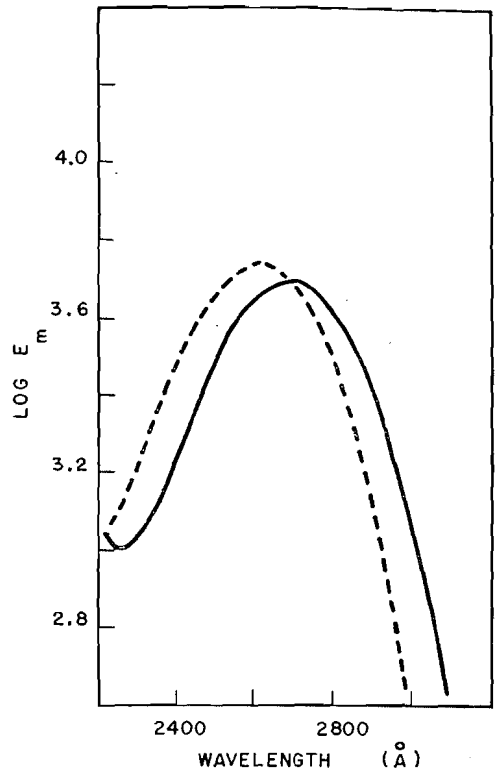

FIG. 4. *Ultraviolet absorption spectra.*
—— *4, 4-Dimethyl-3-amino-5-pyrazolone (neutral).*
- - - - *4, 4-Dimethyl-3-amino-5-pyrazolone (acid).*

where its spectrum is compared with the curve resulting from the addition of the spectrum of α-methylnaphthalene and that of 4-methyl-3-amino-5-pyrazolone (3).

The 4-acethydrazide derivative (Fig. 3) shows an absorption maximum of high intensity at a shorter wave length than those observed for the compounds containing alkyl or cyclohexyl substituents.

4, 4-Disubstituted-3-amino-5-pyrazolones

The spectrum of 4,4-dimethyl-3-amino-5-pyrazolone (Fig. 4) is typical of the spectrometric behavior of all the 4,4-dialkyl derivatives.

Concluding Remarks

The similarity of the spectra of the 4-monoalkyl, 4-cyclohexyl, and 4, 4-dialkyl compounds supports their formulation in terms of the bond structure III in which the cyclic double bond is placed at the 2: 3 position.

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The only effect of the pyrazolone ring on the absorption of 4-(α-naphthylmethyl)-3-amino-5-pyrazolone is to shift the maxima of the naphthalene chromophore towards the visible. Since it cannot be in conjugation with the naphthyl group, its additive contribution to the total absorption of the molecule is negligible.

The spectrum of the 4-acethydrazide pyrazolone is different from those of 4-mono- or 4,4-dialkyl compounds. This is indicative of a difference in the pyrazolone ring since C-alkyl-substituted acethydrazides have been found not to absorb in the same spectral region. It is suggested that the cyclic double bond is at the 3:4 position.

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INFLUENCE OF SHEAR ON THE DIELECTRIC CONSTANT OF LIQUIDS[1]

By B. L. Funt[2] and S. G. Mason[3]

Abstract

The effects of a velocity gradient upon the dielectric constant were studied in solutions of macromolecules, in suspensions and in liquid crystals. Decreases in dielectric constant under shear were observed for polar polymers in polar and nonpolar solvents. For solutions of ethyl cellulose an increase in dielectric constant was obtained. Nonpolar polymers showed no changes of dielectric constant under shear. Large changes in dielectric constant at low rates of shear were observed in carbon black suspensions. The experimental results are discussed on the basis of particle orientation in a velocity gradient and in an electric field.

Introduction

The behavior of asymmetric molecules subjected to external electrical and mechanical forces is of considerable interest. If the molecules are geometrically asymmetric it is reasonable to predict that, in solution, they would become oriented when subjected to a sufficiently high rate of shear. The hydrodynamic principles governing this type of orientation have been extensively investigated for particles of idealized shape in dilute solutions (1). Furthermore, the phenomenon of non-Newtonian viscosity has been predicted from theoretical considerations for systems in which orientation in a velocity gradient occurs (1). A system is considered to be non-Newtonian when the apparent viscosity is a function of the rate of shear at which it is measured. Such behavior, particularly when manifested as thixotropy, is common in solutions of macromolecules and in colloidal systems (3).

An extremely convincing manifestation of the orientation of geometrically asymmetric particles when they are subjected to shear is indicated optically (2). A solution of long-chain cylindrically shaped molecules is normally isotropic. When such a system is subjected to a sufficiently high rate of shear it becomes optically anisotropic, and the phenomenon is termed streaming birefringence.

If, in addition to being geometrically asymmetric, a molecule is also electrically asymmetric, another type of orientation can occur. A molecule possessing a permanent dipole moment will tend to align itself when placed in an electric field. The extent of the electrical orientation can be determined by measurement of the dielectric constant of the material.

It was the purpose of this investigation to determine the interplay of these two possible types of orientation in suitable molecular systems. In particular,

[1] *Manuscript received April 3, 1951.*
Contribution from Chemistry Department, McGill University, Montreal, Que. This work was conducted with the financial assistance of the Defence Research Board.
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[3] *Honorary Lecturer, Department of Chemistry, McGill University.*

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it was thought that, if these two types of orientation opposed one another, a decrease in dielectric constant might be found experimentally, whereas if the orientations were additive, an increase in dielectric constant would be found.

Although orientation cannot be considered the only factor responsible for non-Newtonian behavior, nor indeed for streaming birefringence, it was felt that measurements of the dielectric constant under shear could, in principle, yield useful information regarding these phenomena and the structure of molecular systems. Small but definite changes in some of the systems studied were noted, but for reasons discussed later the interpretation is difficult.

Apparatus

A General Radio type 716C Schering bridge was used for the electrical measurements. The bridge was fed by a Hewlett–Packard audio-frequency oscillator. The null point was determined on an oscilloscope fed from the bridge through an intermediate amplifier and phase shifting network. This arrangement permitted rapid, simultaneous balance of the resistive and capacitative components of the test condenser. A reproducibility of .03 $\mu\mu$f. in measuring 1000 $\mu\mu$f. was obtainable.

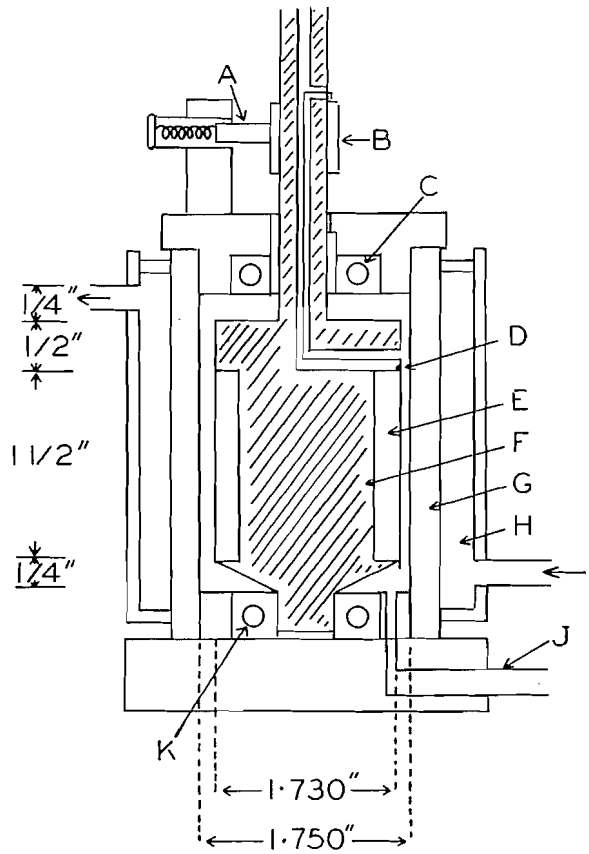

FIG. 1. *Rotating cylindrical condenser.*

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The design of rotating condensers suitable for the proposed measurements presented difficulties. The dimensions and design had to fulfil, amongst others, the requirements of (1) absence of variation in capacitance of greater than 0.2% during rotation, (2) a suitable capacitance and shear gradient, and (3) absence of turbulent flow at the highest rates of shear employed.

Several rotating condensers were used in this work. All were of the coaxial cylindrical type with the inner cyclinder rotating and were designed to avoid the possibility of drawing in air. One of the models used is shown in Fig. 1. Here A and B are the contact brush and contact ring; C, K are ball bearings; E is a brass sleeve on an insulating bakelite shaft, F. G indicates the outer brass cylinder, H the water jacket, and J the filling vent.

Results

Polymers in Nonpolar Solvents

Changes in dielectric constant were found when solutions of polar polymers in nonpolar solvents were subjected to shear.

In Fig. 2 are shown the changes in dielectric constant with shear for ethyl cellulose and polyvinyl acetate in benzene at 10 Kc. The polyvinyl acetate solutions were of two molecular weights commercially designated as Gelva V-15 and V-200. The percentage concentrations, expressed as gm. per 100 ml. of solvent, were 15% for the ethyl cellulose and Gelva V-200, and 30% for the Gelva V-15.

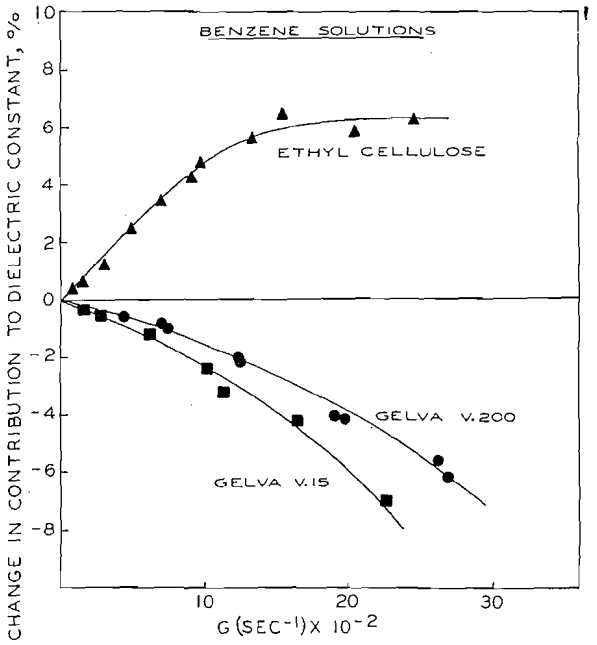

FIG. 2. *Change of dielectric constant with rate of shear for solutions of ethyl cellulose and polyvinyl acetate. Measurements were carried out at 10 Kc.*

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The rate of shear, G, is expressed as $G = R\frac{d\omega}{dR}$ in units of reciprocal seconds. Here ω is the angular velocity of the liquid at the radial distance R.

The changes in dielectric constant are expressed as percentage changes by the relationship

$$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$$

where $\Delta\epsilon$ is the dielectric constant change under shear, ϵ_s is the rest value of the dielectric constant of the solution, and ϵ_0 is the dielectric constant of the pure solvent.

After rotation ceased, the dielectric constants returned to their original values, as shown in Fig. 3.

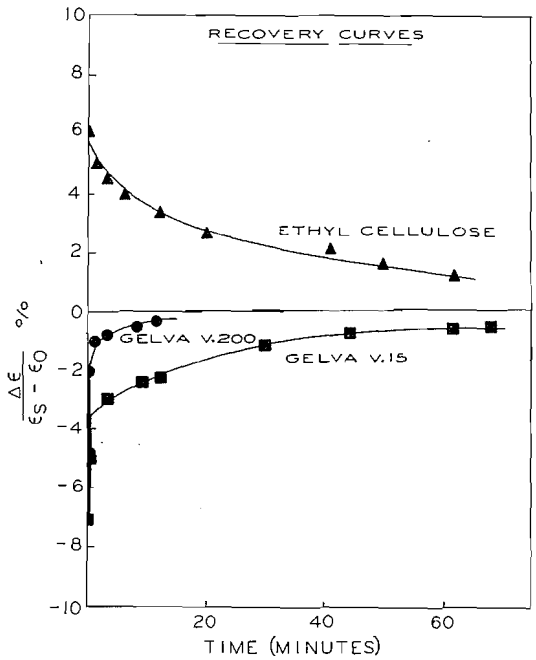

FIG. 3. *Recovery of dielectric constant in quiescent solutions after shearing at 2500 sec.*$^{-1}$.

Polar Polymers in Polar Solvents

Some of the polymer samples would not dissolve in nonpolar solvents. Although the use of polar solvents introduced theoretical complications, some measurements were made on such systems. Table I shows some results obtained for solutions at a 10% concentration.

Nonpolar Polymers in Nonpolar Solvents

Systems of nonpolar polymers in nonpolar solvents would not be expected to show changes in dielectric constant due to orientation. Voet (8), however,

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TABLE I

POLAR POLYMERS IN POLAR SOLVENTS

A. CELLULOSE ACETATE BUTYRATE IN CHLOROFORM.
B. CELLULOSE ACETATE IN 1:2 BUTYL ACETATE: TOLUENE.
C. POLYVINYL FORMAL IN CHLOROFORM.

A		B		C	
G(sec.$^{-1}$)	$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$	G(sec.$^{-1}$)	$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$	G(sec.$^{-1}$)	$\frac{\Delta\epsilon}{\epsilon_s - \epsilon_0} \times 100$
200	− 3.6	200	− 2.2	172	− 2.6
286	− 9.0	389	− 5.6	286	− 5.1
400	−15.3	572	−10.0	400	− 9.8
515	−20.6	800	−13.3	515	−14.9
600	−29.3			685	−18.9
715	−36.0	1141	−22.2	943	−28.9
858	−42.4	1370	−24.4	1030	−49.0
1060	−57.0	1695	−27.8	1200	−63.6

reported changes in the dielectric constants of solutions of polystyrene and polyisobutylene in toluene when these solutions were subjected to shear.

Our investigations of these systems failed to show any change of the dielectric constant under shear. It is also significant that the values of the dielectric constant determined for the solutions at rest differed markedly from those reported (8). Our measurements showed a linear relationship between the dielectric constant and the concentration expressed in volume per cent for these solutions. This contrasted with the sharp rise of the static dielectric constant reported after a critical concentration was reached (9).

Our data at 10 Kc., at 30°C. are shown in Fig. 4 for solutions of polystyrene of varying concentrations in toluene. Although samples of molecular weights of 10-13 × 10^3, 35-40 × 10^3, 65-70 × 10^3, and 100 × 10^3 were used, the experimental points plotted fall on a straight line. This is in essential

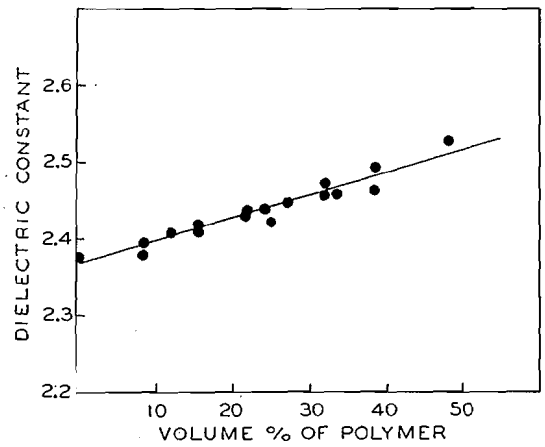

FIG. 4. *Variation with concentration of rest dielectric constants of polystyrene of varying mol. wt. in toluene.*

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agreement with the Debye theory*. Our results have recently been mentioned by Voet in a subsequent note of correction (9).

Carbon Black Suspensions

In view of the marked discrepancy between our results on polymer solutions and those of Voet (7), it was of interest to check Voet's earlier measurements on the effect of shear on the dielectric constant of carbon black–mineral oil suspensions. A sample of printing ink obtained from the Canada Printing Ink Co. was used.

In this system large changes in dielectric constant were obtained at very low rates of shear. Changes in dielectric constant five times as great as those observed in polymer solutions were obtained at rates of shear 1/100th as great as those employed with the polymer solutions. Significant changes in the dielectric constant were observed at a rate of shear of less than 1 sec.$^{-1}$.

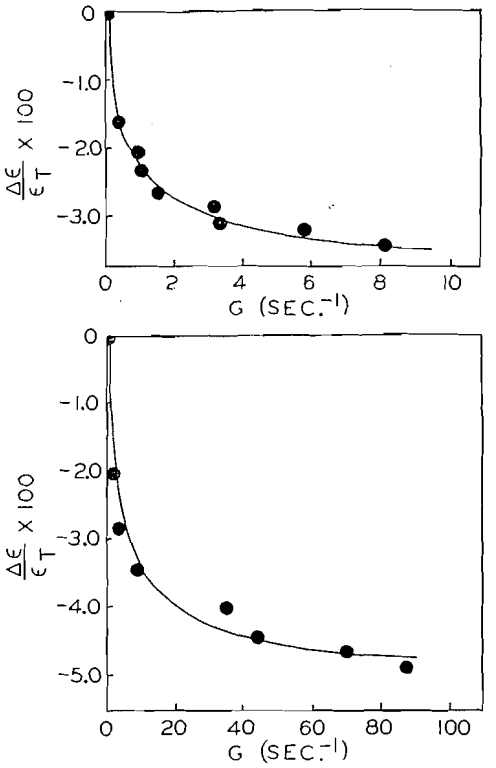

FIG. 5. *Effect of rate of shear upon the dielectric constant of carbon black printing ink. Note in the upper curve the large effect at low rates of shear.*

The data exhibited an exponential relationship between the decrease in dielectric constant and rate of shear. Fig. 5 shows some of the results obtained. The results are expressed as percentage changes: $\Delta\epsilon$ represents the change in dielectric constant under shear, and ϵ_T the total dielectric constant of the suspension at rest.

* *(Added in proof.) P. Debye and F. Bueche. J. Phys. & Colloid Chem. 55: 235. 1951, have recently reported substantially the same results as those in Fig. 4.*

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Liquid Crystals

The anisotropy of liquid crystals in their transition region is well known. It therefore seemed worthwhile to investigate whether a change in dielectric constant under shear occurred in these systems, and for this purpose *p*-azoxyanisole was used. The sample possessed a melting point of 117°C. and a transition point of 132°C.

Dielectric measurements under shear were carried out at 100 and 300 Kc. at temperatures of 122°C. It was not found possible to work at lower frequencies or lower temperatures. At lower frequencies the high conductance of the liquid crystals interfered with the measurements of the dielectric constant. At lower temperatures difficulties were encountered owing to the freezing of the crystals in the bearings of the rotating condenser.

Nevertheless, the measurements were performed in the transition region, and near the melting point of the crystals. On subjecting the system to shear it was found that the bridge balance was disturbed. A careful analysis of many measurements, however, showed that the effect was due to a change in the conductance and that no significant change in the true capacitance of the system occurred up to velocity gradients of 1500 $sec.^{-1}$. It was therefore concluded that the oriented groups were too small to be affected by the shear gradients employed.

Discussion

The results, in general, support the picture of orientation in a shear gradient opposing the orientation in an electric field. For nonpolar polymers where no orientation in an electric field was to be expected no changes were observed.

It should be noted that, with one exception, all systems in which any change in dielectric constant occurred showed decreases in dielectric constant under shear. With ethyl cellulose in benzene, however, an increase in dielectric constant with increasing rate of shear was observed. This would indicate that the orienting effects of the electric field and of the mechanical shear were supplementary. Such a condition could exist if the polar groups of ethyl cellulose were perpendicular to the long axis of the molecules.

It is obvious from the experimental results that the picture is complicated by factors other than orientation. The slow return of the dielectric constant to its original value after rotation had ceased is shown in Fig. 3. If orientation were the only factor, the recovery would, in principle, have been instantaneous. This slow recovery, similar to that often observed for viscosity, probably arises from molecular interaction. Since polymer concentrations of from 10 to 30 gm. per 100 ml. of solvent had to be employed to obtain sufficient sensitivity of measurement, a high degree of particle interaction could be expected.

Under such conditions, considerations of photoelastic behavior may be applicable. For an amorphous linear polymer the mechanical effect of a stress

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is shown in a series of retarded elastic effects in addition to the instantaneous elastic response. The total elastic strain is thus a function of time as well as of stress (4).

The instantaneous response can be regarded as resulting from an elastic strain. By analogy with the photoelastic phenomena this corresponds to a general stretching, with neighboring atoms being pulled apart slightly. This introduces a degree of anisotropy which would be evident as a double refraction corresponding to a change of refractive index in two directions perpendicular to one another. Similarly it can be regarded as giving rise to two dielectric constants perpendicular to one another, of slightly differing magnitudes.

The retarded photoelastic response is regarded as resulting from a time dependent segmental diffusion of the polymer chains. An uncurling and orientation of the polymer chains gives rise to further configurational strains and leads to additional anisotropy. The most significant of such configurational strains is believed to be due to orientation of relatively short segments of molecular chains.

We thus see that, as with streaming birefringence or photoelastic behavior, we may regard the changes in dielectric constant under shear as due to partial orientation of polymeric chains. Although the phenomenon of streaming birefringence lends itself to simpler theoretical treatment, the photoelastic effect seems to offer a basis for a more complete explanation of the experimental data.

Ostwald's conception of "strukturviskositat" (5, 6) appears to support the above views. As an example, the shearing of a dispersion of elastically deformable particles will produce a change in particle shape which will make flow progressively easier, and hence lower the viscosity. The particles need not be elastic. They may be polar and tend, when the system is at rest, to orientate themselves into some type of ordered structure which has to be destroyed before flow can take place. When the stress is removed the particles recover their original orientation. If this recovery is relatively slow, thixotropic behavior may be observed.

With suspensions of carbon black the changes in dielectric constant under shear were very pronounced. The results confirm Voet's work (8) on such systems, and the interpretation is probably best approached as suggested by him. In essence the latter's "agglomeration factor" can be regarded as derived from Ostwald's concept of structural viscosity due to the formation of molecular aggregates.

Acknowledgment

We wish to express our indebtedness to Miss Ruth Seidman for preparation of the sample of *p*-azoxyanisole.

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INFLUENCE OF ALCOHOLS UPON THE UNCATALYZED REACTION BETWEEN RESORCINOL AND FORMALDEHYDE[1]

By R. A. V. Raff[2] and B. H. Silverman[3]

Abstract

The rate of the condensation of an uncatalyzed, equimolecular solution of resorcinol and formaldehyde in water was determined at 60°C. By replacing a portion of the water in this system with aliphatic alcohols, a reduction in the rates of condensation was noted at the same temperature. However, these reaction rates were found to vary widely among themselves, depending on the alcohol used. These results are explained under the assumption of the intermediate formation of hemiacetals from the free formaldehyde and the alcohols. The retarding effect of these alcohols on the resorcinol–formaldehyde condensation is inversely related to their different tendency to form esters with acids, or acetals with aldehydes, as reported by other authors. The general importance of the formation of hemiacetals is emphasized where formaldehyde is applied in the presence of alcohols.

Discussion of Previous Experiments

Previous work (15) on the kinetics of the uncatalyzed reaction of resorcinol and formaldehyde had shown the considerably higher reactivity of resorcinol as compared to phenol and to alkylated monophenols. For the various temperatures and the different ratios of resorcinol to formaldehyde which were investigated, a first order reaction rate constant served best to represent the experimental data. These condensations had been studied on solutions of resorcinol in dioxane and water, to which the calculated amounts of aqueous formaldehyde solutions were added. The charges were prepared in such a way that the combined weights of resorcinol plus formaldehyde (as CH_2O) represented 40% of the total weight of the solutions; the dioxane amounted to 26.7%; 33.3% water was present, partially introduced as part of the aqueous formaldehyde solution. These mixtures were reacted in a resin flask kept in a constant temperature bath, and the progress of the reaction determined from the gradual decrease in free formaldehyde on samples removed during the experiment.

Influence of Solvents

Since it appeared of interest to learn the influence of solvents upon the reaction rate of the uncatalyzed resorcinol–formaldehyde condensation, equimolecular mixtures of resorcinol and formaldehyde were reacted at 60°C., in which the dioxane in the above formulation was replaced by various aliphatic alcohols. One experiment was also carried out in an all aqueous medium, replacing the dioxane by water. As found in dioxane, a first order reaction rate constant served best to represent the experimental data.

[1] *Manuscript received May 21, 1951.*
Contribution from the Mellon Institute of Industrial Research, Pittsburgh, Pa. (Multiple Fellowship on Special Resins, Koppers Company, Inc.).
Paper presented before the third Canadian High Polymer Forum in Kingston, Ont., on May 24, 1951.
[2] *Senior Fellow at Mellon Institute, Pittsburgh, Pa.*
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The solvents used, together with their densities and viscosities, are given in Table I, in the order of increasing reaction rate constants. The values for the pH's obtained for the reaction mixtures at the start and at the end of each experiment are shown to have remained practically unchanged.

Comparing the reaction rate of the condensation in water with the reaction rates obtained in the presence of the various alcohols, the retarding effect of the latter on the condensation rate is quite pronounced. A comparison of the alcohols among themselves shows that their retarding effect decreases from methyl alcohol to normal propyl alcohol, and still further to isopropyl alcohol and tertiary butyl alcohol.

These facts suggest the connection between the retarding effect of these alcohols on the condensation reaction and their molecular structures, involving the reactivity of the alcoholic hydroxyl groups.

Comparison with Esterification Reaction

A reaction of alcohols which is known to involve the alcoholic hydroxyl group and to be dependent upon the structure of the alcohol is the esterification reaction.

Kailan and coworkers (5,6,7,8,9,10) measured the esterification of a number of alcohols in a large surplus of different acids by determining the changes in the melting points of the mixtures during the reaction. Reaction rate constants obtained in measuring the uncatalyzed esterification of the alcohols with which the present work is concerned, in formic and acetic acids, are shown in Table I. From these data it appears that the more easily an alcohol is esterfied, the more it retards the uncatalyzed resorcinol–formaldehyde condensation.

Comparison with Acetalization Reaction

Considering that, according to the accepted modern mechanism, the rate-controlling step in the esterification of carboxylic acids is the addition of the alcohol to the carboxylic carbonyl group, this indirect relationship between the retarding effect of the alcohols upon the condensation reaction and their tendency to form esters suggests the possibility that the alcohols take part in the resorcinol–formaldehyde condensation by forming intermediates with the free formaldehyde. The greater the reactivity of the hydroxyl group in an alcohol, the greater should be its tendency to bind temporarily the free formaldehyde, and the greater its retarding effect upon the resorcinol–formaldehyde condensation.

Reaction products between alcohols and aldehydes are known as acetals and hemiacetals. As far as the formation of acetals is concerned, a comparison of data by Minné and Adkins (13) actually indicates that the conversion to acetals from the various alcohols and acetaldehyde decreases with the tendency of the alcohols to retard the uncatalyzed resorcinol–formaldehyde condensation. This is shown in Table I and graphically represented in Fig. 1.

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TABLE I

COMPARISON OF DATA ON SOLVENTS

Solvent				Resorcinol–formaldehyde condensation			Esterification		Acetal	
Name	Formula	Density $\left(\frac{(20°)}{(4°)}\right)$	Viscosity (c.p.s., 25°)	$K \times 10^4$	pH		K in formic acid	$K \times 10^4$ in acetic acid	Formation K** with acetaldehyde(13)	Hydrolysis $K \times 10^3$ acidic(17)
					Initial	Final				
Methyl alcohol	CH_3-OH	0.791	0.547	2.7	3.52	3.46	Not measured	$12.3_{(8)}$	2.41, 1.95	1.53
Ethyl alcohol	CH_3-CH_2-OH	0.789	1.096	$4.7_{(*)}$	3.45	3.45	$6.5_{(7)}$	$8.4_{(8)}$	1.40, 1.21	13.0
Normal propyl alcohol	$CH_3-CH_2-CH_2-OH$	0.803	1.967	5.3	3.55	3.53	$6.0_{(7)}$	$9.4_{(8)}$	1.06	14.4
Allyl alcohol	$CH_2=CH-CH_2-OH$	0.855	1.215	5.7	3.62	3.58	$3.4_{(5)}$	$4.6_{(10)}$	0.84	Not measured
Iso propyl alcohol	$(CH_3)_2CH-OH$	0.783	2.06	7.5	3.51	3.53	$1.8_{(7)}$	$2.1_{(9)}$	0.10, 0.11	72.3
Tert. butyl alcohol	$(CH_3)_3C-OH$	0.789	4.47	8.6	4.00	3.72	$0.8_{(6)}$	Not measured	0.015, 0.019	Not measured
Water	$H-OH$	0.998	0.894	25.0	3.48	3.43	—	—	—	—

(*) *The corresponding value for phenol has been determined as* $K = 4.5 \times 10^{-5}$. ****Equilibrium constant.*

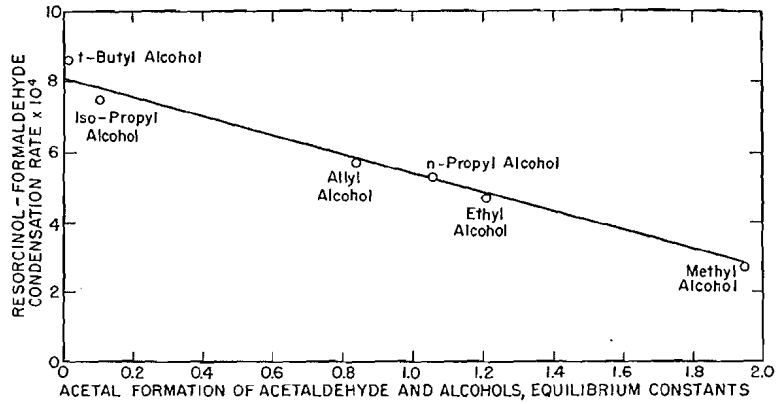

FIG. 1. *Rates of resorcinol—formaldehyde condensation vs. equilibrium constants for acetal formation.*

Accordingly, there appears to be a direct relationship between the data given by Skrabal and Eger (17, 12) on the acidic saponification of the acetals of some of the alcohols under discussion and their retarding effect. The slower the hydrolysis of an acetal, the greater the retarding effect of the related alcohol on the uncatalyzed resorcinol–formaldehyde condensation. This is borne out by the data shown in Table I and in Fig. 2.

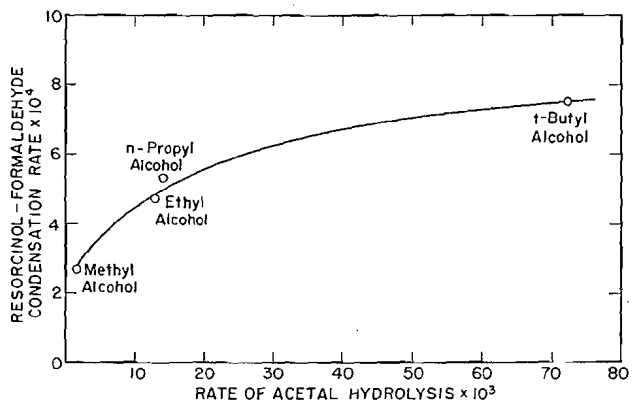

FIG. 2. *Rates of resorcinol—formaldehyde condensation vs. rates of acetal hydrolysis.*

Intermediate Formation of Hemiacetals as the Rate Governing Factor

Although evidence makes it seem likely that the intermediate reaction of formaldehyde with the alcohols is the rate governing reaction when the uncatalyzed resorcinol–formaldehyde condensation is carried out in the presence of these alcohols, the question of whether acetals or hemiacetals are the intermediates remains open.

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To decide between these two possibilities, an experiment was carried out in which an attempt was made to react resorcinol in water by adding formal (methylal), as the source of formaldehyde. Since hardly any condensation reaction took place under this condition, the acetal appears too stable a compound under the prevailing reaction conditions to occur as an intermediate product.

On the other hand, if "Methyl Formcel" (Celanese Corporation of America), a hemiacetal of methanol and formaldehyde, was used as a potential source of formaldehyde in uncatalyzed condensations with resorcinol, the condensation proceeded at the same speed as if the formaldehyde had been added in its free state as an aqueous solution.

It may, therefore, be concluded that hemiacetals and not acetals are the intermediate products if the uncatalyzed resorcinol–formaldehyde condensation is carried out in the presence of alcohols.

Literature Review on Hemiacetals

The formation of hemiacetals from alcohols and acetaldehyde was postulated from refractive indices and densities of such mixtures by Adkins and Broderick (1), and by Schimmel & Co. (16). Abnormalities in the ultraviolet absorption spectra of alcohols and aqueous solutions of carbonyl compounds were assumed by Herold (3) to be due to hemiacetal formation. The extent of this reaction was estimated from absorption measurements and linked with the molecular structure of both components. These ideas were further developed in a paper by Grabowsky and Herold (2) where the reaction mechanism of the hemiacetal formation is discussed on the basis of absorption measurements of alcohol and aldehyde solutions in inert solvents. Hemiacetal formation is considered by Mueller (14) as an intermediate step in the acetal formation and explained by the distribution of the electrons in the aldehyde. Herold and Wolf (4) measured the rate of hemiacetal formation in several aldehyde–alcohol systems by ultraviolet absorption experiments. With propionaldehyde, the rate of reaction was found to decrease in the order: methyl alcohol, ethyl alcohol, butyl alcohol, leading to equilibria containing increasing amounts of aldehyde. These results agree basically with the fact that methanol has a stronger retarding effect on the uncatalyzed resorcinol–formaldehyde condensation than ethanol. Whereas Herold and Wolf found the acetaldehyde–methanol reaction to proceed too rapidly for exact measurements by their method, Lauder (11) investigated this system at 0°C. by the use of a refractometer. He concludes that a reversible reaction, first order in each direction, occurs on mixing the reagents, and assumes that an equilibrium is set up between an alcoholate and the hemiacetal,

such as $CH_3CHO.CH_3OH \rightleftharpoons CH_3 - CH\begin{matrix}\diagup OCH_3 \\ \diagdown OH\end{matrix}$.

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General Remarks

Aldehydes, particularly formaldehyde, are widely applied in the presence of alcoholic solvents. The moderating influence of alcohols in such reactions, the extent of which differs depending on their structure, has only been recognized in isolated cases, although it must be assumed to be of general occurrence and validity. It may be expected that such systems can be further modified by any variation in the amount of water present and by changes in the pH under which such reactions are carried out.

Acknowledgment

Thanks are due to Mr. C. D. Isack[1] for his assistance in the preparation of this paper. The support of this work by Koppers Company. Inc. and the permission by Dr. G. F. D'Alelio, Vice President of Koppers Company, Inc. to publish it are gratefully acknowledged.

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[1]*Research Associate at Mellon Institute, Pittsburgh, Pa.*

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ELECTRONIC INTERPRETATION OF THE UNCATALYZED REACTION BETWEEN RESORCINOL AND FORMALDEHYDE IN ALCOHOLS AND DIOXANE[1]

By A. R. Ingram[2]

Abstract

The condensation of resorcinol and formaldehyde in aqueous alcohols and dioxane is interpreted on the basis of competing electrophilic reactions of the hydroxymethyl carbonium ion with the resorcinol aromatic ring and with the oxygen atoms of the resorcinol and the solvents. The reaction of the carbonium ion and the alcohol groups leads to oxonium ions which may then form hemiacetals.

Introduction

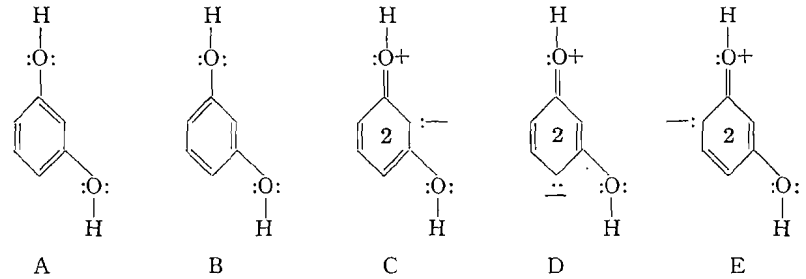
Raff and Silverman (15, 16) have determined the reaction rates of equimolar proportions of resorcinol and formaldehyde in water and in the aqueous solutions of dioxane, methyl alcohol, ethyl alcohol, normal-propyl alcohol, allyl alcohol, iso-propyl alcohol, and tertiary-butyl alcohol, at 60°C. and at pH values lying within the range of 3.5 to 4.0. The organic solvents were found to retard the condensation of resorcinol and formaldehyde and the effect of the alcohols was attributed to their reversible formation of hemiacetals with the formaldehyde.

In this paper an attempt is made to interpret all the reactions involved in terms of the electronic theory of acids and bases (1, 8, 10).

Resonance in Molecular and Ionic Resorcinol

A consideration of the most probable resonance structures of resorcinol is important in order to visualize the electronic distribution responsible for reaction.

(*a*) Un-ionized resorcinol



[1] *Manuscript received May 21, 1951.*
Contribution from the Mellon Institute of Industrial Research, Pittsburgh, Pa. (Multiple Fellowship on Special Resins, Koppers Company, Inc.).
[2] *Fellow at Mellon Institute of Industrial Research, Pittsburgh, Pa.*

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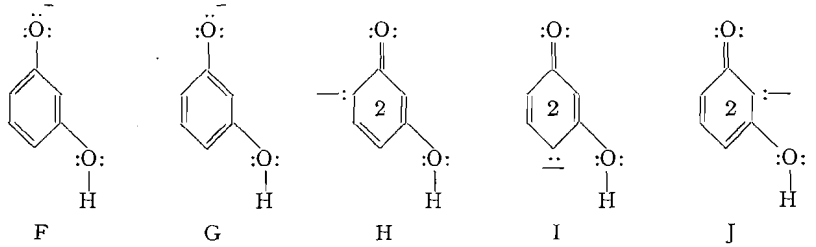
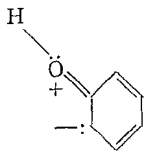
(*b*) Singly charged resorcinolate ion

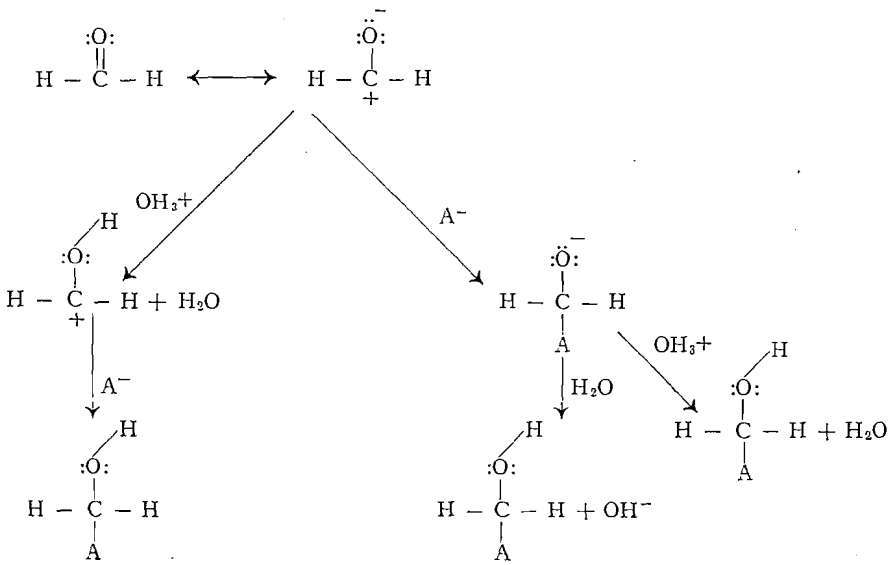


F G H I J

In the system under investigation it is believed that the resorcinolate ion structures represent best the resonance picture for the reactive resorcinol molecule involved in nuclear condensation with formaldehyde. According to Pauling (14), the resonance structures of phenol which involve separated charges such as  are much less stable than the conventional Kekulé structure and contribute only a small amount, 7 kcal. per mole to resonance energy. On the other hand, the resonance energy of the phenolate ion, corresponding to structures F through J with $-H$ in place of $-OH$, is about 8 kcal. per mole greater than that for un-ionized phenol.

Formation and Reaction of Formaldehyde Carbonium Ion

Formaldehyde contains an extremely reactive carbonyl group, capable of reacting with centers of high electron density. In neutral or slightly acid media, these reactions are probable:



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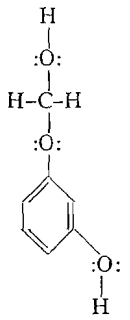
Reaction of Formaldehyde with Resorcinol at the Negative Oxygen Atom in the Resorcinol Ion

Where A^- is the resorcinolate ion, the formaldehyde may make an electrophilic attack at the phenolate oxygen of F or G or at the nucleophilic centers on H, I, or J. The reaction at the phenolate oxygen would then yield the monohemiformal of resorcinol, K.

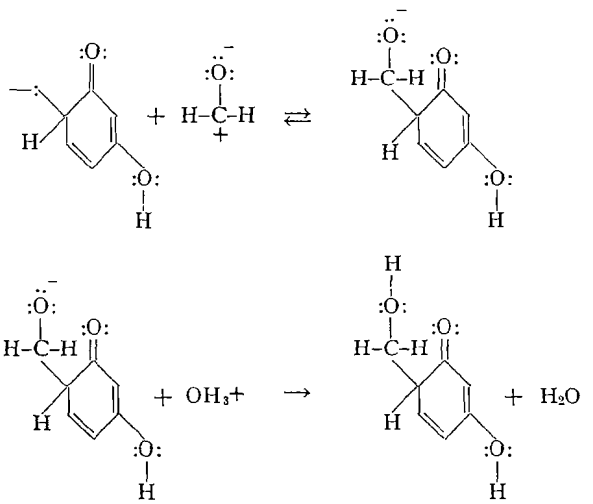


(K)

According to some authors (e.g. 2, 17) the hydroxymethyl group in the phenyl hemiformal, corresponding to K, may migrate to the ring. However, the hemiformal of phenol, because of its instability, has never been isolated.

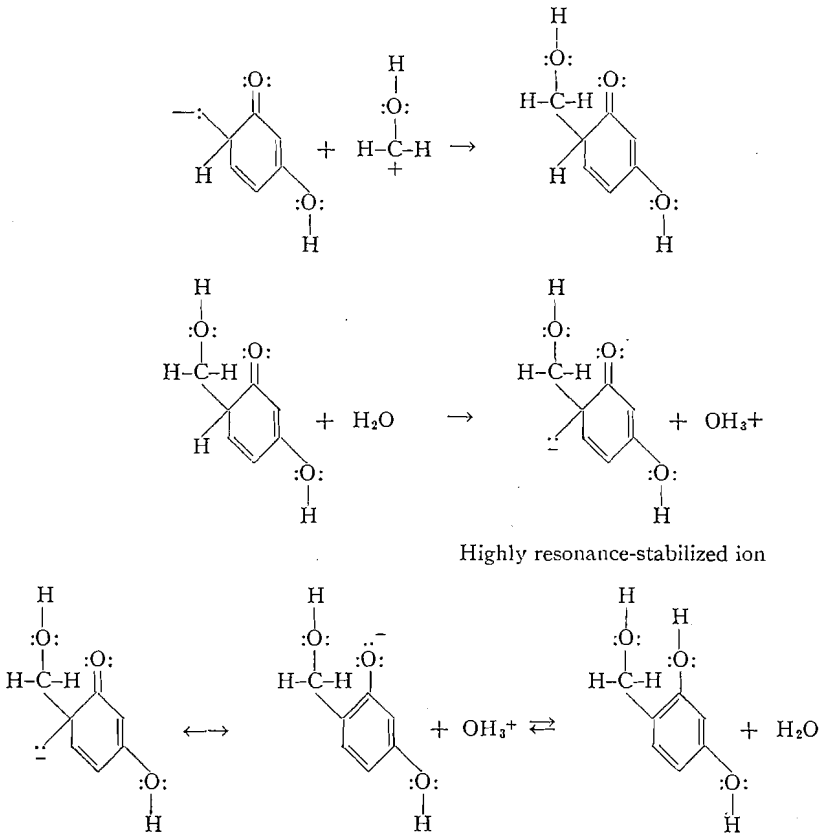
Reaction of Formaldehyde Directly on the Aromatic Ring

Since the attack of the carbonyl group in formaldehyde can occur directly on the electronegative 6-, 4-, or 2-positions in the stable electronic structures, H, I, and J (see below), the postulation of the hemiformal, K, as the important intermediate in the mechanism of nuclear hydroxymethylation seems unessential. The resorcinolate ion, H, is considered to react with formaldehyde as follows:



Strong base

Slightly resonance-stabilized neutralization product

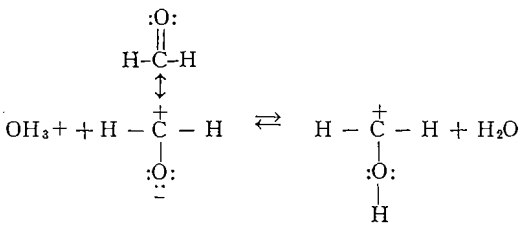


Highly resonance-stabilized ion

Effect of pH on Reaction Mechanism

It should be pointed out that the acidity of the system affects the mechanism by shifting the following two equilibria:

$$H_2O + \text{resorcinol} \rightleftarrows [\text{resorcinolate ion}]^- + OH_3^+$$



Thus, in strongly acid media, the concentration of resorcinolate ion will greatly diminish, but on the other hand the concentration of the hydroxymethyl carbonium ion will increase. In strongly basic media, the resorcinolate ion concentration will increase, and the carbonium ion concentration will decrease. Hultzsch (4) has presented a mechanism for strongly acid catalyzed conden-

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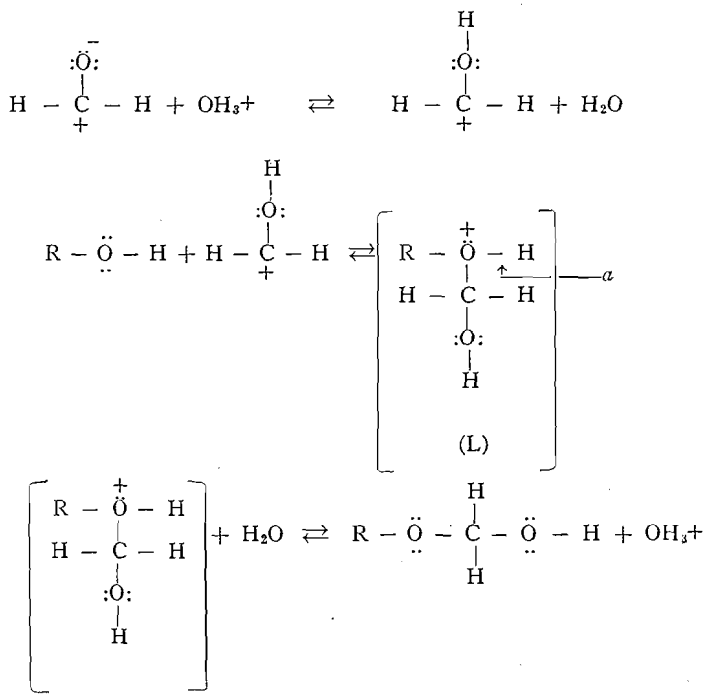
sation of phenol which involves the polarized form of the phenol (such as C through E for resorcinol) as the intermediate reacting through the aromatic nucleus with the carbonium ion ($H-\overset{OH}{\overset{|}{\underset{+}{C}}}-H$). In alkaline media Hultzsch proposes an attack of the negative spots of the phenolate ion on the polarized carbonyl bond of formaldehyde.

Since the reactions studied by Raff and Silverman were carried out in mildly acid media, it is felt that the resonance stabilized ionic structure of resorcinol should play an important role in reacting with formaldehyde either as a carbonium ion or as a polarized carbonyl compound.

Retarding of Resorcinol–Formaldehyde Condensation by Alcohols

If there are added to the aqueous reaction medium, compounds such as alcohols or dioxane which have an electron sharing capacity due to the free electrons on the oxygen atoms, these compounds will then compete with the resorcinolate ion or molecular resorcinol for reaction with the formaldehyde. The reaction of alcohols was recognized by Raff and Silverman (16) as the reversible formation of a hemiacetal, equations for which are given below for reaction under mildly acid conditions:



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It should be pointed out that R-O-H in the above mechanism includes not only the alcohol added to modify the resorcinol reaction but also represents resorcinol itself which is also competing with the resorcinolate ion. Reversible formation of hemiacetals, therefore, is felt to take place between resorcinol and formaldehyde as well as between the added alcohol and formaldehyde.

The mechanism of hemiacetal formation, according to Müller (12), involved splitting the alcohol into H^+ and OR^-, arising from a hydrogen bonding between the alcoholic hydrogen and the oxygen of the carbonyl group. The H^+ and OR^- then added to the carbonyl group. However, it seems much more plausible that the carbonyl group would first add the readily available proton originating from the free acid, thus giving rise to a carbonium ion which would attack the alcoholic oxygen to give a loosely bound oxonium ion, which could in turn eliminate a proton to form the hemiacetal.

The tendency of an alcohol to form an acetal should be indirectly proportional to its electron releasing effect in the direction of the oxygen–hydrogen bond, *a*, in the oxonium complex L. The electron releasing power of the alkyl groups of the alcohols investigated are given in order of the decreasing electron releasing tendency:

$$(CH_3)_3C- \rangle (CH_3)_2\overset{H}{C}- \rangle CH_2=\overset{H}{C}-\overset{H_2}{C}- \rangle CH_3-\overset{H_2}{C}-\overset{H_2}{C}- \rangle CH_3-\overset{H_2}{C}- \rangle CH_3-.$$

This series is in the order of decreasing chain length, branching on the number one carbon, and unsaturation—all factors believed to contribute to electron release. From this series it would be expected that methanol would have the greatest tendency to form acetals and would retard the resorcinol–formaldehyde reaction the greatest. When the rate constants for the condensation of resorcinol and formaldehyde in the various alcohols were plotted by Raff and Silverman against the equilibrium constants of acetal formation as determined by Minné and Adkins (11), a remarkably precise linear inverse relationship was obtained. Other alcohol reaction rates such as those observed in reactions with acids (5, 6, 7), acid chlorides (13), or isocyanates (3) were similarly related to the resorcinol–formaldehyde condensation rate in the given alcohol. These reactions all involve rupture of the O-H bond. The data are summarized in Table I.

TABLE I

RELATION BETWEEN ALCOHOL MODIFIED RESORCINOL–FORMALDEHYDE REACTION AND REACTIVITY OF THE ALCOHOLS

R–	Relative equilibrium constants	Relative rates			Rate constant $\times 10^4$
	A	B	C	D	RFK
CH_3-	1	1	1	1	2.6
C_2H_5-	0.555	0.459	0.96	0.68	4.7
$n-C_3H_7-$	0.486	0.358	0.78	0.76	5.3
$H_2C=\overset{H}{C}-\overset{H_2}{C}-$	0.385	0.372	..	..	5.7
$i-C_3H_7-$	0.046	0.0549	0.31	0.17	7.3
$t-C_4H_9$	0.008	0.0147	0.0032	Not determined	8.6

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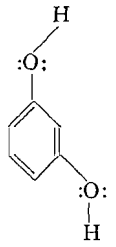
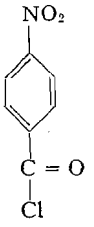
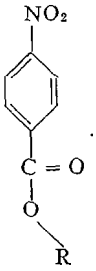
RFK:  + $CH_2O \xrightarrow[H_2O]{ROH}$ (16)

A: $2ROH + CH_3CHO \underset{25°C.}{\leftrightharpoons} CH_3 - \underset{\underset{R}{|O|}}{\overset{H}{\overset{|}{C}}} - OR + H_2O$ (11)

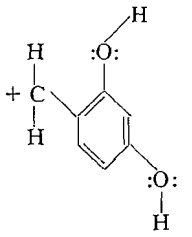
B: $ROH + HO - \overset{O}{\overset{\|}{C}} - CH_3 \overset{25°C.}{\leftrightharpoons} R - O - \underset{O}{\overset{\|}{C}} - CH_3 + H_2O$ (5, 6, 7)

C: ROH +  $\underset{25°C.}{\overset{ether}{\rightleftarrows}}$  HCl (13)

D: $ROH + C_6H_5 - N = C = O \underset{25°C.}{\overset{C_6H_6}{\rightleftarrows}} R - O - \underset{O}{\overset{\|}{C}} - \underset{H}{N} - C_6H_5$ (3)

Effect of Alcohols on Polymeric Chain Growth

The further condensation of the methylol resorcinol with either another methylol group or an electronegative unsubstituted 2-, 4-, or 6- position would involve, according to Lilley (9) or Hultzsch (4), electrophilic attack by the carbonium ion arising from the methylol group, i.e.



Alcohols present here would solvate this carbonium ion to give an oxonium complex, thereby retarding the chain growth of the resorcinol–formaldehyde polymer.

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Retarding of Condensation by Dioxane and *t*-Butyl Alcohol Where Hemiacetal Formation is Restricted

Raff and Silverman did not attempt to explain in their papers (15, 16) the retarding effect of aqueous dioxane on the condensation of resorcinol and formaldehyde. Since dioxane is probably too stable to be ruptured by formaldehyde under these conditions, a chemical reaction in this sense is unlikely. However, the condensation rate was decreased from 25.0 to 10.5 by the addition of dioxane. Since dioxane is known to give stable oxonium compounds, Raff has previously suggested that this effect might be due to the formation of an oxonium compound with formaldehyde at the carbonium ion.

Since *t*-butyl alcohol exhibits practically no tendency to form acetals or to undergo other reactions involving a rupture of the oxygen to hydrogen bond, it would be expected, like dioxane, to retard the resorcinol–formaldehyde reaction mostly by reason of an oxonium complex ion like L. It is interesting to point out that the first order resorcinol–formaldehyde condensation rate in dioxane is 10.5×10^{-4}, compared to 8.6×10^{-4} for *t*-butyl alcohol.

Acknowledgment

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COMPONENT FATTY ACIDS OF RAPESEED OIL[1]

By C. G. Youngs, T. M. Mallard, B. M. Craig, and H. R. Sallans

Abstract

The fatty acid composition of the oil from Argentine rapeseed grown in Western Canada was investigated by converting the glyceride esters to methyl esters and distilling the latter in a Podbielniak Heligrid distillation column. Analyses of the fractions showed 6 to 10% more eicosenoic acid and 7 to 10% less erucic acid than was previously reported for rapeseed oils.

The compositions of rapeseed and other Cruciferae oils have been the subject of a number of investigations in recent years (1, 2, 3, 4, 5, 6) and erucic, oleic, linoleic, and linolenic acids have been established as major constituents in these oils. Hopkins (5) first showed the presence of eicosenoic acid in hare's-ear mustard oil and more recent work (2, 6) has confirmed the presence of this acid in rapeseed oil.

Hydrolysis of rapeseed oil liberates acids which differ both in chain length and in degree of unsaturation. A complete fatty acid analysis requires an initial separation on the basis of chain length or unsaturation. A number of workers have obtained partial separation by distillation of the methyl or ethyl esters and further analyses were based on heart cuts of these fractions. Norris and Terry (7) indicated that the Podbielniak Heligrid distillation unit (8) effected nearly complete separation of these esters. A similar unit was used in the present investigation.

Rapeseed oil obtained from Prairie Vegetable Oils Ltd., Moose Jaw, Sask., was alkali refined and bleached to give a clear golden yellow oil.

The methyl esters were first prepared according to the following conventional procedure. The oil was saponified with alcoholic potassium hydroxide and the fatty acids were liberated with sulphuric acid. The fatty acids were washed free of mineral acid and converted to the methyl esters by refluxing with methanol containing 1% of concentrated sulphuric acid. The yields obtained varied from 88 to 96%, with a free fatty acid content of 1 to 2%. Quantitative recovery (99.4%) of the acids as their methyl esters was, however, obtained by converting the soaps to methyl esters with dimethyl sulphate (10). The free fatty acid content of the product was 0.2%. The esters prepared by the dimethyl sulphate procedure were divided into two portions, one of which was hydrogenated to an iodine value of 0.3 units. A small amount (0.02%) of N.D.G.A. was added to the nonhydrogenated esters prior to distillation.

A Podbielniak Heligrid distillation unit with a 25 mm. by 3 ft. column was used for the distillation. The column was operated at a head pressure of 10 mm.,

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a pressure drop across the column of 10 mm., and a reflux setting of 15 to 1. Adiabatic conditions were closely approached by covering the vacuum jacket of the column with an electrically heated mantle maintained at a temperature just below that at the head of the column.

The analytical values of the original oils and esters are given in Table I. Fig. 1 shows the distillation curves for the hydrogenated and nonhydrogenated esters prepared by the dimethyl sulphate procedure. Cuts between the fractions were made at the beginning of each transition. The material which distilled over during each transition represented about 1% of the total sample. The weights per cent of the corresponding fractions of hydrogenated and nonhydrogenated esters agreed within 0.3%, indicating that there was negligible carry over of the unsaturated esters due to association. The first three fractions, the C_{16}, C_{18}, and C_{20} esters, were collected and the pot fraction was assumed to be C_{22} esters.

TABLE I

ANALYTICAL VALUES OF OIL AND ESTERS

	Original oil	Conventional esters		Original oil	Dimethyl sulphate esters	
		Found	Calc.*		Found	Calc.*
Iodine value	105.1	104.6	104.7	104.7	103.9	104.2
Saponification value		175.8		174.3	174.0	173.8
Unsaponifiable, %	0.7	0.7	0.7	0.8	0.8	0.8
Linolenic, %	9.2	9.2	9.2	8.7	8.5	8.7
Linoleic, %	15.1	14.5	15.1	15.7	15.7	15.7
Yield of esters, %		88	100		99.4	100
Free fatty acid, %		0.8	0		0.2	0

* *Calculated from the values found for the original oil.*

The analytical values of the distilled fractions of the esters prepared both by the conventional and dimethyl sulphate procedures are given in Table II. The diene and triene acids were determined by ultraviolet analysis (9), using a Beckmann Model DU spectrophotometer. Iodine values were measured by the Wijs method with one-half hour reaction time. Weights per cent and saponification values for fractions from the hydrogenated esters are included in Table II for comparison. In Table III the weighted totals of the analytical values found for the distilled fractions are compared to the values for the original esters. A small amount of destruction of the diene and triene acids occurred during the distillation, which was verified by the slight decrease in iodine value. The amounts destroyed were of the order of 0.5% which would not materially affect the final acid analysis.

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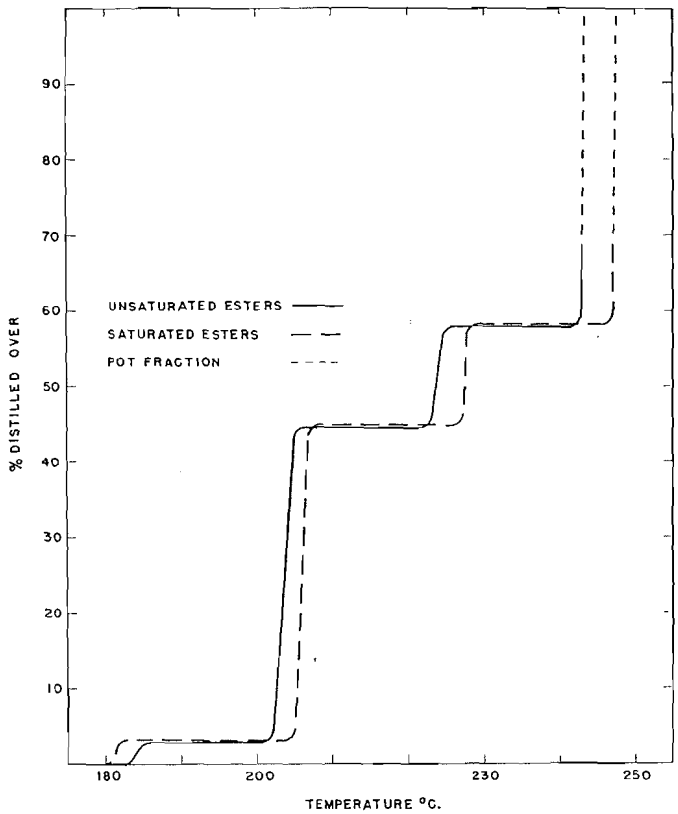

FIG. 1. *Distillation curves for hydrogenated and nonhydrogenated methyl esters of rapeseed oil prepared by dimethyl sulphate procedure.*

TABLE II

ANALYTICAL VALUES OF DISTILLED FRACTIONS

	Weight %	Iodine value	Saponification value	Triene acid, %	Diene acid, %
Fraction 1					
Conventional	2.7	23.3	208.7	3.4	1.4
$(Me)_2SO_4$	2.9	23.3	206.7	3.8	3.2
Hydrogenated	3.1	–	208.6	–	–
Fraction 2					
Conventional	41.2	145.5	191.2	18.7	33.1
$(Me)_2SO_4$	41.5	145.9	189.9	19.2	33.1
Hydrogenated	41.7	–	187.8	–	–
Fraction 3					
Conventional	13.7	87.1	175.7	4.6	4.1
$(Me)_2SO_4$	13.4	83.2	173.5	2.4	5.1
Hydrogenated	13.3	–	171.8	–	–
Fraction 4					
Conventional	42.4	74.2	156.6	–	0.9
$(Me)_2SO_4$	42.2	73.9	156.2	–	1.6
Hydrogenated	41.9	–	154.8	–	–

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TABLE III

COMPARISON OF PROPERTIES OF ORIGINAL ESTERS WITH SUMMATION OF DISTILLED FRACTIONS

Property	Dimethyl sulphate		Conventional	
	Original esters	Total from fractions	Original esters	Total from fractions
Iodine value	103.9	103.6	104.6	104.0
Saponification value	174.0	174.0	175.8	174.9
Diene acid, %	15.69	15.19	14.50	14.50
Triene acid, %	8.54	8.41	9.20	8.40
Naturally conj. diene	0.21	0.40	0.26	0.45
Naturally conj. triene	0.16	0.02	0.02	0.01

Table IV summarizes the distribution of the acids in the four fractions on the basis of the whole oil. Diene and triene acids in Fractions 1 and 3 were considered to be linoleic and linolenic acids which carried over from Fraction 2. The diene acid in Fraction 4 was considered to be docosadienoic acid. The amounts carried over in all cases were small on the basis of the whole sample, so that carry over of acids other than linoleic and linolenic was neglected. The monoethenoid acids in Fractions 1, 2, 3, and 4 were taken as hexadecenoic, oleic, eicosenoic, and erucic, respectively. The amount of each acid was calculated from the iodine value of the fraction and the diene and triene acid content. The saturated acids, palmitic, stearic, arachidic, and behenic were

TABLE IV

DISTRIBUTION OF THE ACIDS IN FRACTIONS

	Percentages*									
	Fraction 1		Fraction 2		Fraction 3		Fraction 4		Total	
Fatty acid	Conven.	Me_2SO_4	Conven.	Me_2SO_4	Conven.	Me_2SO_4	Conven.	Me_2SO_4	Conven.	Me_2SO_4
Palmitic	2.1	2.4							2.1	2.4
Hexadecenoic	0.3	0.2							0.3	0.2
Linoleic		0.1	13.6	13.7	0.6	0.7			14.2	14.5
Linolenic	0.1	0.1	7.7	8.0	0.6	0.3	0.8	.008	9.2	8.4
Oleic			15.7	15.4					15.7	15.4
Stearic			2.3	2.5					2.3	2.5
Arachidic					0.7	0.8			0.7	0.8
Eicosenoic					11.2	11.0			11.2	11.0
Behenic							0.9	1.3	0.9	1.3
Erucic							37.8	37.6	37.8	37.6
Docosadienoic							0.4	0.7	0.4	0.7
Unsaponifiable							1.8	1.9	0.7	0.8

* *Calculated on the basis of whole oil.*

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determined by difference. Small amounts of lignoceric acid have been reported in rapeseed oil by Hilditch (2) and Kapur (6). In view of the small amount of saturated acid in Fraction 4 no attempt was made to establish the presence of this acid.

The values in Table IV were calculated to a fatty acid basis and are compared in Table V to data reported by Hilditch (2) and by Kapur (6) for other rapeseed oils. The erucic acid content is 7 to 10% lower and the eicosenoic acid content 6 to 10% higher in the present investigation. The value for eicosenoic acid is of the same magnitude as that reported by Hopkins (5) for hare's-ear mustard seed oil.

TABLE V

COMPARISON OF FATTY ACID COMPOSITIONS OF RAPESEED OIL

Acid	Hilditch(2)	Kapur(6)	Present investigation*	
			Conventional	Me_2SO_4
Myristic		0.6		
Palmitic	2.6	1.0	2.2	2.5
Hexadecenoic	0.6		0.3	0.2
Stearic	1.0	0.2	2.4	2.6
Oleic	16.0	17.7	16.6	16.3
Linoleic	12.5	13.8	15.0	15.3
Linolenic	9.9	9.1	9.7	8.9
Arachidic	0.6	0.4	0.7	0.8
Eicosenoic	6.0	3.1	11.8	11.6
Behenic	2.1	2.6	1.0	1.4
Erucic	47.3	50.4	39.9	39.7
Docosadienoic	0.9		0.4	0.6
Lignoceric	0.5	1.2		

* *Calculated to fatty acid basis.*

The close agreement between the fatty acid analysis of the esters prepared by the two methods indicates that although only an 88% yield was obtained by the conventional procedure a representative sample of esters was obtained. The presence of unsaturated acids did not appreciably affect the separation obtained by fractional distillation as shown by the weight per cent of corresponding fractions from the hydrogenated and nonhydrogenated esters. This, coupled with the small loss of diene and triene acids, would indicate an error in the final analysis of less than 1% for the major constituent acids.

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THE ADDITION COMPOUNDS OF SILICON TETRACHLORIDE AND AMINES[1]

By W. R. Trost

Abstract

Addition compounds formed between silicon tetrachloride and some amines have been prepared and analyzed. Molecular ratios of 4/1, 2/1, and 1/1 were established for amine to silicon tetrachloride in these compounds. It is suggested that these molecular compounds use 4*s*, 3*d*, 4*p* orbitals only, in forming the coordinate bonds that establish the compound, and that the configuration of the silicon tetrachloride remains essentially undisturbed. Use of these assumptions permits definite structural predictions to be made about the compounds.

In preliminary experiments with silicon tetrachloride and amines, the formation of addition compounds was noted whenever an amine was mixed with silicon tetrachloride. The following amines were used: diethylamine, triethylamine, butylamine, dibutylamine, tributylamine, piperidine, morpholine, ethanolamine, diethanolamine, pryridine, dimethylaniline, and aniline. When silicon tetrachloride was added to excess amine, in the ratio of 1/10 by volume, a voluminous usually white precipitate formed, extensive enough to transform the liquid mixture into a grease. When amines were added to excess silicon tetrachloride, in the ratio of 1/10 by volume, colored solids (frequently yellow) precipitated from the colorless liquid. These exothermic reactions occurred as rapidly as the mixing process, but the large heat of reaction varied considerably, seeming to decrease with the strength of the base and with the number of hydrogen atoms on the amine nitrogen. The compounds, once formed, could be kept indefinitely with no further change.

Of these compounds, those derived from pyridine, aniline, and dimethylaniline could be most conveniently analyzed.

Experimental

The addition compounds of pyridine, aniline, and dimethylaniline with silicon tetrachloride were prepared by mixing equimolar solutions of the amines and the chloride with each other in varying ratios by volume. The reactants, with petrol ether or benzene as solvents, were kept as cold as was possible without a change in phase. Because they react with moist air, the molecular compounds that formed were analyzed in the solvent. They were also analyzed as dry solids, for these could be recovered by filtering and washing the precipitates in an atmosphere of nitrogen, followed by complete drying *in vacuo*. The same analytical method was used for the analyses of the addition compounds, whether they were dry solids, or were still immersed in anhydrous solvent.

[1] *Manuscript received June 6, 1951.*
Contribution from the Department of Chemistry, Dalhousie University, Halifax, Canada, with financial assistance from the National Research Council of Canada.

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Analysis

The addition compounds decompose in dilute aqueous acid giving silica, hydrochloric acid, and the acid salt of the amine.

$$SiCl_4.(NR_3)_n + nH^+ + 2H_2O \rightarrow SiO_2 + 4HCl + nHNR_3^+ \quad (1)$$

If the amines[2] are bases whose dissociation constants have values between 10^{-6} and 10^{-10}, the strong and weak acids in the mixture resulting from the decomposition Equation (1) can together be analyzed by means of a two end-point titration using standard sodium hydroxide and the indicators methyl orange and phenolphthalein. Each mole of silicon tetrachloride produces four moles of hydrochloric acid. Silicon tetrachloride was therefore equated to one-quarter of the net increase in acidity resulting from the decomposition and measured at the phenolphthalein end point.

$$\text{Moles } SiCl_4 = \frac{\text{Moles (base} - \text{acid)}}{4} \quad (2)$$

The amine was identified with the amount of base needed to carry the mixture from a methyl orange to a phenolphthalein end point.

$$\text{Moles } NR_3 = \text{moles base (methyl orange to phenolphthalein)} \quad (3)$$

The mole ratio, n, was obtained from (2) and (3)

$$n = \frac{\text{Moles } NR_3}{\text{Moles } SiCl_4} \quad (4)$$

The net result of the acid decomposition and the two end-point titration with the base was

$$SiCl_4.(NR_3)_n + 4OH^- = SiO_2 + 4Cl^- + 2H_2O + nNR_3 \quad (5)$$

Pyridine, aniline, and dimethylaniline are bases whose constants have suitable values for the analysis. The method was confirmed for these amines by titrating known mixtures of silicon tetrachloride and amine, and by titrating knowns of each of the amines and of silicon tetrachloride separately.

Addition Compounds with Pyridine

Pyridine and silicon tetrachloride were made up as 1.74 M solutions in petrol ether. The two solutions were combined in different volume ratios. The precipitate that formed was centrifuged and washed repeatedly with petrol ether until all free amine and chloride had been removed. The solid, still immersed in petrol ether, was next decomposed by 25.00 ml. 0.1500 N hydrochloric acid, and the decomposed mixture titrated with 0.1000 N sodium hydroxide to methyl orange and phenolphthalein end points. The results of these analyses are presented in Table I. The composition of the solution in which the reaction occurred is given in the first three columns, and the composition of the precipitate resulting from the reaction is recorded in the last three columns.

A. $SiCl_4.(Pyridine)_2$

The data for the analysis of the diaminate are given for the compound as it occurs in the solvent (Table I), and as a dry solid (Table IV). This yellow

[2]*NR_3 is used to represent any amine.*

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TABLE I

ANALYSIS OF $SiCl_4$.(PYRIDINE)$_n$ PRECIPITATES IN PETROL ETHER

Reaction mixture			Precipitate			
Pyridine / $SiCl_4$	Moles × 10^3		Moles × 10^3		Pyridine / $SiCl_4$	Color
	Pyridine	$SiCl_4$	Pyridine	$SiCl_4$		
1/39	0.348	13.55	0.35	0.17	2.1/1	Yellow
1/11	0.348	3.83	0.34	0.17	2.0/1	Yellow
1/7	1.10	7.70	1.08	0.53	2.0/1	Yellow
1/3	1.74	5.22	1.39	0.73	1.9/1	Yellow
5/3	4.35	2.61	4.27	1.94	2.2/1	Mixed
3/1	5.22	1.74	4.07	1.72	2.4/1	Mixed
6/1	6.00	1.00	2.53	0.94	2.7/1	Mixed
19/1	6.61	0.35	0.97	0.27	3.6/1	Mixed
39/1	13.55	0.35	1.42	0.36	4.0/1	White
50/1	43.5	0.87	2.39	0.61	3.9/1	White
100/1	97.5	0.97	1.48	0.37	4.0/1	White

microcrystalline compound was recovered from silicon tetrachloride and pyridine solutions mixed in the ratio of 12/1. The dry yellow solid quickly turns white in moist air, and then liquifies, while acid fumes are given off. In dry air, decomposition begins at about 100°C., accompanied by acid odors, the darkening of the solid which ends up as an ash, and the appearance of a colorless liquid that freezes into white crystals.

B. $SiCl_4$.(Pyridine)$_4$

This compound is a white powder, soluble in pyridine and hygroscopic, adding water quickly to become a white odorless grease. All of the water except about two molecules per mole can be easily removed. When heated the compound does not melt, but begins to decompose at about 200°C., giving some pyridine among other products, and leaving an infusible ash. The analyses for this compound are reported in Tables I and IV.

Addition Compounds with Dimethylaniline

When dimethylaniline is added to silicon tetrachloride in such a way that no mixing occurs, the diffusion of the two liquids into one another quickly establishes three distinct zones in the interface region. The bottom zone consists of a flocculent pink precipitate which slowly curls off to fall through the liquid silicon tetrachloride. Above this a curdy, olive green precipitate forms, while a thick yellow agglomeration colors the third zone which fades into the liquid amine above. The separation and suspension of the three zones, as diffusion proceeds, is maintained by the different densities of the precipitates, but the pink compound is just heavy enough to collect in the silicon tetrachloride phase. This is fortunate, as the pink compound adds more amine and turns green when the amine concentration is more than about 0.2% of the chloride. The analyses of these three addition compounds, recorded in Table II, identifies the pink precipitate as the monoaminate, the green precipitate as the diaminate, and the yellow precipitate as the tetraminate.

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TABLE II

ANALYSIS OF $SiCl_4.(Me_2ANILINE)_n$ PRECIPITATES IN PETROL ETHER

Reaction mixture			Precipitate			
$\frac{Me_2Aniline}{SiCl_4}$	Moles × 10^3		Moles × 10^3		$\frac{Me_2Aniline}{SiCl_4}$	Color
	$Me_2Aniline$	$SiCl_4$	$Me_2Aniline$	$SiCl_4$		
1/100	0.25	25	0.26	0.25	1.0/1	Pink
1/100	0.25	25	0.18	0.14	1.3/1	Pink
1/100	0.25	25	0.24	0.245	1.0/1	Pink
1/14	0.87	12.2	0.375	0.190	2.0/1	Green
14/1	12.2	0.87	0.34	0.084	4.0/1	Yellow

A. $SiCl_4.(Me_2Aniline)_1$

The pink compound was prepared in pure silicon tetrachloride and analyzed in petrol ether (Table II), and as a dry solid (Table IV). The monoaminate decomposes when heated, giving off acid fumes, and changing color from pink to yellow at about 80°C. No liquid appears and the final product is a gray powder. The compound reacts with water vapor, turning orange and giving acid fumes.

B. $SiCl_4.(Me_2Aniline)_2$

The green compound prepared in petrol ether (Table II) turns red when dried (Table IV) but the color change does not affect the composition. Both forms are, analytically, diaminates. On heating, the red compound gives off acid fumes and turns yellow at about 70°C. It then melts, and its subsequent decomposition is much like that of the tetraminate. On exposure to water vapor, the red compound turns yellow, becomes greasy, and gives acid fumes.

C. $SiCl_4.(Me_2Aniline)_4$

A yellow addition compound analyzed in petrol ether (Table II) or as a dried solid (Table IV) was identified as the tetraminate. This compound, like the diaminate, shows two colors. The yellow solid, refluxed at 60°C. for one hour in a mixed petrol ether–cyclohexane solvent containing excess dimethylaniline, transformed into a brown product. The analysis of the brown form was similar to that of the yellow (Table IV). Both are soluble in dimethylaniline and neither give color to the solution. Both behave in the same way on heating, changing into thick brown liquids at about 65°C. that become thin enough to run at about 80°. Further heating causes frothing, amine odors, and another color change from brown to green. Colorless liquids distill off and very strong odors develop. In moist air, both forms melt, change color, and pick up water at about the same rate, and similarly lose it until about two molecules of water per mole remain.

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Addition Compounds with Aniline

When aniline is added to a large excess of silicon tetrachloride a transient red precipitate appears. This compound, which might be the monoaminate, could not be recovered. Apart from this, yellow and white solids were prepared and analyzed.

A. $SiCl_4.(Aniline)_2$

The yellow precipitate, analyzed in benzene (Table III) and as a dry solid (Table IV) corresponds to the diaminate. It reacts quickly with water vapor turning white and giving acid fumes.

TABLE III

ANALYSIS OF $SiCl_4.(ANILINE)_n$ PRECIPITATES IN BENZENE

Reaction mixture			Precipitate			
$\frac{Aniline}{SiCl_4}$	Moles × 10^3		Moles × 10^3		$\frac{Aniline}{SiCl_4}$	Color
	Aniline	$SiCl_4$	Aniline	$SiCl_4$		
1/30	2.0	60.0	1.62	0.82	2.0/1	Yellow
14/1	12.2	0.87	2.25	0.57	4.0/1	White

TABLE IV

ANALYSIS OF $SiCl_4.(NR_3)_n$ AS DRY SOLIDS

Compound	Analysis			Mass balance		Color
	Moles × 10^3		$\frac{Amine}{SiCl_4}$	Grams weighed	Grams found	
	Amine	$SiCl_4$				
$SiCl_4.(Pyridine)_2$	1.16	0.546	2.12/1	0.1818	0.1805	Yellow
$SiCl_4.(Pyridine)_4$	2.17	0.545	3.98/1	0.2700	0.2650	White
$SiCl_4.(Me_2Aniline)_1$	0.249	0.243	1.02/1	0.0705	0.0710	Pink
$SiCl_4.(Me_2Aniline)_2$	0.394	0.202	1.95/1	0.0812	0.0825	Red
$SiCl_4.(Me_2Aniline)_4$	3.39	0.850	3.98/1	0.5540	0.5560	Brown
$SiCl_4.(Me_2Aniline)_4$	0.889	0.221	4.02/1	0.1452	0.1459	Yellow
$SiCl_4.(Aniline)_2$	0.909	0.429	2.12/1	0.1610	0.1575	Yellow
$SiCl_4.(Aniline)_4$	2.47	0.620	3.99/1	0.3335	0.3345	White

B. $SiCl_4.(Aniline)_4$

The white precipitate, analyzed in benzene (Table III), or as a white powder (Table IV), confirms the tetraminate formula. The compound is unaffected by water vapor, neither gaining nor losing weight in the course of several days exposure. On heating, it begins to decompose at about 185°C., giving aniline hydrochloride and leaving an infusible ash.

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Stability of the Addition Compounds

All of the addition compounds are indefinitely stable when kept in dry air, or in an anhydrous inert solvent. But few of them have enough stability to manage a phase change. The thermal decompositions are complicated processes though they may begin simply, when the amine nitrogen carries no hydrogen, with a partial regeneration of chloride and amine. The diaminates and the monaminate give heavy acid fumes at temperatures below 100°C., and leave large ashes. The tetraminates decompose at temperatures below 200°C. Amines, or amine hydrochlorides, appear together with other products and a substantial ash is left. Exposed to water vapor the diaminates undergo disruptive chemical reactions which may indicate the addition of water to the exposed silicon tetrachloride, for hydrogen chloride is eliminated. The compounds with four amine groups may add water when exposed to the vapor but are not apparently degraded by it. The diaminates react with excess amine to form the tetraminates. The tetraminates dissolve in excess amine. In summary, the tetraminates are more stable and less reactive than the corresponding diaminates.

The Structures of the Addition Compounds

It will be assumed that the analyses definitely establish[3] the occurrence of the compounds $SiCl_4.(NR_3)_1$, $SiCl_4.(NR_3)_2$ and $SiCl_4.(NR_3)_4$. In addition, the compound $SiCl_4.(NH_3)_6$ is known (2). An attempt to explain the valences and predict the structures of these molecular compounds will be made.

In dealing with the structures and valences shown by complex ions, it is usually sufficient to treat all of the bonding orbitals as a group, and to find, from the resonance among them, that stable hybrid configuration that will explain the properties of the complex (1). But this method may not be satisfactory when applied to the molecular compounds formed between silicon tetrachloride and the amines. For the most part, the bonds that establish the chloride–amine compounds can probably be thought of as coordinate bonds in which electron-pairs from nitrogen atoms fill vacant orbitals in the silicon atom. The possibility for resonance among these bonds and the covalent Si-Cl bonds is not promising. On the one hand, it would be required that $3s$, $3p$ orbitals mix with $4s$, $3d$, $4p$ orbitals, and on the other, that the asymmetry introduced by the amine molecules (as compared to the chlorine atoms) still be overcome. In addition, a coordination number of 10, which is thought to be impossible for silicon, would have to be explained if the hexammonate is included. Again, the steric implication that the already crowded silicon tetrachloride molecule can add extra groups into itself is so unlikely as to practically eliminate the argument.

[3]*The reviewer has drawn the attention of the author to the work of A. Hardin, J. Chem. Soc. 51: 40. 1887, who reported 2: 1 addition compounds between pyridine and silicon tetrachloride, and quinoline and silicon tetrachloride.*

The molecule silicon tetrachloride has tetrahedral symmetry and uses four sp^3 bonds. This gives silicon an electron structure $3s^23p^6$, and requires silicon to use $4s$, $3d$, $4p$ orbitals if it is to become involved in further bonding. Because of the electronegativity of the chlorine atoms, the unused silicon orbitals ($4s$, $3d$, $4p$) would be expected to be more available in silicon tetrachloride than in other silicon compounds, excepting silicon tetrafluoride. Specifically, the group theoretical treatment (1) states that there are two d orbitals in silicon tetrachloride that can form two strong π bonds, plus an additional two d orbitals that can form two weak π bonds, and that the Si-Cl bonds themselves achieve some double bond character, for unshared pairs from the chlorine atoms are thought capable of forming π bonds by occupying the d orbitals of the silicon. This description might lead to the expectation that silicon tetrachloride would form a stable addition compound with two amine groups, and perhaps also an unstable addition compound with n equal to 4. These predictions are not fulfilled by the amine compounds, for the tetraminate is more stable than the diaminate and in addition monoaminate and hexammonate addition compounds occur.

Considering these difficulties, it is suggested that the amine groups add to the silicon tetrachloride molecule by using stablest hybrids from the $4s$, $3d$, $4p$ silicon orbitals, that no mixing occurs with the $3s$, $3p$ orbitals, and that silicon tetrachloride retains its sp^3 configuration. This would permit the formation of stronger coordinate bonds at greater distances from the silicon atom. In addition, only deformations of a secondary type (molecule–dipole interactions, etc.) would be required in the silicon tetrachloride molecule as amine groups add to it. In a way, the silicon tetrachloride molecule can be thought of as an atom, with the amine groups adding to form an envelope around it. It is assumed that the $4s$, $3d$, $4p$ orbitals of silicon provide the usual hybrid orbitals (1).

$SiCl_4.(NR_3)_1$

The silicon orbital from $4s$, $3d$, $4p$ that will form the most stable bond with one electron-pair is $4s$. This would not be, in itself, a directed bond. But greater penetration, with a corresponding increase in stability, would result if the amine molecule approached the silicon tetrachloride in the direction of the center of one of the faces of the tetrahedron. This could lead to some distortion, principally displacements of the three chlorine atoms. Some definition in structure would therefore be expected, the amine group being long bonded and opposite one chlorine atom, with the other three chlorine atoms pushed up out of their tetrahedral positions. The molecule should have a large dipole moment.

$SiCl_4.(NR_3)_2$

The ds configuration would be the stablest for two bonds. This is an angular arrangement, suggesting the possibility that both amine groups could approach tetrahedral faces. Molecule–dipole interactions should cause some distortion in the silicon tetrachloride. The resulting molecular compound would have a

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large dipole moment, as it lacks symmetry with regard to the distribution of electrons. Alternatively, however, the bonds could be called d^2 bonds. This arrangement is also angular (1), and would correspond to the amines' use of the two strong d orbitals supposedly resident in the normal silicon tetrachloride molecule.

$SiCl_4.(NR_3)_4$

For four bonds the d^3s is the stablest selection from the $4s$, $3d$, $4p$ group. This is a tetrahedral arrangement (1) which will be satisfied if the four amines are imagined to sink into the hollows in the four faces of the silicon tetrachloride tetrahedron. A description of the structure of the molecular compound would be that of a large tetrahedron (the four amine groups) enclosing a small tetrahedron (silicon tetrachloride). The two tetrahedra would be so rotated that the corners of one were perpendicular to the faces of the other. Because of its symmetry, the tetraminate would not be expected to have a dipole moment.

$SiCl_4.(NR_3)_6$

Six bonds formed from s, p, d, orbitals almost always have the octahedral d^2sp^3 arrangement (1). This would enable each amine in the hexaminate to approach an edge of the silicon tetrachloride tetrahedron and to lodge, as it were, in the hollow between two chlorine atoms; d^5s could also accommodate six bonds, but this arrangement is irregular (1). If d^2sp^3 is correct, the addition compound would possess no permanent dipole moment.

For all of these compounds it has been assumed that the Si-Cl bonds retain their sp^3 character. They will necessarily lose whatever double bond properties they possess, however, when the addition compounds form, and might be expected for this reason to become weaker and longer.

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PHYSICAL CONSTANTS AND ESTIMATION OF STEREOISOMERIC 2,3-BUTANEDIOLS[1]

By R. W. Watson, J. A. R. Coope, and J. L. Barnwell

Abstract

The refractive index – temperature relation for optically active and *racemic* diols is linear, with $n_D^{t*} = 1.4310 - 0.00036\ (t - 25)$ from 25° to 40°C.: for the *meso*-isomer $n_D^t = 1.4372 - 0.00034(t - 25)$ from 25° to 50°C. The specific rotation $[\alpha]_D^{25} \cong \pm 13.2°$. Measurements of n_D^t and α_D^t in suitably purified mixtures of stereoisomers allow calculation of the percentage of each isomer present. Tests of the method on known mixtures of all three stereoisomers show an experimental error of $\pm 3\%$. Analyses of five diol samples from pilot plant fermentations of beet molasses by *Aerobacter aerogenes* reveal 65–87% *meso*-, from 2 to 16% *dextro*-, and from 0 to 33% *racemic* 2,3-butanediol.

Refractive indices from 1.4306 to 1.4322 at 25°C. have been reported for optically active and *racemic* 2,3-butanediols. Wide variations also occur in the recorded values of specific rotations and densities as shown in Table I. Specific rotations for the *levo*-isomer reportedly range from −12.85° to −13.34°. The present investigation aims to establish more accurate values for these constants and to develop a simple physical method, based on their use, for rapid estimation of isomeric ratios.

Two methods for the estimation of isomers in mixtures of isomeric 2,3-butanediols have been described in the literature. Tipson (16) successfully used the procedure of conversion to isopropylidene derivatives followed by fractional distillation. The *meso*-derivative was readily separated in this way. Robertson and Neish (13) described a method in which the isomers in a 1 gm. sample were converted to their di-*p*-nitrobenzoates by a modified Schotten–Baumann reaction, dissolved in chloroform, measured polarimetrically to determine the concentration of optically active isomers, and fractionally crystallized for estimation of relative amounts of *dl*- and *meso*-esters. Four to six crops of crystals provided 90 to 95% recovery, from which the different components were separated by hand and weighed. This method has the unique advantage of simultaneously identifying the isomers, although several days are required for a determination. A simple procedure is described in the present communication which requires only 0.5 gm. of suitably purified diol, is accurate to ±3%, and may be completed within half an hour.

The variations noted in the reported values of physical constants have probably arisen from measurements on impure or mixed isomers. Removal of acids, esters, ketones, and ketals as well as prevention of isomerization and absorption of water comprise the main difficulties in obtaining the pure com-

[1] *Manuscript received June 14, 1951.*
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* t = °C.

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TABLE I

PREVIOUSLY REPORTED PHYSICAL CONSTANTS OF STEREOISOMERIC 2,3-BUTANEDIOLS

Constant \ Isomer	*levo-*	Ref.	*dextro-*	Ref.	*racemic*	Ref.	*meso-*	Ref.
Refractive index	$n_D^{25} = 1.4307$	19	$n_D^{25} = 1.4306$	7	$n_D^{25} = 1.4310$	11	$n_D^{25} = 1.4364$	14
	$n_D^{25} = 1.4308$	3					$n_D^{18} = 1.4387$*	8
	$n_D^{25} = 1.4309$	7					$n_D^{25} = 1.4384$*	19
	$n_D^{25} = 1.4310$	22, 20					$n_D^{35} = 1.4324$	7
	$n_D^{26} = 1.4318$	9					$n_D^{35} = 1.4325$	10
	$n_D^{18} = 1.4340$	8						
Specific rotation	$[\alpha]_D^{23} = -12.85$	8			$[\alpha]^{26} = 0.000$	10	$[\alpha]_D^{20} = +0.80$*	3
	$[\alpha]_D^{25} = -13.0$	19					$[\alpha]_D^{25} = +1.0$ *	19
	$[\alpha]_D^{20} = -13.1$	3					$[\alpha]_D^{25} = +1.06$*	8
	$[\alpha]_D^{25} = -13.17$	5						
	$[\alpha]_D = -13.19$	7						
	$[\alpha]_D^{26} = -13.34$	10						
Density and specific gravity	$d_{20}^{20} = 0.992(2)$	3	$d^{25} = 0.9872$	7			$d^{20} = 1.0033$	14
	$d_4^{25} = 0.9873$	3					$d^{20} = 1.004$	10
	$d^{25} = 0.9069$	7					$d^{25} = 0.990$	8
	$d_{15}^{26} = 0.9880$	9					$d^{25} = 0.9939$	7
	$d_{30}^{30} = 0.983(8)$	3						
	$d_{40}^{40} = 0.9750$	3						

**Aerobacter diol.*

pounds. The preparation of stereoisomeric diols of high purity is described in the experimental section. All purified samples gave negative tests for acetyl groups (2), esters (4), ketones, and ketals (6). Water contents, estimated by the Karl Fischer method (15) did not exceed 0.046%. Accurately determined physical constants of the isomers are reported in Table II.

Close agreement between the refractive indices of optically active and *racemic* diols prepared by different methods (Table II) is evidence for their accuracy to the fourth place. The value of n_D^{25} for the *dextro-*, *levo-*, and *racemic* forms is therefore 1.4310. The refractive index of *meso*-diol at 25°C. was obtained by direct reading on the supercooled liquid. The same value (± 0.0001) is obtained (*a*) by extrapolation of readings on a series of *meso–dl-*

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TABLE II

PHYSICAL CONSTANTS OF STEREOISOMERIC 2,3-BUTANEDIOLS FOUND IN THE PRESENT INVESTIGATION

Isomer	*levo-*			*racemic*		*meso-*
	Sample A	Sample B	Sample C	Sample A	Sample B	
Water, % / Constant	0.046	0.028		0.040		0.042
Refractive index n_D^{25}	1.43095	1.43100	1.4310	1.43109	1.43095	1.43719
Optical rotation α_D^{25} (1 dm.)	−12.75	−12.73	−12.99	−0.005	0.00	0.00
Specific rotation $[\alpha]_D^{25}$	−12.92	−12.90	−13.16	−0.005	0.00	0.00
Density d_4^{25}	0.9873					

and *meso–levo-* mixtures (Fig. 1) as well as (*b*) by extrapolation of a series of readings on the pure diastereoisomer at temperatures above the melting point (Fig. 2). The value of n_D^{25} for *meso*-diol is therefore 1.4372 ± 0.0001.

Changes in refractive index with temperature have not previously been determined. Values of n_D^t for the *racemic*, *levo-*, and *meso*-forms over the range from 25° to 50°C. are given in Table III. These readings are plotted versus

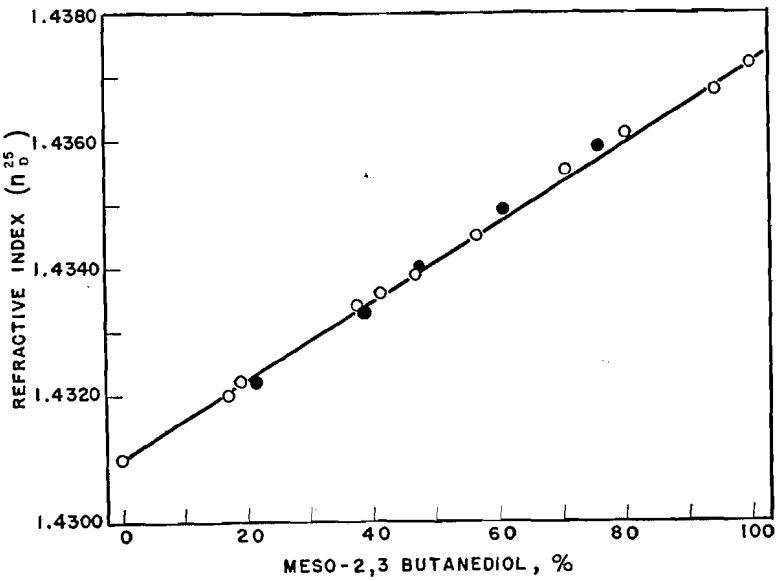

FIG. 1. *Refractive index vs. per cent meso-2,3-butanediol in meso–levo-mixtures (open circles) and meso–dl-mixtures (solid circles).*

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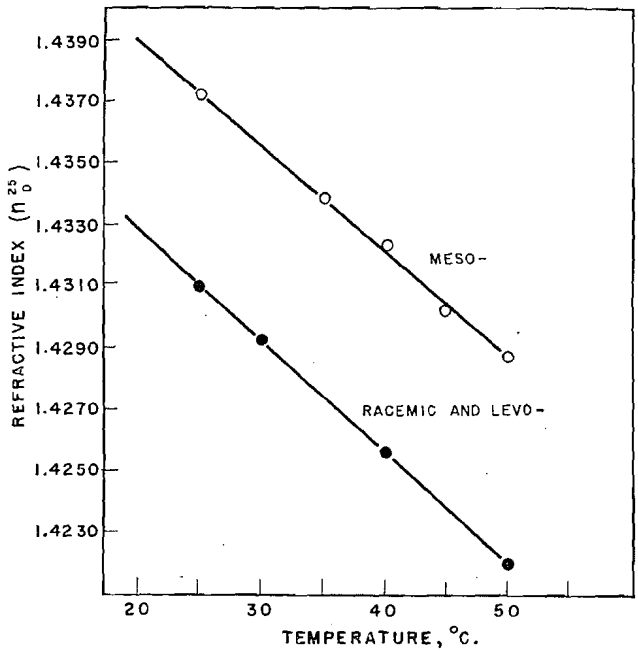

FIG. 2. *The temperature–refractive index relation for racemic, levo-, and meso-2,3-butanediols.*

temperature in Fig. 2 and show strictly linear relations. Conversion coefficients for the refractive indices of (*a*) *levo-* and *racemic* forms from 25° to 40°C. and (*b*) the *meso*-isomer from 25° to 50°C. are therefore −0.00036 and −0.00034 respectively per degree Centigrade rise in temperature.

The specific rotation $[\alpha]_D^{25} = -12.92°$, obtained for the first supposedly pure sample (A, Table II) of *levo*-diol was viewed with suspicion. The experience of other investigators indicated that this value was probably too low (see Table I). Accordingly the entire procedure of preparation and purification was repeated, with care being taken to prevent metal contamination and isomerization (21). Polarimetric measurement of the second sample (B, Table II) merely served to confirm the value obtained for the specific rotation of Sample A. A third sample, prepared with special care from an-

TABLE III

REFRACTIVE INDICES OF ISOMERS AT VARIOUS TEMPERATURES

Temp., °C.	*levo-*	*racemic*	*meso-*
25	1.4310	1.4310	1.4372
30	1.4293	1.4293	
35			1.4339
40	1.4256	1.4256	1.4323
45			1.4303
50	1.4220	1.4220	1.4287

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other fermentation of wheat by *B. polymyxa* (23) had $n_D^{25} = 1.4310$, $[\alpha]_D^{25} = -13.16°$. In view of the fact that the refractive indices of these three samples are almost identical it seems probable that *B. polymyxa* produces a small variable amount of the *dextro*-isomer and that the true specific rotation is nearer $-13.16°$ (9). The recent work of Garner and Lucas (5) gives $[\alpha]_D^{25} = -13.17°$ for the *levo*-isomer. Although this constant cannot yet be accepted as established, any error which may remain in its measurement is too small to effect a variation of more than $\pm 2\%$ in the results of a physical method for the estimation of isomeric ratios.

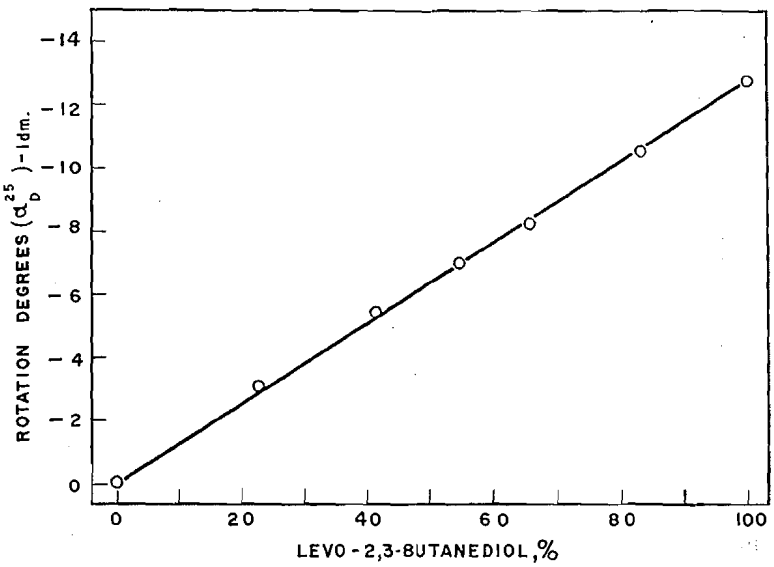

FIG. 3. *Relation between optical rotation and per cent levo-2,3-butanediol in meso–levo-mixtures.*

The density of the pure *levo*-isomer was stated by Clendenning (3) to be $d_4^{25} = 0.9873$. Repetition of this measurement using Sample A of *levo*-diol exactly confirmed the previous determination as shown in Table II. Moreover, the value reported for the density of *dextro*-diol is almost identical (see Table I), so that $d_4^{25} = 0.9873$ was used in calculations of the specific rotation.

The refractive indices of a series of *meso–levo-* and *meso–dl-* mixtures are given in Tables IV and V respectively. These values are plotted in Fig. 1 and show a linear relation between concentration and refractive index at 25°C. The weight per cent of *meso*-2,3-butanediol in a mixture of stereoisomers whose D-line refractive index at 25.0°C. = x may therefore be calculated from the expression,

$$\%\ meso\text{-} = \frac{x - 1.4310 \times 100}{0.0062}.$$

The comparatively narrow gap of 0.0062 divisions between the refractive indices at 25°C. of the internally compensated and other isomers makes

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TABLE IV

REFRACTIVE INDICES OF *meso-levo*-MIXTURES

No.	*levo*-, gm.	*meso*-, gm.	*levo*-, %	*meso*-, %	n_D^{25}
1	100.0	....	100.0	0.0	1.4310
2	3.1350	0.6471	82.9	17.1	1.4320
3	0.8799	0.2088	80.8	19.2	1.4322
4	2.3342	1.4113	62.3	37.7	1.4334
5	0.8919	0.6263	58.7	41.3	1.4336
6	0.6443	0.4552	58.6	41.4	1.4336
7	2.0422	1.8016	53.1	46.9	1.4339
8	1.6279	2.1102	43.5	56.5	1.4345
9	1.1632	2.8177	29.2	70.8	1.4355
10	0.1963	0.7897	19.9	80.1	1.4361
11	0.0518	0.8393	5.8	94.2	1.4368
12	0.0	100.0	0.0	100.0	1.4372

TABLE V

REFRACTIVE INDICES OF *meso–dl*-MIXTURES

No.	*dl*-, gm.	*meso*-, gm.	*dl*-, %	*meso*-, %	n_D^{25}
1	100.0	0.0	100.0	0.0	1.43102
2	1.0625	0.2934	78.4	21.6	1.43219
3	0.5471	0.3432	61.5	38.5	1.43334
4	0.4811	0.4353	52.5	47.5	1.43396
5	0.3326	0.5200	39.0	61.0	1.43486
6	0.3114	0.9676	24.4	75.6	1.43592
7	0.0	100.0	0.0	100.0	1.43719

accurate determination of the fourth place necessary. Without special precautions this may be obtained under ordinary conditions from a series of readings with an Abbé refractometer.

Specific rotation is independent of dilution (Fig. 3). Since errors in polarimetry need not exceed $\pm 0.02°$, and a range of approximately 13.0° occurs between the rotations (1 dm.) of optically active and inactive diols, direct estimates of the percentage of an optically active isomer present in a mixture in excess of its enantiomer may be made with an error $< \pm 2\%$. The optical rotations (1 dm.) of a series of *levo–dl*-mixtures at 25°C. are shown in Table VI.

TABLE VI

OPTICAL ROTATIONS (1 DM.) OF *levo–dl*-MIXTURES

No.	*levo*-, gm.	*dl*-, gm.	*levo*-, %	*dl*-, %	α_D^{25}
1	0.0	100.0	0.0	100.0	0.00
2	0.8628	2.9149	22.8	77.2	− 3.04
3	1.6648	2.3446	41.5	58.5	− 5.32
4	2.1663	1.7983	54.7	45.3	− 6.98
5	2.5917	1.3668	65.5	34.5	− 8.30
6	3.3890	0.6834	83.2	16.8	−10.58
7	100.0	0.0	100.0	0.0	−12.74

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These values are plotted in Fig. 3, and show a linear relation between concentration and optical activity. The weight per cent of either optically active isomer in a mixture whose optical rotation (1 dm.) at 25°C. = $\pm y$ may therefore be obtained from the equation:

$$\% \text{ optically active isomer} = \frac{\pm y \times 100}{\pm 13.0}.$$

The percentage of the *racemic* mixture is obtainable by difference.

Tests of the method on mixtures containing all three stereoisomers, with refractive indices measured in room air, are reported in Table VII. The isomeric composition, calculated from measurements of the refractive index and optical rotation, are within $\pm 3\%$ of the known values.

TABLE VII

TEST OF METHOD ON KNOWN MIXTURES

No.	n_D^{25}	α_D^{25}	Known weight % of isomers in mixture			Weight % of isomers calculated from n_D^{25} and α_D^{25}		
			levo-	*dl-*	*meso-*	*levo-*	*dl-*	*meso-*
1	1.4312	−5.29	41.4	56.8	1.8	41.5	55.2	3.2
2	1.4324	−3.68	29.8	49.0	21.2	28.9	48.5	22.6
3	1.4328	−3.82	30.6	40.9	28.5	31.4	39.6	29.0
4	1.4331	−4.86	40.0	28.9	31.1	38.2	27.9	33.9
5	1.4338	−2.42	20.7	37.1	42.2	19.0	35.8	45.2
6	1.4340	−5.99	50.9	2.4	46.8	47.0	4.7	48.3

The method was applied to the mixed 2,3-butanediols produced by *Aerobacter aerogenes*. Walpole (18) originally reported that this organism formed a *meso–racemic* mixture with a small positive rotation. Böeseken and Cohen (1) also showed that certain samples may contain an unstated percentage of the *racemic* mixture; and Tipson (16) recently reported the presence of D-(*levo*)-2,3-butanediol in the mixed 2,3-butanediols from the normal fermentation of glucose by *A. aerogenes*. Pilot plant samples of 2,3-butanediol, all obtained from the fermentation of beet molasses by *A. aerogenes* Strain M148, were purified (see experimental section). Karl Fischer determinations on two of the purified samples showed 0.02% and 0.065% of water respectively. Isomeric ratios obtained by the physical method were checked for one sample by fractional crystallization of the di-*p*-nitrobenzoyl esters. Results are shown in Table VIII. The percentage of *racemic* diol reported by the ester method for Sample 2 is known to be too high because of the difficulty of removing fine *meso*-crystals from *dl*-buttons. The proportion of *meso*-diol reported by the physical method varies from 65–87%, of the *dextro-* isomer from 2 to 16%, and of the *racemic* mixture from 0 to 33%. Whether this variation exists in the diol produced by the organism, or whether it arises during the recovery process in the pilot plant has not been determined.

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TABLE VIII

ISOMERIC COMPOSITION OF *Aerobacter* DIOLS

No.	n_D^{25}	a_D^{25}	Weight % of isomers calculated from n_D^{25} and a_D^{25}			Weight % of isomers from di-*p*-nitrobenzoyl esters (13)		
			meso-	*dextro-**	*racemic*	*meso-*	*dextro-**	*racemic*
1	1.4350	+0.31	65	2	33			
2	1.4359	+0.4	79	3	18	73	2	25
3	1.4362	+2.09	84	16	0			
4	1.4364	+1.66	87	13	0			
5	1.4367	+0.8	92	6	2			

* *In excess of the enantiomer.*

Experimental

Preparation of Isomers

1. D-(*levo-*)-*2,3-Butanediol*

Levo-diol, produced in the pilot plant from the fermentation of wheat by *Bacillus polymyxa* (23) was refluxed overnight at pH 8 with an equal volume of reagent benzene, the water removed in a Barrett distilling receiver, and the benzene distilled off through a Vigreux column at atmospheric pressure. The residual diol was distilled *in vacuo* (0.2 to 0.5 mm. Hg) at pH 8-9, treated with activated charcoal (Anachæmia H-73), and redistilled without fractionation under a pressure of 0.2 to 0.5 mm. Hg into a dry receiver that was sealed off under vacuum. The receiver was so designed that the distillate could be evaporated without ebullition into a dry test tube, which was sealed off in turn. The supposedly pure isomer had $n_D^{25} = 1.43095$; $[a]_D^{25} = -12.92°$; and contained 0.046% water. Other samples of *levo*-diol prepared in the same way had the physical constants and water contents shown in Table II.

2. Meso-2,3-Butanediol

Diol obtained from a pilot plant fermentation of beet molasses by *Aerobacter aerogenes* N.R.C. strain M148, was adjusted to the phenolphthalein end point with sodium hydroxide, and distilled through a Vigreux column at about 1 mm. pressure. Mixed propionals, prepared from this diol by Neish and MacDonald's procedure (12), were fractionated through a 100-plate Podbelniak Hyper-Cal column. From 1230 ml. of mixed propionals, 230 ml. of pure *meso*-propional (b.p. 134.5°C.; $a_D < +0.005°$) was obtained. *Meso*-propional (2-ethyl, 4,5-dimethyl, 1,3-dioxacyclopentane) refluxed with 530 ml. of 1.65% hydrochloric acid for about two hours, was distilled to remove propionaldehyde, and the mixture neutralized with sodium hydroxide. Glycerol was added as a still-pot base, propionaldehyde and water were removed by distillation, and the diol finally distilled through a semimicro-Todd (17) column into a dry receiver. The product had $a_D^{26} = -0.005$: $n_D^{25} = 1.4371$.

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A second sample of pure *meso*-diol, prepared from dimethyl ketals (12) by a similar procedure, had $n_D^{25} = 1.4373$.

The two samples of crystalline *meso*-diol were combined and recrystallized at 10°F. from three and one-half volumes of isopropyl ether. The crystals were finally distilled *in vacuo* through a semimicro-Todd column (17) into a dry receiver. The final product had $\alpha_D^{25} = 0.00 \pm 0.003$; $n_D^{25} = 1.43719$; water content = 0.042% (Karl Fischer); m.p. = 34.5°C. (24).

3. Racemic 2,3-Butanediol

Pure *racemic* diol was prepared by hydrolysis of the *dl*-propional. Samples of the propional, obtained during fractionation of the mixed propionals from *Aerobacter* diol, were mixed and refractionated through the Podbelniak column to $\alpha_D^{26.5} = +4.05$; $n_D^{25} = 1.4010$. *Levo*-propional ($\alpha_D = -14.0$) was added until the optical rotation of the mixture was 0.00 in a 2 dm. tube. Propionaldehyde was removed continually by fractional distillation during the hydrolysis. The final distillate had $\alpha_D = +0.23$ (2 dm.). Pure *levo*-diol was added until the mixture became optically inactive ($\alpha_D^{25} = 0.00$). The diol was finally redistilled and stored as previously described ($\alpha_D = -0.005° \pm 0.003°$ (1 dm.); $n_D^{25} = 1.43109$; water content = $0.040 \pm 0.006\%$.

Measurement of Physical Constants

The pure isomers were stored in glass tubes sealed from distillation receivers *in vacuo*. The tubes were opened, and transfers to polarimeter tubes and precision pycnometers (25) were made in a specially constructed air-tight box-desiccator containing Anhydrone and fitted with a Plexiglass window and neoprene gloves. A current of dry air was passed over the prisms of the Phoenix precision refractometer while refractive indices were being measured.

Purification of Aerobacter Diols and Estimation of Isomers

Five samples of diol from the pilot plant fermentation of beet molasses by *A. aerogenes* were prepared as follows: 2,3-butanediol (50 ml.), reagent benzene (50 ml.), and several glass beads were placed in a 250 ml. round-bottom flask fitted with a Barrett distilling receiver and reflux condenser. The mixtures were refluxed overnight to remove water. Benzene was largely removed by distillation at atmospheric pressure through an 18 in. Vigreux column. The pH of the diol was maintained at 8.5–9.0 during subsequent distillation (without fractionation) at 1–5 mm. pressure, and the distillate collected in a dry receiver. Karl Fischer determinations on two samples prepared in this way showed 0.065% and 0.020% of water respectively. Refractive indices at 25°C. were measured in room air with an Abbé refractometer, and optical rotations were determined with a Hilger polarimeter.

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HYDROGEN PEROXIDE AND ITS ANALOGUES

IV. SOME THERMAL PROPERTIES OF HYDROGEN PEROXIDE[1]

By William T. Foley[2] and Paul A. Giguère

Abstract

Using a Bunsen ice calorimeter the following thermal data were obtained for pure hydrogen peroxide:

Specific heat of liquid between 0° and 25°C.	0.632 ± 0.003 cal. per gm. per degree
Specific heat of solid between −20° and −10°C.	0.41 ± 0.02 cal. per gm. per degree
Latent heat of fusion at melting point, −0.46°C.	85.83 ± 0.18 cal. per gm.
Latent heat of vaporization at 0°C.	370.17 ± 0.18 cal. per gm.

The freezing points of very concentrated solutions of hydrogen peroxide calculated from these data agree closely with the experimental ones. Preliminary measurements of the heat of decomposition of hydrogen peroxide catalyzed by platinum black were also made at 0° and at various concentrations. The results point to 23.54 ± 0.04 kcal. per mole for the heat of the reaction

$$H_2O_2(l) = H_2O(l) + \tfrac{1}{2} O_2 (g),$$

a value slightly higher than those found by previous experimenters.

A recent investigation (7) has shown conclusively that hydrogen peroxide and water do not form solid solutions together. Therefore the discrepancy which was observed (9) between calculated and measured freezing points of concentrated hydrogen peroxide solutions seemed abnormal, more especially since dilute peroxide solutions exhibit no such deviations. This suggested that the accepted value for the latent heat of fusion of hydrogen peroxide, 74 cal. per gm. (14), was possibly in error and should be revised. For that purpose an ice calorimeter was used and a number of other thermal properties of hydrogen peroxide were determined at the same time.

Experimental

Because the freezing point of hydrogen peroxide is so close to that of water the ice calorimeter was the logical choice for these measurements. Furthermore, it is easy to make and operate and yet it is capable of high precision (11). The model described by Bartholomé and Clusius (2) was adopted except that the vacuum jacket was not silvered. The central well, 27.5 cm. long and 1.4 cm. in diameter, was topped with a 19/38 ground glass joint. The amount of mercury displaced was estimated by weighing.

The water and mercury used to fill the calorimeter were carefully redistilled and thoroughly degassed under vacuum. The calorimeter proper was placed in a tall Pyrex jar and packed to the top in finely shaved ice made from distilled

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water. The jar, wrapped in thick cotton insulation, fitted snugly inside a large stainless steel vacuum container. In operation the water from the melting ice was removed periodically through a siphon and replaced by an equivalent quantity of fresh ice. It was found by practice that the best results were obtained when the ice mantle in the calorimeter was formed at night and the ice in the jar completely replaced the next morning. One hour later the observations on the rating of the calorimeter could be started. The thermal leak was always small, never exceeding 0.3 cal. per hour; on some days it was zero and on others it was negative, but more often it was positive. The calibration factor was that found by Ginnings and Corruccini (11), 64.631 cal. per gm. of mercury, where 1 cal. = 4.1833 international joules.

The central well of the calorimeter contained some thin mineral oil as heat-transfer fluid. To form an ice mantle a narrow glass test tube containing some acetone was lowered into the well and small pieces of dry ice were dropped into it. The ice mantle thus formed was optically clear and had the usual shape (11). The response of the calorimeter to addition or removal of heat seemed instantaneous, although it was noted that when the tube containing the dry ice came in contact with the inner wall of the calorimeter the mercury receded for an instant before advancing again. This was caused by a slight contraction of the glass suddenly cooled below the temperature of the ice. As reported previously (11) the ice mantle developed tiny hairlike cracks radiating from the glass wall after some heat had been added to the calorimeter.

Specific Heat of the Liquid

The mean specific heat of liquid hydrogen peroxide was first determined in the temperature interval 25° to 0°C. The sample tube, 10 cm. long and 0.8 cm. in diameter, was fitted with a 7/25 ground glass joint and stopper having a small capillary vent. This tube was suspended in the central well of a portable constant-temperature jacket by means of a thread passing through a hook and leading to the outside (Fig. 1A). Water from a large thermostat was circulated through the jacket at the rate of 100 ml. per minute. The temperature of the water in the jacket was estimated to 0.01° on a thermometer calibrated by the National Bureau of Standards. For a determination the water jacket containing the sample tube was placed directly above the ice calorimeter, the two central tubes being separated by a plastic diaphragm. After a two-hour rating period for determining the thermal leak the diaphragm was removed and the sample tube was quickly lowered into the calorimeter. Then the diaphragm was replaced and the calorimeter was allowed to reach equilibrium for a period of 30 min. after which the mercury cup was replaced. The determination was concluded with another two-hour rating period. Thus the amount of mercury corresponding to the cooling of the empty sample tube from 25° to 0° was found to be 0.680 ± 0.001 gm.

A sample of hydrogen peroxide, obtained by fractional distillation of a 90% commercial solution (Becco), was recrystallized; on analysis it was found to

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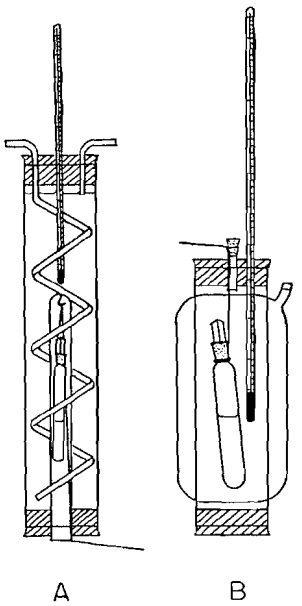

FIG. 1. *Constant-temperature jackets used for measuring the specific heat of the liquid (A) and the heat of fusion of the solid (B) hydrogen peroxide.*

be 99.8% pure. This was deemed satisfactory as the heat capacity changes very slowly with concentration. Furthermore this quantity need be used only in the temperature interval −0.46° to 0°C. for the determination of the heat of fusion. The results in Table I give an idea of the degree of precision of the measurements.

Specific Heat and Heat of Fusion of the Solid

For these determinations a very pure sample was needed as any impurity would result in "premelting." Measurements were made with the sample originally at two different temperatures, −10° and −25°C., in order to obtain the specific heat of the solid and then, by difference, the heat of fusion. These

TABLE I

SPECIFIC HEAT OF LIQUID HYDROGEN PEROXIDE BETWEEN 0° AND 25°C.

Weight of H_2O_2, gm.	Weight of mercury, gm.	Weight of mercury, per gm. H_2O_2, gm.	Specific heat, cal./gm./deg.
6.2788	1.5374	0.2449	0.633
6.1413	1.5023	0.2446	0.632
6.7580	1.6482	0.2439	0.631
6.2728	1.5329	0.2444	0.632
6.4150	1.5769	0.2458	0.636
5.7390	1.3957	0.2432	0.629
	Mean	0.2444 ± 0.001	0.632 ± 0.003

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two temperatures had to be taken far enough apart for good accuracy on the specific heat of the solid. On the other hand a temperature too close to the freezing point would have exaggerated the importance of the slightest premelting whereas too low a temperature would have increased the experimental difficulties.

A 1 lb. sample of 99.6% hydrogen peroxide was subjected to six fractional crystallizations after which it was found to freeze at −0.51°C. From the freezing-point curve (7) the composition at that stage was 99.95%. It was then recrystallized three more times and again before each determination. Unfortunately not enough was left for a freezing-point determination although volumetric analysis with potassium permanganate gave the following values: 100.09%, 99.94%, and 99.99%. In order to cool it to the selected temperature the sample tube was placed inside a larger tube (Fig. 1B) with double walls, the space between the latter being filled with a 40% solution of glycerol in water. This container was closed with two rubber bungs and was immersed in a low temperature bath described before (10). The temperature was measured with a calibrated mercury-in-glass thermometer. Crystallization of the cooled sample of peroxide was initiated by seeding as it was feared that application of a very low temperature at one point might result in an unstable form of the solid. The necessary corrections for the seeding operation were always applied. The sample was kept for at least one hour in the low-temperature bath before being transferred to the calorimeter in the manner described above. It took about eight hours for the sample to reach 0° from −25°. From the results given in Table II the thermal data are obtained as follows:

Specific heat of solid between −25.1° and −9.6°C.:

$$\frac{96.23 - 89.88}{25.1 - 9.6} = \frac{6.35}{15.5} = 0.41 \pm 0.02 \text{ cal. per gm. per degree.}$$

From this datum and the specific heat of the liquid the heat of fusion is found to be $89.88 - (0.41 \times 9.1) - (0.632 \times 0.46) = 85.83 \pm 0.18$ cal. per gm.

TABLE II

HEAT REQUIRED TO BRING SAMPLE TO 0°C.

Initial temperature, °C.	Weight of H_2O_2, gm.	Weight of mercury, gm.	Calories per gm.	Average
−25.1	2.8033	4.1786	96.34	96.23
−25.1	3.0400	4.5207	96.11	
−9.6	3.3579	4.6764	90.01	89.88
−9.6	3.0341	4.2130	89.75	

Heat of Vaporization

To measure this quantity it was only necessary to connect the sample tube by means of a ground glass joint to a liquid-air trap and a high-vacuum pump. Some perfluoromethylcyclohexane was used in the calorimeter well for good heat transfer. The sample was allowed to stand in the calorimeter for 30 min.

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before the rating period was begun. Once the thermal leak was determined the vacuum pump was started; after about five hours the outflow of mercury stopped abruptly indicating that the sample had all evaporated. The results are summarized in Table III. By combining this result with that for the heat of fusion and the heat capacity of the liquid, the latent heat of sublimation of hydrogen peroxide at its freezing point is obtained. The heat capacity of the vapor may be taken without appreciable error as 0.3 cal. per gm. per degree (8). Therefore the heat of sublimation is $85.83 + (0.63 \times 0.46) + 370.17 - (0.3 \times 0.46) = 456.2$ cal. per gm.

TABLE III

HEAT OF VAPORIZATION OF HYDROGEN PEROXIDE AT 0°C.

Weight of H_2O_2, gm.	Weight of mercury, gm.	Calories per gm.
0.9670	5.5369	370.07
0.9691	5.5544	370.44
0.8886	5.0872	370.00
	Mean	370.17 ± 0.18

Heat of Decomposition

A number of determinations of the heat of decomposition of hydrogen peroxide have been reported but none was made at 0°C. Because of the availability of the ice calorimeter and of some very pure hydrogen peroxide it was thought worthwhile to carry out a few measurements of this quantity at various concentrations. Some difficulty was encountered in preparing a catalyst with the right activity. Indeed, with a very active catalyst there was the danger that the evolved gas might leave the calorimeter at a higher temperature than 0°; on the other hand a low activity meant a very slow reaction with greater experimental error. Finally the following procedure

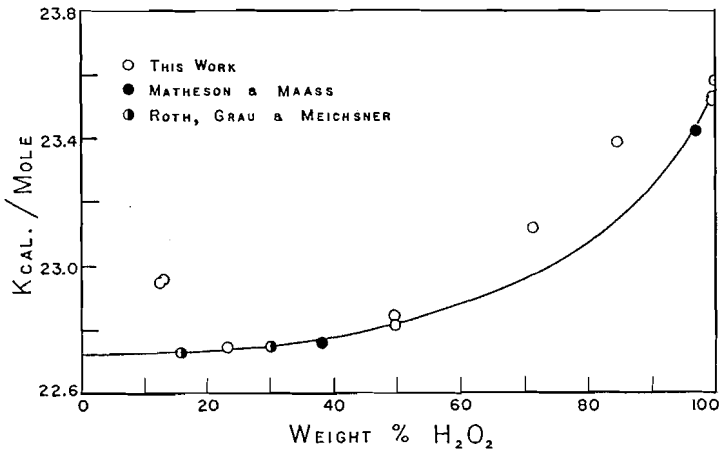

FIG. 2. *Heat of decomposition of hydrogen peroxide at 0°C.*

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was adopted. The sample tube was fitted with a length of glass tubing for the escaping gas. From the mouth of this tube were suspended by means of threads a tiny glass capillary and, inside it, a length of platinized platinum wire sealed to a thin glass rod. The function of the capillary shield was to prevent particles of platinum black from falling prematurely into the peroxide. After thermal equilibrium was established in the calorimeter the catalyst was taken out of the capillary and lowered into the liquid peroxide. Following a brief induction period the decomposition proceeded briskly as indicated by a hissing noise. The catalyst was then raised for a moment and lowered again, and so on, until the hydrogen peroxide was so diluted that it decomposed quietly.

Obviously the end of the reaction could not be ascertained as definitely as in the other thermal measurements; the reaction died away, not gradually but in irregular spurts. In addition, the remaining liquid had to be transferred quantitatively to a dilute sulphuric acid solution and titrated for the undecomposed peroxide. In correcting for the latter quantity it was assumed that the total heat effect measured was the sum of the heat of decomposition of most of the sample plus the heat of dilution, from the original concentration, of the unreacted fraction. The uncertainty resulting from this procedure will be discussed below. The corrected values thus obtained are tabulated in the last column of Table IV.

TABLE IV

HEAT OF DECOMPOSITION OF HYDROGEN PEROXIDE AT 0°

% H_2O_2	Weight of sample, gm.	Weight of H_2O_2, gm.		Time of reaction, hr.	Weight of mercury, gm.	ΔH (kcal./mole)	
		Total	Unreacted			Uncorrected	Corrected
100	0.4333	0.4333	0.0204	3.5	4.4276	23,578	23,535
100	1.2393	1.2393	0.0295	7	12.9858	23,600	23,580
99.85	0.7814	0.7801	0.0839	6	7.4802	23,624	23,528
99.85	0.6107	0.6098	0.0159	9.5	6.3570	23,535	23,514
84.52	0.4898	0.4140	0.0396	8	3.9914	23,440	23,388
71.50	0.6725	0.4808	0.0025	5	5.0554	23,187	23,130
49.71	1.0241	0.5091	0.0376	5	4.8998	22,850	22,842
49.55	1.1436	0.5666	0.0368	5	5.4997	22,824	22,816
23.15	1.4438	0.4636	0.0032	4	4.7613	22,749	22,749
12.63	3.5097	0.4431	0.0001	8	4.6273	22,962	22,962
12.50	2.8468	0.3560	0.0412	5.5	3.2862	22,953	22,953

Discussion

The only measurements of the thermal properties of hydrogen peroxide to be found in the literature are those of Maass and Hatcher (14). Using a Richard's adiabatic calorimeter these authors found the values 0.57 and 0.46 cal. per gm. per degree respectively for the specific heat of the liquid and the solid, and 74 cal. per gm. for the latent heat of fusion. Their stated accuracy was of the order of 2-4%. An analysis of their results reveals that the sample they used must have contained some water as its freezing point

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was −1.7°C. and it could be cooled to −32° without freezing. This condition would result in serious "premelting" thus leading to a low value for the heat of fusion and a high value for the specific heat of the solid, as borne out by the present results.

With an average thermal leak of less than 0.3 cal. per hour the precision of the measurements reported here was of the order of 0.25% for the specific heat of the liquid and the latent heats of fusion and vaporization. The experimental values usually check to better than this. A much larger discrepancy was to be expected in the case of the specific heat of the solid for this quantity was obtained as the difference between two large numbers. Here an error of 0.1° in estimating one temperature resulted in an uncertainty of about 6%, as was indeed observed. From the present data the cryoscopic constant of hydrogen peroxide is calculated to be 1.72°C. The freezing points of very concentrated solutions of hydrogen peroxide are now found to agree quite well with those calculated by the well known equation

$$-\ln N_1 = \frac{\Delta H_f (T_0 - T)}{R\, T_0\, T}.$$

In fact the agreement is better than for the dilute solutions as shown in Table V.

TABLE V

FREEZING POINTS OF SOLUTIONS OF HYDROGEN PEROXIDE AND WATER

Mole fraction H_2O_2	Freezing points		Mole fraction H_2O_2	Freezing points	
	Obs.	Calc.		Obs.	Calc.
0.01	−1.05°	−1.03°	0.99	−0.98°	−0.97°
0.02	−2.22°	−2.07°	0.98	−1.51°	−1.48°
0.03	−3.60°	−3.11°	0.97	−2.05°	−2.00°
0.04	−4.90°	−4.13°	0.96	−2.61°	−2.51°
0.05	−6.20°	−5.18°	0.95	−3.20°	−3.03°

No actual determination of the heat of vaporization of hydrogen peroxide has been reported previously. From their vapor-pressure measurements Maass and Hiebert (15) calculated it to be 341.5 cal. per gm. at the boiling point, 152°. The more recent data of Kavanagh (12) lead to 370 cal. per gm. at 25°; this quantity is slightly higher than the present result recalculated to the same temperature, 362. cal. per gm. It is well known, however, that experimental measurements of the heat of vaporization usually give more accurate results than the indirect method (17). The above data combined with the vapor pressure of pure hydrogen peroxide at the triple point (0.26 mm. Hg from Kavanagh's equation) make it possible to calculate the slope of the three phase-equilibrium curves at that point. For these calculations the density of the solid was taken as 1.70 gm. per cm.^{3} from a recent X-ray investigation (1). These various constants are given in Table VI along with the corresponding ones for water (5).

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TABLE VI

THERMAL PROPERTIES OF HYDROGEN PEROXIDE AND WATER

	H_2O	H_2O_2
Specific heat of liquid (cal./gm./deg.)	1.002	0.632
Specific heat solid (cal./gm./deg.)	0.505	0.41
Heat of fusion (cal./mole)	1435	2920
Heat of vaporization at 0° (cal./mole)	10740	12593
Melting point (°C.)	0.000	−0.461
Cryoscopic constant	1.86	1.72
dp/dt, fusion (atm./deg.)	−134	143
dp/dt, vaporization atm./deg.	4.4×10^{-4}	2.9×10^{-5}
dp/dt, sublimation atm./deg.	4.8×10^{-4}	3.6×10^{-5}

Numerous determinations of the heat of decomposition of hydrogen peroxide have been reported since the first one by Favre and Silbermann (6) one hundred years ago. Their results, as well as those of their successors, Berthelot (3), Thomsen (20), and de Forcrand (4) seem widely scattered by present standards and need not be considered here. Among the more recent data those of Matheson and Maass (16) and of Roth, Grau, and Meichsner (19) are the most reliable. These two groups of experimenters followed the same technique, using an adiabatic calorimeter at about 20° and solid manganese dioxide as catalyst. In addition the German workers measured the heat of dilution of hydrogen peroxide at four different concentrations. From an analysis of their results Mickley (18) concluded that the most probable value for the heat of the reaction

$$H_2O_2\ (l) = H_2O\ (l) + \tfrac{1}{2}\ O_2\ (g)$$

was 23.47 kcal. per mole at 20°. This may be compared as such with the average of the first four results in Table IV, 23.54 kcal. per mole, since the temperature coefficient of the reaction is practically zero for the pure peroxide. For aqueous solutions, however, the temperature coefficient is not negligible, so that the two sets of data mentioned above had to be recalculated to 0° for comparison with the present ones. As shown in Fig. 2 most of the points fall closely on a smooth curve except for the four ones at 12.5, 12.6, 71.5, and 84.5%. The first two of these measurements must be given less weight as they were done on successive days using the same, somewhat unstable, solution. At that level a difference of 0.1% in the concentration of hydrogen peroxide is sufficient to bring the two points down on the curve. As to the other two erratic results, no obvious explanation could be found for them after a careful scrutiny of the experimental procedure. (The data of Kavanagh (12) and Kubaschewski and Weber (13) confirm that the curve should be concave as drawn.) The degree of reproducibility of the other thermal measurements reported above is sufficient indication that the calorimetric technique itself was free from serious systematic errors.

The necessity of correcting for the undecomposed peroxide introduced some uncertainty because the heat of dilution varies appreciably with concentration (13) and it was not possible to tell whether there remained droplets of

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relatively concentrated hydrogen peroxide sprayed on the wall of the reaction tube or whether the total residual liquid was a very dilute solution. Because of the long time taken to complete a determination the first occurrence seemed more probable and the correction was applied accordingly. At any rate this correction seldom amounted to more than a few parts per thousand. Time was not available to extend the work much further but in view of the importance of this datum in thermochemical calculations another attempt will be made, along somewhat different lines, to obtain a more accurate and reliable value.

Acknowledgment

This work was done during the tenure by one of the authors (W.T.F.) of a summer fellowship of the National Research Council. The Buffalo Electro-Chemical Co. has generously supplied the 90% hydrogen peroxide.

Résumé

Les propriétés thermiques suivantes du peroxyde d'hydrogène ont été mesurées avec un calorimètre à glace de Bunsen. Chaleur spécifique du liquide: 0.632 cal./g./deg. entre 0° et 20°C.; chaleur spécifique du solide cristallin: 0.41 cal./g./deg. entre −20° et −10°; chaleur latente de fusion: 85.83 cal./g. au point de fusion, −0.46°; chaleur latente de vaporisation 370.17 cal./g. à 0°. La constante cryoscopique du peroxyde d'hydrogène, 1.72, obtenue à partir de ces nouvelles données, permet de calculer le point de fusion des solutions très concentrées de peroxyde d'hydrogène. L'accord avec les valeurs expérimentales déterminées récemment est excellent.

La chaleur de décomposition du peroxyde d'hydrogène catalysée par le noir de platine a également été mesurée à différentes concentrations dans le calorimètre à glace. Les résultats ne sont pas définitifs mais ils tendent vers une valeur de 23.54 kcal./mole pour la décomposition du peroxyde pur.

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THE STRUCTURE OF RYANODINE. I[1]

BY R. B. KELLY,[2] D. J. WHITTINGHAM,[3] AND K. WIESNER

Abstract

Ryanodine consumes one mole of periodic acid and gives oxoryanodine $C_{25}H_{33}O_9N$. Splitting off water from ryanodine gives anhydroryanodine $C_{25}H_{33}O_8N$. The analyses of these two derivatives are therefore in agreement with the formula for ryanodine $C_{25}H_{35}O_9N$. Alkaline hydrolysis of ryanodine gives pyrrole-α-carboxylic acid and an alcohol $C_{20}H_{32}O_6$. This alcohol splits off water to give a compound $C_{20}H_{30}O_7$. Alkaline hydrolysis of oxoryanodine consumes three moles of alkali and gives a mixture of low molecular acidic products. Alkaline fusion of oxoryanodine gives a neutral aromatic nitrogen-free crystalline substance.

Folkers and associates (1) have isolated from the flacourtiaceous plant *Ryania speciosa* Vahl. the insecticidal principle ryanodine. They formulated it tentatively as $C_{25}H_{35}NO_9$ or $C_{26}H_{37}NO_9$. It melts at 219-220°C., is neutral to litmus, and shows six or seven active hydrogens. The ultraviolet absorption maximum is at 268.5 mμ.

We have repeated the isolation of ryanodine and the substance, purified by a nine-funnel countercurrent distribution between ether and water, analyzed reasonably well for $C_{25}H_{35}NO_9$. This formula is substantiated by two derivatives which are much more easily purified and analyzed.

Upon oxidation with periodic acid or lead tetraacetate, ryanodine consumes one mole of each reagent, respectively, and gives a compound which we call oxoryanodine $C_{25}H_{33}NO_9$, m.p. 227°C. No volatile carbonyl compound could be detected.

Oxoryanodine can be differentiated from ryanodine by its sparing solubility in alcohol, from which it can be obtained in high purity. Treatment of ryanodine with acids in ether, for instance sulphuric acid, gives a beautiful crystalline compound, anhydroryanodine $C_{25}H_{33}NO_8$, m.p. 275°C., which can be sublimed without decomposition for analysis.

Both oxoryanodine and anhydroryanodine have ultraviolet spectra identical with ryanodine. The infrared spectrum of ryanodine shows a single carbonyl peak at 1684 $cm.^{-1}$. Oxoryanodine, in addition to this, shows a second carbonyl

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Contribution from the Chemistry Laboratories of the University of New Brunswick, Fredericton, N.B. Presented at the 3rd Summer Seminar in the Chemistry of Natural Products, July 10th-14th, Fredericton.
[2] *Holder of a Beaverbrook Graduate Scholarship.*
[3] *National Research Council of Canada Postdoctorate Fellow.*

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peak at 1719 cm.$^{-1}$. Anhydroryanodine shows in addition to the original carbonyl peak a second one at 1735 cm.$^{-1}$. The splitting off of water is therefore connected with the appearance of a new carbonyl group.

However, the group splitting off water is different from the grouping which is oxidized by periodic acid since anhydroryanodine consumes, as does ryanodine, one mole of periodic acid or lead tetraacetate.

The ultraviolet spectrum of ryanodine is, as can be seen from Fig. 1, closely related to the spectrum of pyrrole-α-carboxylic ester. Also, the infrared spectra of both compounds show several parallel bands. Alkaline saponification of ryanodine results in the consumption of one mole of alkali and gives pyrrole-α-carboxylic acid, identified by the melting point of the ester and its ultraviolet spectrum.

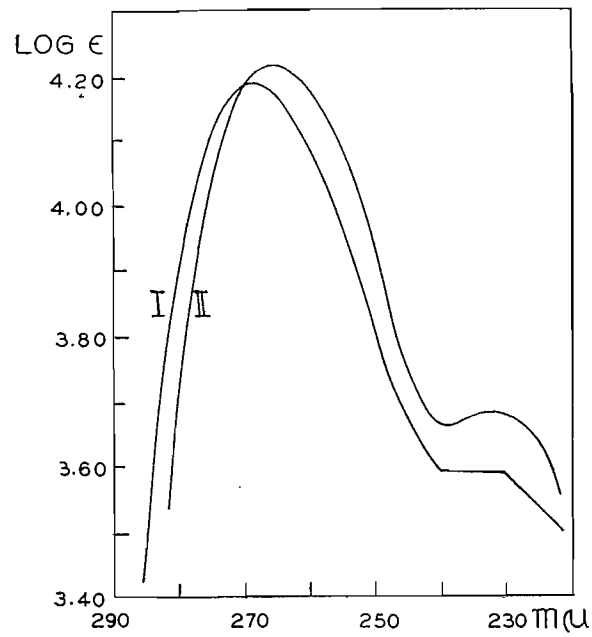

FIG. 1. *Ultraviolet spectra in alcohols. I. Ryanodine. II. Pyrrole-α-carboxylic methyl ester.*

Prolonged continuous extraction of the alkaline hydrolysis mixture gives a beautifully crystalline compound, m.p. 252°C., which analyzes well for $C_{20}H_{32}O_8$. Active hydrogen determinations on this compound show a content of five or possibly six active hydrogens. A microhydrogenation failed to show the presence of double bonds. The compound has no ultraviolet absorption. The infrared spectrum of the compound suggests, in spite of the results of the microhydrogenation, the presence of double bonds, possibly of the $R_2-C=CH-R$ and $RHC=CHR$ type and besides this, of course, a strong peak due to bonded $-OH$ is observed. The compound does not show carbonyl absorption.

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If the aqueous solution of the C_{20} alcohol is acidified, the compound can be extracted in a much shorter time on a continuous extractor. The compound thus obtained is difficult to crystallize but crystallizes on sublimation in high vacuum and melts then at 220°C. It analyzes for $C_{20}H_{30}O_7$. The infrared spectrum of this compound shows a carbonyl peak at 1720 cm.$^{-1}$. Although this is not the exact value of the second carbonyl peak of anhydroryanodine, it seems reasonable to assume that the two compounds are in the same relationship as ryanodine and anhydroryanodine.

Alkaline saponification of oxoryanodine was also investigated. Somewhat surprisingly, the compound consumes three moles of alkali and gives a mixture of low molecular acidic products.

Alkali fusion of oxoryanodine gives besides pyrrole-α-carboxylic acid a neutral substance, m.p. 158°C. (in a low yield), which can be obtained in beautiful crystals and sublimed for analysis.

The ultraviolet (λ_{max} 258, 280 log ϵ 4.00, 3.90) and infrared spectrum point to an aromatic compound.

The analysis checks best to $C_{12}H_{14}O_2$ although the formula $C_{18}H_{20}O_3$ has still to be considered.

Experimental Part

Ryanodine

The amyl acetate residue (6 gm.), prepared from 2400 gm. of *Ryania* powder according to the procedure of Folkers *et al.* (1), was dissolved in 300 ml. of ether and placed in a separatory funnel. Into a second and a third separatory funnel were placed 300 ml. of ether. After shaking the first funnel with 300 ml. of water, the water layer was transferred to the second funnel and a new 300 ml. portion of water was added to the first funnel. The process was repeated as in an ordinary countercurrent distribution until six portions of water had passed through the three funnels. The combined water layers were then evaporated *in vacuo* to a smaller volume and extracted six times with ether. The ether solution was evaporated to dryness, yielding 3 gm. of pure white foam. This material crystallized easily from ether, and after four recrystallizations attained a constant melting point of 228-229°C. It was dried at 80°C. for 24 hr. in high vacuum. Calc. for $C_{25}H_{35}NO_9$: C, 60.84; H, 7.15; N, 2.84%. Found: C, 60.44; H, 7.28; N, 2.88; active H, 1.36%.

Titration with lead terraacetate or periodic acid gave a consumption of 0.83 mole of either reagent in 15 min. An extended reaction period did not alter this consumption.

Anhydroryanodine

Pure ryanodine (310 mgm.) was dissolved in 300 ml. of absolute ether and 0.5 ml. of concentrated sulphuric acid and 9 gm. of anhydrous copper sulphate were then added. The mixture was allowed to stand for three days. At the end

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of this period the acid was neutralized by adding powdered sodium carbonate, and the ether solution was washed with a 5% sodium carbonate solution. The aqueous washings were extracted several times with ether, and the combined and dried ether extracts were taken to dryness. In this way 245 mgm. of a substance was obtained, which, after four crystallizations from methanol–chloroform, melted at 275°C.; further recrystallization did not alter the melting point. For analysis the compound was sublimed in high vacuum at 190°C. The melting point of the sublimate was 275°C. Calc. for $C_{25}H_{33}NO_8$: C, 63.14; H, 7.00; N, 2.95%. Found: C, 62.63, 62.65, 63.12; H, 6.96, 6.82, 7.17; N, 2.99, 2.89; active H, 1.26%.

Oxoryanodine

Ryanodine (250 mgm.) was dissolved in 5 ml. of methanol and to this solution was added 5 ml. of 0.5 *M* periodic acid and 2 ml. of water. After approximately ten minutes, oxoryanodine started to crystallize in shining rodlike crystals. In two hours the crystals were collected on a filter and washed with water. Upon drying the yield was 243 mgm. and the melting point 205-207°C. After six recrystallizations from methanol the compound melted constantly at 227°C. and gave a strong depression with ryanodine. For analysis it was dried at 110°C. for 24 hr. in high vacuum. Calc. for $C_{25}H_{33}NO_9$: C, 61.09; H, 6.77; N, 2.85%. Found: C, 61.26, 60.76, 60.69; H, 6.76, 6.64, 6.58; N, 3.21, 2.99, 3.33, 2.82; active H, 1.21%.

A nine-funnel countercurrent distribution of oxoryanodine between ether and water (200 ml. of each phase) gave the following result:

Funnel No.	Weight of substance
1	868 mgm.
2	67
3	1
4, 5, 6, 7, 8, 9	0

Alkali Fusion

Oxoryanodine (4.5 gm.) was added in small portions with stirring to 30 gm. of fused potassium hydroxide at 320-330°C. in a nickel crucible. After cooling, the melt was dissolved in 250 ml. of water and ice, and the solution was continuously extracted with ether for 24 hr. The ether extract was dried over anhydrous sodium sulphate, the greater portion of the ether was removed by distillation through a 12-in. Vigreaux column, and the final traces of solvent were removed *in vacuo* at 10°C. The residue (167 mgm.) was dissolved in ether and this solution was chromatographed in ether on alumina. The residue from the eluate (98 mgm.) was sublimed at 40-60°C./0.15 mm. Part of the oily sublimate crystallized from petroleum ether in red-coated warts. This material (20 mgm.) was recrystallized twice and sublimed at 110°C./0.015 mm. to give white needles which melted at 158°C. Calc. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%; calc. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%. Found: C, 75.35; H, 7.18%.

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The aqueous solution, which had been continuously extracted with ether, was acidified to Congo red with sulphuric acid and then extracted continuously with ether for 24 hr. After removal of the ether, 2.5 gm. of a dark resinous material was obtained. This material was sublimed at 80°C./0.15 mm. to give a white solid. Three recrystallizations from ether – petroleum ether and resublimation at 95°C./0.015 mm. gave a pure substance which sublimed at 175-180°C. when subjected to a melting point determination. A positive test was obtained with alcoholic ferric chloride solution. Calc. for $C_5H_5NO_2$: C, 54.05; H, 4.53; N, 12.61%, Found: C, 54.15, 54.31; H, 4.40, 4.28; N, 12.54, 12.72%. The ultraviolet spectrum in alkaline alcohol showed λ_{max} 253 mμ; log ϵ 4.14 and in acidic alcohol showed λ_{max} 264 mμ; log ϵ 4.23.

The acidic substance (124 mgm.) was converted to the methyl ester with methanol and an ethereal solution of diazomethane. The product was recrystallized once from ether – petroleum ether, and then sublimed at 50°C./0.015 mm. to give beautifully crystalline rods, m.p. 73-74°C. alone and in admixture with an authentic specimen of the methyl ester of α-pyrrole carboxylic acid. Calc. for $C_6H_7NO_2$: C, 57.60; H, 5.64; N, 11.19%. Found: C, 57.59, 57.33; H, 5.31, 5.20; N, 10.87, 10.71%.

Saponification of Ryanodine

Ryanodine (2.7 gm.) was refluxed with 50 ml. of 5% alcoholic potassium hydroxide for six hours. After evaporation of the alcohol *in vacuo*, 50 ml. of water was added and the solution extracted continuously with ether for a week. Evaporation of the ether gave a white foam which crystallized in beautiful prisms from ether. The yield was 1.4 gm. After six crystallizations the m.p. was sharp and constant at 252°C. It was dried for analysis at 80°C. in high vacuum. Calc. for $C_{20}H_{32}O_8$; C, 59.97; H, 8.07%. Found: C, 59.97, 59.90; H, 7.95, 7.99%; active H, 1.27%; N, 0.00%.

Microhydrogenation: no uptake in glacial acetic acid with Adams catalyst.

From the exhausted residue pyrrole-α-carboxylic was extracted after acidification and identified by spectrum and mixed melting point of the methyl ester.

In another experiment performed analogously the hydrolysis mixture was immediately acidified, and extracted six times with ether which removed the pyrrole-α-carboxylic acid.

After this an 18-hr. continuous extraction gave a quantitative yield of a white foam which could only be precipitated as a powder by petroleum ether from ether and after a few reprecipitations crystallized on sublimation (m.p. 220°C.) Calc. for $C_{20}H_{30}O_7$: C, 62.80; H, 7.92%. Found: C, 62.53; H, 7.87%; N, 0.00%.

The analyses were performed in the microanalytical laboratory of Dr. R. Dietrich, Zurich.

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Acknowledgments

The infrared spectra were taken partly in the National Research Council Laboratories, Ottawa, through the courtesy of Dr. R. Norman Jones and partly by Dr. Bohon in the Anderson Physical Laboratory; to them we are also indebted for their interpretation. The work was performed on a grant from the National Research Council, Ottawa.

We also wish to thank S. B. Penick and Company for a gift of powdered *Ryania* stems.

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STUDIES IN THE POLYOXYPHENOL SERIES

V. PREPARATION FROM PYROGALLOL OF THE ISOMERIC CYCLOHEXANE-1,2,3-TRIOLS AND -1,2-DIOLS, AND OF SEVERAL ISOPROPYLIDENE AND MONOMETHYL DERIVATIVES[1]

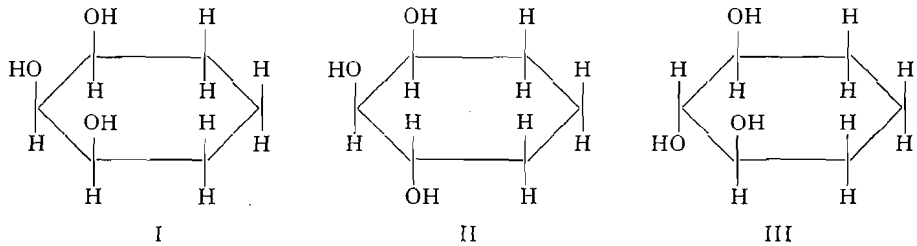
By W. R. Christian,[2] C. J. Gogek,[3] and C. B. Purves

Abstract

A study of the high pressure hydrogenation of pyrogallol over nickel, copper – chromium oxide, and palladium catalysts showed that yields of 35% to about 60% of *cis-cis-cis*-cyclohexane-1,2,3-triol were attainable, but that the *cis-cis-trans* and *cis-trans-cis* isomers were formed only in minor amount. Partial hydrogenolysis of these primary products incidentally yielded some *cis*-cyclohexane-1,2-diol, a smaller amount of the *trans* form, but none of the 1,3-diols. The following derivatives were prepared apparently for the first time: *cis-cis*-isopropylidene-*cis*-cyclohexane-1,2,3-triol, an oil, and its monobenzoate, m.p. 103°C.; *cis-cis*-isopropylidene-*trans*-cyclohexane-1,2,3-triol, m.p. 51°C., and its monobenzoate, m.p. 72° to 76°C.; *cis*-monomethyl-*cis-cis*-cyclohexanetriol, m.p. 71°C., and its *bis*-3,5-dinitrobenzoate, m.p. 190°C.; *trans*-monomethyl-*cis-cis*-cyclohexane-1,2,3-triol, m.p. 37°C.; and isopropylidene-*trans*-cyclohexane-1,2-diol, an oil. Formation of the latter compound occurred when *p*-toluenesulphonic acid, and not the customary hydrogen chloride, was used as catalyst in the condensation of the *trans* diol with acetone.

Introduction

The high pressure hydrogenation of pyrogallol led Lindemann and de Lange (15) to the three isomeric cyclohexane-1,2,3-triols (Structures I. II, III) which were separated and characterized in a satisfactory way for the first time.



I II III

The three cyclohexane-1,2,3-triols

cis-cis-cis	*cis-cis-trans*	*cis-trans-cis*
(γ-pyrogallitol)	(β-pyrogallitol)	(α-pyrogallitol)
m.p. 148°C.	m.p. 124°C.	m.p. 110°C.

These authors realized that the *cis-cis-trans* isomer could be identified because it was the only one capable of being resolved into D and L forms, but their failure to establish this fact decisively made their allocations of structure doubtful. In 1944 McRae and Moir (17) reviewed the literature and arrived

[1] *Manuscript received June 7, 1951.*
Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from Ph.D. Theses submitted in September 1946 (W.R.C.) and in April 1947 (C.J.G.).
[2] *Present address: Colgate–Palmolive–Peet Company, Jersey City, N.J.*
[3] *Present address: Corn Products Refining Company, Argo, Ill.*

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at the correct allocations by applying modern theory to the published data. This review will be given in a forthcoming article. In 1947 Posternak and Ravenna (23) published the first direct experimental proof of the configurations and their work included a resolution of the *cis-cis-trans* raceme by microbiological methods. The object of the present work was to determine the yields, unreported by Lindemann and de Lange, of cyclohexanediols and -triols obtainable by hydrogenating pyrogallol, and to study the possibility of separating the triols by the selective formation of their cyclic isopropylidene acetals. Posternak and Ravenna sought in vain to prepare such derivatives. Their data on the relative rates with which lead tetraacetate and the periodate ion oxidized the three triols were also supplemented by larger-scale experiments, since these rates differentiated the *cis-cis-cis* from the *cis-trans-cis* form.

A series of comparable high pressure hydrogenations of pure pyrogallol in ethanol were carried out at 100° ± 3°C. over Raney nickel instead of over the nickel–copper–cobalt catalyst used by Lindemann and de Lange (15). After various times aliquots of the filtered solutions were used to estimate unreacted pyrogallol. Destruction of the latter in the remainder of the products by air and alkali then left black liquors from which fractional distillation at 0.15 mm. pressure recovered the cyclohexanediols (b.p. 85° to 90°C.) and -triols (b.p. 119° to 123°c.). The yields were corrected for distillation losses but could not be regarded as precise. Fig. 1 (filled circles) shows that the maximum yield of cyclohexanetriols (42%) occurred after about 1.6 hr., or when about 70% of the pyrogallol had reacted. The formation of cyclohexanediols passed through a clearly marked induction period (open circles)

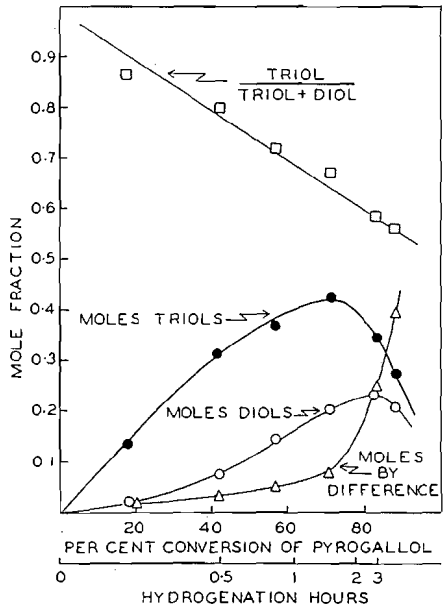

FIG. 1. *High pressure hydrogenation of pyrogallol over Raney nickel at 100 ± 3°C. to cyclohexane-1,2,3-triols and -1,2-diols.*

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and the molar ratio of triols alone to diols *plus* triols, when plotted against the percentage of pyrogallol reacted, gave a nearly linear relationship (squares). A somewhat questionable extrapolation of this ratio suggested that its value was unity at zero time, or that diols were not then present. These observations made it extremely likely that pyrogallol was first reduced to the cyclohexanetriols, and that the latter then underwent hydrogenolysis of hydroxyl groups to yield the diols. More volatile fractions, not recovered quantitatively, contained cyclohexanol (triangles). The difficulty of hydrogenolysis was encountered in an acute form by Packendorff (22), whose platinum oxide catalyst gave cyclohexane and cyclohexanol as the main products from catechol, resorcinol, and pyrogallol.

In larger-scale preparations at 130° to 140°C. in a bigger autoclave, it was found convenient to isolate the crude cyclohexanetriols by first evaporating the alcohol from the filtered hydrogenated liquor, and then extracting products of hydrogenolysis and unchanged pyrogallol with ether from an aqueous solution of the residue. As Lindemann and de Lange (15) reported, dilution of the re-distilled product with acetone separated much of the *cis-cis-cis*-cyclohexanetriol in crystalline form, and the pure *cis-cis-trans* and *cis-trans-cis* isomers could be isolated as crystalline tribenzoates from the mother liquors. Trial showed that these separations were not clean-cut and mother liquors had to be re-worked by benzoylation and debenzoylation in a very tedious manner. The final yields (Table I) were nevertheless sufficiently accurate

TABLE I

YIELDS OF THE CYCLOHEXANE-1,2,3-TRIOLS FROM HYDROGENATED PYROGALLOL*

Catalyst, 100–145°C.	*cis-cis-cis* M.p. 108°C. %	As tribenzoates	
		cis-cis-trans M.p. 184°C. %	*cis-trans-cis* M.p. 142°C. %
Raney Ni**	12–24	0.3–6	0–1.1
Ni – Supercel***	6.3	0.8	0.7
Cu – Cr – O†	17	6.8	3.2
Pd – $SrCO_3$††	70–77	~5†††	0†††

* *Hydrogenated at 2400 to 3100 p.s.i. initial pressure until residual pyrogallol was 10 to 30%.*
** *Five runs using 25 to 316 gm. of pyrogallol at 100° to 140°C.*
*** *Used at 140°C.*
† *Experiment at 140° to 145°C. by C. Gleason.*
†† *Experiment in pure 1,4-dioxane at 130° to 135°C. by J. F. C. Dixon.*
††† *Larger-scale separations by N. S. Whittall.*

to confirm the fact that the hydrogenation of pyrogallol with nickel catalysts was a practical preparative method for *cis-cis-cis*-cyclohexanetriol. Such catalysts, however, were of doubtful utility for the other two isomers, which were recovered in improved, but still unsatisfactory, yields by hydrogenating over copper – chromium oxide. A new palladium–strontium carbonate catalyst (19) promoted comparatively little hydrogenolysis but the crude cyclo-

hexanetriols consisted overwhelmingly of the *cis-cis-cis* isomer and none of the *cis-trans-cis* isomer was isolated from special larger scale experiments carried out recently in this laboratory by Mr. N. S. Whittall.

The preponderance of the *cis-cis-cis* form in all the hydrogenations studied could be accounted for by the "normal" or "one-sided" addition of hydrogen to pyrogallol molecules adsorbed plane to the flat surface of a crystalline catalyst (12). The occurrence of the *trans* forms, however, would seem to require either a multi-stage hydrogenation of the aromatic ring, or a keto-stage, or a thermal isomerization. Although such a thermal isomerization actually took place when *cis*-1,2-dimethyl cyclohexane was passed over nickel at 170°C. (18, 27), a keto-stage mechanism seemed more probable in the present case because Coussemant and Jungers (6) isolated up to 18% of cyclohexanone as an intermediate in the high pressure hydrogenation of phenol. The recovery of *cis-cis-cis*-cyclohexanetriol exclusively from the hydrogenation of optically active *cis*-2,3-dihydroxycyclohexanone over platinum oxide (23), however, raised an objection to this analogy.

On one occasion the entire cyclohexanediol fraction was found to reduce the amount of periodate calculated for the exclusive presence of 1,2-diols (see below). Cyclohexane-1,3-diols, which would be stable to periodate, were therefore present, if at all, in extremely small amount, as was expected from the known tendency for hydrogenolysis to eliminate hydroxy groups in a β, rather than an α, position to others (1, p. 69). The predominance of *cis*-1,2-diol over the *trans* form (mole ratio 2: 1) reflected the much greater amount of *cis-cis* triol initially produced by the hydrogenation.

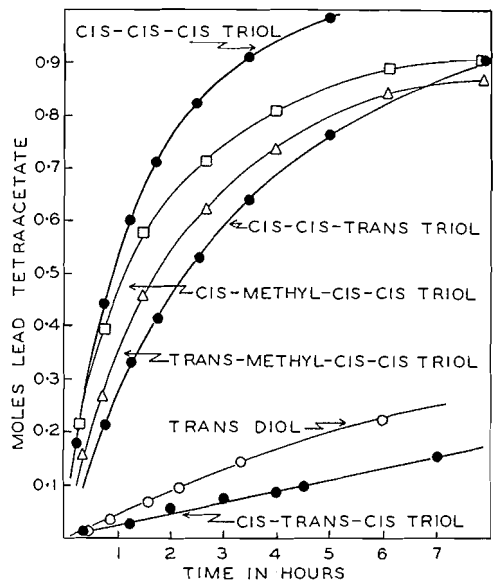

FIG. 2. *Rates of oxidation, in glacial acetic acid at 18.6°C., of 0.0025 M solutions of the cyclohexane-1,2,3-triols and -1,2-diols; triols with 0.00665 M, and diols with 0.005 M, lead tetraacetate. Plot for the cis diol (not shown) was superposable on that for the cis-cis-cis triol. Similar oxidations of the monomethyl ethers at 20°C.*

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Criegee's (7) oxidations of the cyclohexanediols with lead tetraacetate at 18°C. proceeded with second order rate constants of $10^3 K = 80$ and 25 (liters/mole/sec.), respectively, for the *cis* and *trans* forms. A repetition of this work (Fig. 2 and Table II) gave a divergent result for the *cis* diol, but such rates were shown to be sensitive to small amounts of water in the lead

TABLE II

SECOND ORDER RATE CONSTANTS FOR OXIDATIONS WITH LEAD TETRAACETATE AND THE PERIODATE ION

Substance	$Pb(OAc)_4$		KIO_4*** $10^3 K$**
	C × 10³*	$10^3 K$**	
Cyclohexanediols			
cis	4.98	54 80†	1.5
trans	5.00	27 25†	0.22
Cyclohexanetriols			
cis-cis-cis	3.30 6.63 13.1	36 36 30	120
cis-cis-trans	3.30 6.63 13.1	14 14 12	0.59
cis-trans-cis	6.69	1.0	0.12
3-Methoxycyclohexane-1,2,-diols††			
cis-cis-cis	5.7	21	
cis-cis-trans	5.7	48–26	

* *Concentration C in mole per liter at 18.6°C. Glycol 0.003 M in all cases.*
** *Second order rate constant K in liter/mole/sec.*
*** *A 0.004 M solution at pH 11.6 and 20.0°C.; glycol concentration 0.0025 M.*
† *Criegee's results as 18.0°C. (Ref. 7).*
†† *At 20°C. for 0.0024 M glycol solutions.*

tetraacetate–acetic acid solution (8). The *cis* form was also oxidized much more rapidly than the *trans* form by aqueous sodium periodate at pH 11.6, as Price and Knell (24) had previously shown, although the figure they used to publish their data did not lend itself to a quantitative comparison with the present results (Fig. 3 and Table II). The oxidations of the cyclohexane-1,2,3-triols were carried out with the same experimental conditions and the *cis-cis-cis*, *cis-cis-trans*, and *cis-trans-cis* isomers reacted at diminishing rates, both with lead tetraacetate and sodium periodate, as expected from the work of Posternak and Ravenna (23). Although each mole of triol should in theory consume two moles of either oxidant and liberate one mole of formic acid, the utilization of the second mole was slow and the oxidations in their later stages failed to follow the second order rate constants noted in Table II. It is apparent from Fig. 3 that traces of the *cis-cis-cis* and *cis-cis-trans* forms could be removed from the *cis-trans-cis* triol by a selective oxidation with periodate, although no use was made of this observation in the present research.

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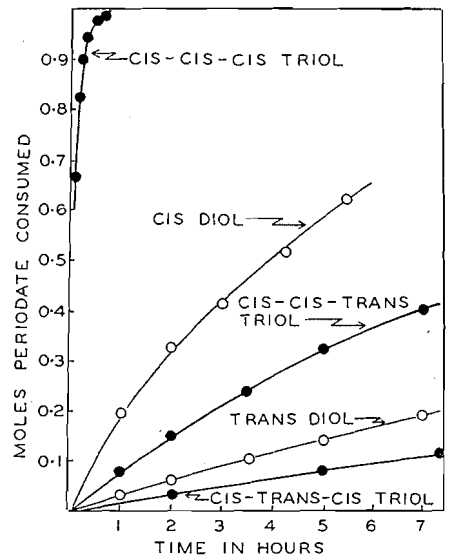

FIG. 3. *Rates of oxidation, by 0.004 M aqueous periodate at pH 11.6 and 20°C., of 0.003 M solutions of the cyclohexane-1,2,3-triols and -1,2-diols.*

By condensing glycols, usually in presence of hydrogen chloride as a catalyst and anhydrous sodium sulphate as a dehydrating agent (Method B) Böeseken (3) established the generalization that cyclic isopropylidene derivatives would form only with 1,2-diols in which the contiguous hydroxy groups were in favorable proximity and in the same plane as the carbon atoms to which they were attached. This rule explained the existence of isopropylidene derivatives from *cis*-1,2,-cyclopentanediol and *cis*-1,2-cyclohexanediol, but not from the corresponding *trans* isomers. The cyclohexanediols were separated very efficiently on several occasions (2, 9, 26) by taking advantage of this circumstance. An attempt was made to apply the same principle of separation to a mixture of the cyclohexanetriols, but the condensation with acetone happened to be carried out with *p*-toluenesulphonic acid as catalyst and a continuous azeotropic distillation with ligroin as the means of dehydration (21) (Method A). Acid hydrolysis of the mixed isopropylidene derivatives, however, yielded a little *cis-trans-cis*-cyclohexanetriol and it was plain that this all-*trans* isomer had unexpectedly undergone the condensation. It then transpired that Method A readily produced a 67% yield of the hitherto unknown isopropylidene acetal from *trans*-cyclohexane-1,2-diol as an oil with a strong peppermint odor, whereas Method B yielded not more than 3%. The attempts of Maan (16) to obtain isopropylidene acetals from several substituted *trans*-cyclohexane-1,2-diols resulted in traces of volatile oils which were assumed, probably in error, to be condensation products of acetone itself. *cis-cis-cis*-Cyclohexanetriol, however, gave with both methods nonquantitative yields of uncrystallized, very readily hydrolyzed acetals (I*a*, R = H) which were separately methylated with silver oxide and methyl iodide. Since some

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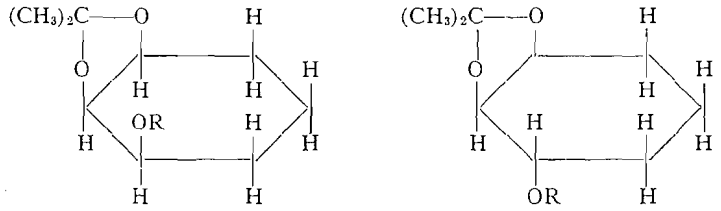

Isopropylidene cyclohexane-1,2,3-triols

Ia. *cis-cis-cis*
R = H, CH_3 or COPh

IIa. *cis-cis-trans*
R = H, CH_3 or COPh

hydrolysis of the labile acetal bonds probably occurred during this process, the crude monomethyl derivatives (I*a*, R = CH_3) were straightway hydrolyzed with dilute acid, and yielded one and the same crystalline monomethyl cyclohexanetriol. The behavior of the *cis-cis-trans*-cyclohexanetriol was similar, although in this case the isopropylidene derivative (II*a*, R = H) was crystalline and the crystalline monomethyl ether of the triol was distinguished by its great hygroscopicity. Both of the cyclohexanetriols yielded crystalline isopropylidene monobenzoates. The ready oxidation of the *cis-cis-cis* monoether with lead tetraacetate (Fig. 2) proved that it still contained an unsubstituted 1,2-glycol group and confirmed the structure (I*a*, R = CH_3) assigned to its isopropylidene derivative. Moreover, since the glycol unit in this case was obviously *cis*, and since the oxidation proceeded almost as quickly with the monomethyl ether of *cis-cis-trans*-cyclohexanetriol (Table II, Fig. 2) the latter also retained the unsubstituted *cis*-1,2-glycol unit. This argument checked the validity of the structures (II*a*).

It was, of course, recognized many years ago that an occasional *trans*-1,2-glycol, such as that from cycloheptane (4, 9), yielded an isopropylidene derivative when condensed with acetone according to the general method A. The present work shows that with *trans*-cyclohexanediol Method B succeeded and Method A failed, and that in consequence Böeseken's generalizations about the formation of isopropylidene derivatives may not apply with the same force when the method of condensation is radically changed.

Experimental

Hydrogenation of Pyrogallol

With Raney Nickel Catalyst (20)

(*a*). The data summarized in Fig. 1 were based on uniform hydrogenations each employing 25.2 gm. of resublimed pyrogallol, 150 cc. of absolute ethanol and 5.0 gm. (wet with ethanol) of catalyst. A Parr high pressure hydrogenation apparatus with a 500 cc. stainless steel bomb was used. After flushing out the system several times with hydrogen, the pressure was adjusted to 2400 p.s.i., the bomb was rapidly heated to 100°C. and maintained within ± 3°C. of that temperature. As the temperature reached 100°C. the shaking device was set in motion and hydrogenation was assumed to have begun at

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that moment. After four hours or less, the bomb was rapidly quenched in cold water, the contents were filtered to remove the catalyst, and filtrate and washings were made up to 280 cc. with ethanol.

Gardner and Hodgson's method (11) was used to determine the unreduced pyrogallol in 0.1 cc. aliquots of the above solution. Each aliquot was added to 25 cc. of 0.1 *N* iodine – potassium iodide solution and strong caustic soda was then added drop by drop until the mixture just failed to give a blue color with a starch indicator. Thirty minutes later 100 cc. of water and 5 cc. of concentrated hydrochloric acid were added, and the liberated iodine was titrated with 0.1 *N* sodium thiosulphate. If the reagent blank was x cc., the titer of the original pyrogallol solution, y cc., and that of the solution after the hydrogenation, z cc., then the residual pyrogallol was 100 $(x-z)/(x-y)\%$ of the original amount. Control experiments showed that the estimation was reliable to $\pm$ 5% even in the presence of ethanol, cyclohexanediols and triols, and the substances arising from the alkaline oxidation of pyrogallol (see below). The amount of iodine required by one mole of pyrogallol, however, was almost 5 moles; not 3 moles, as stated by Gardner and Hodgson, or 3.85 moles as calculated from the example they gave.

The remainder of the hydrogenation liquor was diluted with three 50 cc. volumes of strong aqueous ammonia, added over a period of five hours while oxygen gas was bubbled through the mixture to destroy any pyrogallol. Evaporation of solvents from the resulting black liquor, followed by fractional distillation at 15 mm. pressure, yielded the cyclohexanediol fraction, b.p. 85° to 90°C. and the triol fraction, b.p. 119° to 123°C. Both fractions gave a negative ferric chloride test for phenols. Trials with known mixtures showed that the loss of cyclohexanediols in the fractionation was about 2%, and that of the triols about 6%. The data in Fig. 1 were corrected accordingly.

(*b*). Hydrogenations on a larger scale (Table I) were carried out in a 2-liter Aminco stainless steel bomb and with a more convenient method of isolation. In a typical run, 316 gm. (2.5 moles) of pyrogallol dissolved in 1000 cc. of ethanol were hydrogenated over 50 gm. (wet) of Raney nickel for three hours at 140°C. and 3000 p.s.i. of hydrogen. The hydrogen absorbed was 8.5 moles, instead of the 7.5 moles required for a quantitative conversion to cyclohexane triols. After removal of the catalyst and the ethanol, distillation of the residue yielded 290 gm. of a clear, partly crystalline fraction boiling at 90°to 135°C. at 0.05 mm. pressure. A solution, 500 cc., of this product in water was then extracted continuously with ether to remove cyclohexanediols and also 30 gm. (10%) of unreduced pyrogallol. Evaporation and fractional distillation of the aqueous residue then yielded 90.7 gm. (33%) of cyclohexanetriols boiling at 120° to 140°C. at 0.02 mm. pressure.

With Copper – Chromium Oxide Catalyst (5)

The catalyst, 20 gm., was added to 63 gm. (0.05 mole) of pure pyrogallol dissolved in 200 cc. of pure 1,4-dioxane and hydrogenation was with 3100 p.s.i. of hydrogen at 140° to 145°C. for 150 min. Hydrogen absorbed was 1.68 moles,

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or about 10% in excess of theory. The crude cyclohexanetriols, isolated as in (*b*) and weighing 20.2 gm. (30.6%) were separated as described below into the three isomers, all with correct melting and mixed melting points (Table I).

With a Palladium – Strontium Carbonate Catalyst

As the originators noted (19), this catalyst was very readily inactivated by adventitious impurities, which had to be rigorously eliminated from the reagents. Inactivation uniformly occurred in a 2-liter Aminco stainless steel bomb but not in one of 500 cc. capacity, even when the rates of heating were equalized and the same solutions and catalyst were used. The catalyst, 12 gm. containing 2% of palladium, 33.3 gm. of pyrogallol, 200 cc. of dioxane, and hydrogen initially at 2400 p.s.i. were kept at 75° to 80°C., little or no hydrogen being absorbed at a lower temperature. After two hours of hydrogenation the theoretical amount had been absorbed and the reaction apparently ceased. Much of the *cis-cis-cis*-cyclohexanetriol formed was found to have crystallized and concentration of the mother liquor raised the recovery to 17.6 gm. (50%). The residues when worked up as in (*b*) yielded a further 27% of the mixed *cis-cis-cis* and the *cis-cis-trans* isomers. In larger scale experiments the residual mixture was benzoylated, but extensive fractional crystallization of the tribenzoates revealed no trace of the *cis-trans-cis* form.

Separation of the Cyclohexanetriols

The method of Lindemann and de Lange (15) was followed in principle. A crude cyclohexanetriol fraction, 84 gm., b.p. 135° to 140°C. at 0.25 mm. pressure, was heated under reflux with 1400 cc. of acetone for 10 min. and the mixture was then kept at −15°C. Next day the undissolved portion (45.5 gm.) on recrystallization from an acetone–ethanol mixture yielded 31.7 gm. of the *cis-cis-cis* isomer with the correct melting point of 147° to 147.5°C. In other runs the recrystallizations were more advantageously carried out from ethyl acetate–acetone mixtures. Small amounts of the other two isomers were recovered as the tribenzoates from the final mother liquors.

The acetone-soluble portion, about 40 gm., after recovery was heated on the steam bath for one hour with benzoyl chloride, 110 cc., and pyridine 100 cc. Solution of the semisolid benzoates in 750 cc. of hot ethanol, followed by cooling overnight to room temperature, caused the deposition of the crude crystalline *cis-cis-trans* tribenzoate, which was extracted with 250 cc. of hot ethanol. The tribenzoate, 35.8 gm., was then nearly pure and was conveniently recrystallized to the proper melting point of 182°C. (uncorr.) from glacial acetic acid. The alcohol mother liquors from the crude tribenzoate were kept overnight at −15°C. to bring about the crystallization of the crude *cis-trans-cis* isomer (12.1 gm.). Two recrystallizations from methanol, preferably containing about 5% of water, yielded 5.4 gm. of this isomer with the correct melting point of 139° to 140°C. Mother liquors from all the above crystallizations were then combined, de-benzoylated, and recycled to yield a further 15.1 gm. of *cis-cis-cis*-cyclohexanetriol, 14.1 gm. of the *cis-cis-trans-*

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tribenzoate, and 0.8 gm. of the *cis-trans-cis*-tribenzoate. The final residues from another run were shown to contain a trace of *trans*-cyclohexanediol, which was isolated as the isopropylidene derivative.

The hydrolyses of the two tribenzoates with five volumes of 10% methanolic potassium hydroxide at 45°C. was allowed to continue for several hours after solution was complete, and the products were isolated as Lindemann and de Lange described. A yield of 78% of *cis-cis-trans*-cyclohexanetriol, with the correct melting point of 124°C. was obtained after recrystallization from ethyl acetate. The *cis-trans-cis* isomer (73% yield) melted at 110° to 110.5°C. after recrystallization from ethyl acetate, whereas the recorded m.p. was 108°C. Unlike the other two isomers, the *cis-trans-cis* form was noticeably hygroscopic.

Separation of cis and trans Cyclohexanediols

The crude diol fraction, melting at 76° to 85°C., when triturated with benzene left a residue of the crude *cis* isomer, which could be recrystallized to the proper m.p. of 99°C. from a hot solution of the same liquid. After recovery from the benzene mother liquors, the residue on recrystallization from a 1:2.5 acetone–ligroin mixture deposited the crude *trans* diol, which attained the correct m.p. of 103° to 104°C. when recrystallized from ethyl acetate. The identity of the *cis* and *trans* cyclohexanediols was confirmed by mixed melting points with authentic specimens obtained by oxidizing cyclohexene with potassium permanganate (16) and hydrogen peroxide (26) respectively.

A much more satisfactory method was to separate the *cis* as its more volatile isopropylidene derivative from the *trans* diol, according to the procedure of Rothstein (25). A 46.9 gm. sample of the mixed diols from a large-scale hydrogenation of pyrogallol yielded 39.9 gm. of isopropylidene *cis*-1,2-cyclohexanediol boiling at 70° to 71°C. (12 mm.), together with a still residue from which 13.8 gm. of pure *trans* diol was recovered by crystallization from hot benzene. Hydrolysis of the isopropylidene derivative by heating for two hours with 100 cc. of acetone and 10 cc. of concentrated hydrochloric acid gave 28.5 gm. of the *cis* diol, which was recrystallized from an acetone – petroleum ether mixture cooled to −15°C.

Condensations with Acetone

Method A

A 5 gm. to 7 gm. sample of the pure diol or triol was heated under reflux with about 0.1 gm. of *p*-toluenesulphonic acid monohydrate, 150 cc. of purified acetone and 150 cc. of petroleum ether (b.p. 30° to 60°C.). The apparatus, similar to that of Newman and Renoll (21), consisted of a 500 cc. round-bottomed flask attached by a glass joint to a condenser half-filled with water This condenser returned acetone vapor to the flask but permitted the water formed in the reaction to pass (as an azeotrope with petroleum ether) into a

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second, more efficiently cooled condenser and to be removed by a trap from the system. The condensation was judged to be complete when water ceased to accumulate in the trap. A small amount of anhydrous sodium acetate was added to the residual liquors to neutralize the sulphonic acid before they were evaporated under reduced pressure.

Method B

Five gm. of the diol or triol and 3 gm. of anhydrous sodium sulphate were mechanically shaken with 300 cc. of pure acetone containing 1% or less of dry hydrogen chloride (3), usually for 24 hr. The acid was neutralized with basic lead carbonate; the filtrate from this operation was made definitely alkaline with dry ammonia gas and was evaporated *in vacuo*.

cis-cis-Isopropylidene-cis-Cyclohexanetriol

Method A after two days of heating under reflux gave a still residue which was extracted with benzene. Fractional distillation of the extract returned a 92% yield of the product as a clear colorless oil boiling at 113° to 115°C. (18 mm. pressure). Method B using 1% hydrogen chloride gave a 69% yield (b.p. 111° to 114°C. at 16 mm.), but toward the end of the fractionation white crystals, presumably of regenerated triol, appeared in the neck of the distillation flask. The product from both preparations was soluble in common organic liquids but was practically insoluble in water. All attempts to crystallize the oil failed. Its instability was such that a sample kept for two weeks in a tightly stoppered flask had hydrolyzed completely to the cyclohexanetriol with the correct m.p. of 148°C. after recrystallization. Incipient decomposition was probably the cause of difficulties encountered in the combustion of the isopropylidene derivatives, the best of several results being C, 62.4; H, 8.9%. Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.4%.

cis-cis-Isopropylidene-trans-Cyclohexanetriol

After 60 hr. of heating under reflux, the product from Method A was an oil boiling at 128° to 131°C. at 19 mm. pressure. The oil crystallized completely and recrystallization from ligroin left a 53% yield of fine white needles melting at 50° to 51°C., not depressed by admixture with the product from Method B (0.2% hydrogen chloride). This specimen was initially isolated in 70% yield but two recrystallizations from ligroin at less than 0°C. reduced the amount of pure material, m.p. 51°C., to 45%. Found: C, 63.0; H, 9.5%. Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.4%.

The compound had the solubilities of the *cis* isomer but was much more stable, a sample stored in a tightly stoppered tube deteriorating only very slightly during several weeks.

Isopropylidene-trans-Cyclohexanediol

Method A and 60 hr. of heating yielded 67% of a colorless oil boiling at 77° to 78°C. at 20 mm. pressure, with a density, d_4^{20}, 0.9787 and a refractive index, n_D^{20} 1.4468. Found: C, 69.6; H, 10.3%; mol. refraction, 42.65. Calcd.

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for $C_9H_{16}O_2$: C, 69.2; H, 10.3%; mol. refraction, 42.66. Unreacted *trans*-cyclohexanediol was recovered in 9% yield from a benzene extract of the still residue.

The isopropylidene derivative could not be induced to crystallize, had a strong peppermint odor, and was freely soluble in common organic liquids. A 1-gm. sample, when heated under reflux for one hour with 50 cc. of ethanol and 3 cc. of concentrated hydrochloric acid, gave 0.73 gm. (98%) of *trans*-cyclohexanediol with the proper melting point of 103° to 104°C., not depressed by admixture with an authentic specimen.

Method B with 0.1% hydrogen chloride and shaking for five days gave a product which was extracted with 100 cc. of low-boiling petroleum ether. Three recrystallizations of the residue from benzene recovered 54% of unchanged *trans* diol in a pure condition. The petroleum ether extract, when distilled at 23 mm. pressure, gave 3% of a colorless oil boiling at 76° to 78°C. and having the strong odor characteristic of the isopropylidene *trans* diol. Hydrolysis as described above removed the isopropylidene group and left 2.2% of the *trans* diol, whose purity and identity were confirmed by a mixed melting point. A similar condensation, employing 1% hydrogen chloride in acetone, yielded 11% of volatile material, from which only 0.7% of the original *trans* diol was recovered after acid hydrolysis.

cis-Monobenzoyl-cis-cis-Isopropylidene Cyclohexanetriol

A solution of the acetal, 5 gm., in 15 cc. of chloroform, 15 cc. of pyridine, and 5 cc. of benzoyl chloride was worked up by customary methods after standing at room temperature for 24 hr. After five recrystallizations from ethanol, the melting point of the 3.5 gm. of product (43%) became constant at 101.5° to 103.5°C. The portion analyzed was sublimed at 0.02 mm. pressure and then melted at 103.5°C. Found: C, 69.2; H, 7.4%. Calcd. for $C_{16}H_{20}O_4$: C, 69.5; H, 7.3%. The benzoate was soluble in common organic liquids but not in water.

trans-Monobenzoyl-cis-cis-Isopropylidene Cyclohexanetriol

A repetition of the above benzoylation with 5 gm. of the isomeric isopropylidene acetal yielded 7.4 gm. (92%) of crude product but large losses occurred during several recrystallizations from 50% aqueous ethanol. These recrystallizations yielded 1 gm. of white needles which failed to melt sharply, a typical observation being m.p. 71.5° to 76°C. Sublimation at 0.02 mm. pressure gave a sample with m.p. 72° to 75.5°C. Found: C, 69.5; H, 7.5%. Calcd. for $C_{16}H_{20}O_4$: C, 69.5; H, 7.3%. This monobenzoate, like its isomer, was soluble in organic liquids but not in water.

cis-Monomethyl-cis-cis-Cyclohexanetriol

A 2.5 gm. sample of *cis-cis*-isopropylidene-*cis*-cyclohexanetriol was dissolved in 20 gm. of methyl iodide and 5 gm. of freshly prepared, dry silver oxide was added. After being warmed under gentle reflux for eight hours, the mixture

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was extracted twice with hot methanol. Hydrolysis of the isopropylidene ether contained in the filtered extract was brought about by adding 2 cc. of concentrated hydrochloric acid and by heating under reflux for one hour. Neutralization, filtration, and evaporation left a brown residue that distilled at 0.02 mm. pressure. The distillate soon solidified. After sublimation at 65°C. and 0.02 mm. pressure and two recrystallizations from petroleum ether the average yield was 1.0 gm. or 47%. Specimens were prepared from isopropylidene derivatives made from the cyclohexanetriol by each of the Methods A and B. Each of these specimens melted at 69.5° to 71°C. and a mixed melting point was not depressed. Found: C, 57.8; H, 9.4%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.7%. The monomethyl cyclohexanetriol was soluble in water, alcohol, benzene, and acetone but dissolved very sparingly in petroleum ether.

bis-(3,5-Dinitrobenzoate) of cis-Monomethyl-cis-cis-Cyclohexanetriol

The monomethyl ether, 0.752 gm., was heated under reflux with 3,5-dinitrobenzoyl chloride, 0.752 gm., and pyridine, 3.5 cc., for 30 min. Recrystallization of the product from 30 cc. of ethanol and 20 cc. of ethyl acetate left 0.5 gm. of pure product, m.p. 190°C. Found: C, 46.9; H, 3.5; N, 10.6%. Calcd. for $C_{21}H_{18}O_{13}N$: C, 47.2; H, 3.4; N, 10.5%. An attempt to crystallize the corresponding dibenzoate failed.

This compound was prepared by R. Y. Moir and was analyzed by Marie A. Moir.

trans-Monomethyl-cis-cis-Cyclohexanetriol

The substance was prepared from the corresponding isopropylidene derivative, 2.5 gm., as already described for the *cis*-monomethyl isomer, and in 57% yield. The clear, colorless gum, distilled at 66° to 67°C. at 2 mm. pressure, crystallized completely as white needles when kept *in vacuo* over phosphorus pentoxide. Unlike the *cis* isomer, the present product was extremely hygroscopic and the melting point of 36° to 37°C. had to be taken in a highly evacuated Pyrex tube of 3 mm. diameter. No depression was observed in a mixed melting point of samples prepared from isopropylidene cyclohexanetriols made by Methods A and B. Found: C, 57.1; H, 9.6%. Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.7%.

Determination of Rates of Oxidation

With Lead Tetraacetate

A stock 0.1 *M* solution of the tetraacetate in redistilled, aldehyde-free glacial acetic acid was prepared and standardized iodometrically with 0.02 *N* sodium thiosulphate according to the directions of Hockett and McClenahan (13). The oxidations were carried out, exactly as described by these authors (14), with 100 cc. volumes 0.00025 *M* with respect to the diol or triol and about 0.005 *M* with respect to the lead tetraacetate. Blanks were run and temperature controlled to 18.6 ± 0.5°C. When *a* and *b* were the initial molar

concentrations of the tetraacetate and the glycol, the rate constant K for a second order reaction was given by

$$K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}.$$

The data (Table II) fitted this equation up to consumptions of 0.89 and 0.22, 0.91, 0.91, and 0.15 moles of tetraacetate, respectively, per mole of *cis* and *trans* cyclohexanediol, *cis-cis-cis*, *cis-cis-trans*, and *cis-trans-cis* triol, the slower reactions not being followed to completion. The monoethers of the *cis-cis-cis* and *cis-cis-trans* triols consumed 0.94 and 0.97 moles of tetraacetate per mole in 23 hr. at 20 ± 0.1°C. and 1.02, 1.05 mole after 50 hr.

With Sodium Periodate

The procedure was adapted from the oxidations of the cyclohexanediols by Price and Knell (24). Twenty cubic centimeters of a stock 0.02 M solution of recrystallized periodic acid was mixed in a 100 cc. volumetric flask with 5.0 cc. of 0.045 N sodium hydroxide and 54 cc. of distilled water. At 18.6°C. and zero time, 20 cc. of an aqueous solution containing 0.00030 mole of the cyclohexanediol or -triol was added and the solution (pH 11.6) was made up to the mark with water and rapidly mixed. After various times, 10 cc. aliquots were titrated for remaining periodate by Fleury and Lange's sodium arsenite – iodine method (10). The data fitted the second order rate equation until the molar consumptions by the *cis* and *trans* diols, the *cis-cis-cis*, *cis-cis-trans*, and *cis-trans-cis* triols were at least 0.63 and 0.24, 0.99, 0.41, and 0.51 moles of periodate, respectively.

Acknowledgments

The authors thank the National Research Council of Canada for helping to defray the cost of the research and for awarding Studentships in 1944 and 1945 to one of them (C.J.G.). Another author (W.R.C.) wishes to thank the D. S. and R. H. Gottesman Foundation of New York for the Fellowship held in 1944.

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RELATIVE STABILITIES OF THE ISOMERIC CYCLOHEXANE-1,2,3-TRIOL TRINITRATES AND 1,2-DIOL DINITRATES[1]

By W. R. Christian[2] and C. B. Purves

Abstract

Of the above trinitrates, the *cis-cis-cis* and the *cis-trans-cis* isomers melted at 70° and 88°C., respectively, but the racemic *cis-cis-trans* form remained as a colorless viscid oil. When dissolved in excess 0.105 *N* aqueous–alcoholic sodium hydroxide at 20°C., the *cis-cis-cis* isomer hydrolyzed most rapidly but formed least nitrite, and the solution developed most color. The same isomer evolved the smallest amount of oxides of nitrogen when kept at 106°C., but was more readily detonated by shock than was the *cis-trans-cis*-trinitrate. The relative reactivities toward alkali and heat of the much more stable *cis* and *trans*-cyclohexane-1,2-diol dinitrates, which melted at 24° and 18.5°C., respectively, were as described for the trinitrates, but their relative sensitivities to shock were no less. All five compounds were new.

Introduction

Although it is generally conceded that the explosive properties of an aliphatic nitrate increase with the number of nitrate groups, correlations between these properties and the details of chemical structure and reactivity are still highly incomplete. Much of the available information on chemical reactivity concerns the decomposition of various aliphatic nitrates in alkali, and the early work in this field was reviewed by Lowry, Browning, and Farmery (15). The cleavage of nitrate groups in alkali generally proceeded on both sides of the ester oxygen atom, $\vdots\!\!-\!\!\vdots\ O\ \vdots\!\!-\!\!\vdots\ NO_2$, to yield either the parent alcohol and nitrate, or nitrite together with the corresponding aldehyde or ketone. Nitroglycerine, for example, gave nitrate and nitrite; Berl and Delpy (2) found a glycerol dinitrate among the products, but no mononitrate or glycerol. Conventional hydrolysis to an alcohol dominated in acidic conditions, or when a reducing agent was present in the alkali. Lachman (12) confirmed these principles for nitrotartaric acid, and found that the amount of nitrite formed from nitromalic acid was independent of the temperature, of the concentration and excess of alkali, but varied with the solvent (13).

According to kinetic studies by Lucas and Hammett (16), the cleavages of *t*-butyl nitrate and of *t*-butyl chloride to the alcohol and isobutene in acid, neutral, and alkaline dioxane–water mixtures were so similar that the same mechanisms of solvolysis and elimination could be postulated. Although more benzyl alcohol was produced from benzyl nitrate than from benzyl chloride by solvolysis, the mechanisms were otherwise similar, with the exception that none was suggested for the redox cleavage producing benzaldehyde

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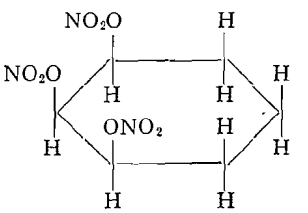
and nitrite from the benzyl nitrate. The hydrolysis of simple alkyl halides was also compared by Gand (8) with that of ethyl nitrate in neutral and slightly acidic systems containing potassium nitrate or silver iodide. Ethyl nitrate was observed to consume alkali more rapidly than its rate of hydrolysis would suggest. Other workers (9) found that the alkaline saponification of methyl-2,3,4-triacetyl-*α*-glucopyranoside-6-nitrate swiftly gave an almost quantitative yield of the methyl-3,6-anhydroglucoside, and that other mononitrates in the glucose series also yielded anhydro derivatives when the nitrate group could be eliminated by a mechanism of the Walden inversion type. When this mechanism was not available, as in methyl-2,3,4-trimethyl-*β*-glucoside-6-nitrate, saponification of the nitrate group was difficult, about 20% of nitrite was formed and the 2,3,4-trimethyl glucoside was recovered in about 75% yield. The other organic product was a resin presumably derived from trimethyl glucoside whose primary alcohol group had been oxidized to an aldehyde unit. Since these results were qualitatively the same as those obtained by saponifying halides and sulphonates in the sugar series, the analogy between aliphatic nitrates, halides, and sulphonates was strengthened. This analogy made it very probable that the mechanisms of elimination, solvolysis and substitution, described for halides and sulphonates in a series of articles by Winstein and his collaborators (24), would eventually find their counterparts for nitrate esters. The particular mechanism favored in a given reaction often depended upon the details of *cis-trans* isomerism and other spatial relationships.

The slow thermal decomposition of several simple aliphatic nitrates gave as principal initial products nitrogen dioxide and the aldehyde or ketone corresponding to the original nitrate (6), the final products from methyl nitrate containing nitric oxide and formaldehyde (1) or carbon dioxide, water, and nitrogen after explosive decomposition (25). Nitroglycerine yielded nitrogen dioxide as an initial product (22), and later work confirmed the fact that first order kinetics were obeyed (1, 21, 23); control experiments with added nitrogen dioxide, nitric acid, or moisture showed that the reaction was catalyzed by its products (23). The initial thermal decomposition of aliphatic nitrates thus appeared to resemble one of the mechanisms of saponification in being a redox reaction leading to carbonyl compounds and the elements of nitrous acid, including nitrogen dioxide.

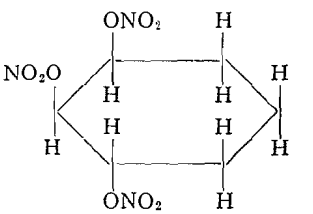
As a result of calculations based on dipole moments, de Kreuk (5) concluded that liquid nitroglycerine existed as various *cis-trans* conformations originating in free rotation about the carbon–carbon bonds and in proportions depending on the solvent. A consideration of the forces of repulsion existing between the nitrate groups suggested that the *cis-cis-cis* would be less stable than the *cis-trans-cis* conformation by an energy factor equivalent to 6330 cal. per mole. The all-*cis* conformation was then tentatively assigned to nitroglycerine in the "labile" crystal habit melting at 2°C., because Hibbert and Fuller (11) had shown that the spontaneous change of this form to the "stable" type of melting point 12.8°C. caused the evolution of practically the same amount of

heat, 6356 cal. The "stable" crystals were more sensitive to detonation by shock than the lower melting form, but results for liquid nitroglycerine were conflicting (7, 10, 11). This irregularity might possibly have been caused by the occlusion in the nitroglycerine of varying numbers of extremely minute gas bubbles (3). The "stable" allotrope had the greatest brisance (7), but the difference between the rates of detonation of the two crystal forms was small (7, 10). Explosion of 1 gm. of the "labile" crystals, on the other hand, produced more gaseous products, 560 cc., than the amounts, 518 cc. and 390 cc., obtained from the "stable" type and liquid nitroglycerine, respectively (7). If de Kreut's inferences were valid, *cis-trans* relationships between nitrate groups produced differences in explosive properties, either in a direct way, or indirectly through their effect on spatial relationships in crystal lattices.

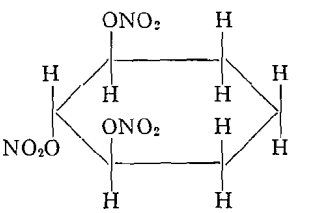
Recent researches (4, 17) accumulated supplies of the three isomeric cyclohexane-1,2,3-triols and made it possible to assign the proper stereochemical configuration to each. The present article describes the behavior of the three corresponding trinitrates, and also of *cis-* and *trans*-cyclohexane-1,2-diol dinitrates, toward alkali, together with some observations on their explosive properties. These trinitrates (structures I, II, and III) were regarded as conformations of nitroglycerine that were rendered capable of independent existence because the presence of the cyclic structure abolished, or very greatly restricted, free rotation about the carbon–carbon bonds.



I. *cis-cis-cis*
(γ-Pyrogallitol trinitrate)



II. *cis-cis-trans*
(β-Pyrogallitol trinitrate)



III. *cis-trans-cis*
(α-Pyrogallitol trinitrate)

Experimental

cis-cis-cis-Cyclohexane-1,2,3-triol Trinitrate

A 5 gm. sample of the pure *cis-cis-cis* triol, melting correctly at 148°C., was added slowly, at 0°C. with stirring, to 20 parts by weight (67 cc.) of 98% nitric acid in which 15 gm. of phosphorus pentoxide had been dissolved. After one hour at 0°C. the mixture was stirred into 1 liter of ice and water, and several

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hours later the product was recovered, washed free of acid, and dried. Yield, 8.5 gm., or 84%; melting point 73° to 74°C. Recrystallizations from hot ligroin caused the material to separate as large thin plates belonging to the monoclinic, or possibly the triclinic, system, and melting at 74° to 74.5°C. Other organic liquids dissolved the substance freely at room temperature. Calc. for $C_6H_9N_3O_9$: C, 27.0; H, 3.4; N, 15.7%. Found: C, 26.9, 27.1; H, 3.8, 4.0; N(Dumas), 15.6, 15.7%; N(micro-Kjeldahl), 15.6, 15.7%.

Similar crude yields resulted in this case when the phosphorus pentoxide was omitted from the nitration mixture; also when the latter was replaced with glacial acetic acid, 100 cc., acetic anhydride, 38 cc., and 98% nitric acid, 18 cc. Nitrations with this mixture lasted from 15 min. to 16 hr. without influencing the yield.

cis-cis-trans-Cyclohexane-1,2,3-triol Trinitrate

A similar nitration of 5 gm. of the pure *cis-cis-trans* triol, melting correctly at 123.5° to 124.5°C., yielded an oil which was made acid-free by repeated washing in distilled water near 0°C.; the oil being recovered on the centrifuge after each wash. A solution of the oil in ether was decolorized with absorbent carbon, was dried over anhydrous sodium sulphate, and was evaporated under reduced pressure. After being kept *in vacuo* over phosphorus pentoxide, 7.6 gm. (75%) of a clear, very faintly yellow oil remained with a refractive index of n_D^{21}, 1.4895. Calc. for $C_6H_9N_3O_9$: N, 15.7%. Found: N, 15.6, 15.6%.

The substance showed no tendency to crystallize from solvents, nor after being kept for six months at −5°C. It was a colorless glass at −40°C.

cis-trans-cis-Cyclohexane-1,2,3-triol Trinitrate

A similar nitration of the pure *cis-trans-cis* triol, melting correctly at 109° to 110°C., was for one hour at −5°C. The crude product (66% yield and m.p. 83° to 84°C.) when recrystallized from hot ligroin yielded large rodlike prisms of either the monoclinic or triclinic systems and melting at 88° to 88.5°C. Calc. for $C_6H_9N_3O_9$: N, 15.7%. Found: N, 15.8, 15.6%.

cis-Cyclohexane-1,2,-diol Dinitrate

The pure *cis* diol, 10 gm. of m.p. 99°C., when nitrated at −5°C. for 30 min. gave an oil which was washed and dried as described above for the *cis-cis-trans* triol trinitrate. The product, 14.7 gm. or 83%, melted at 23° to 25°C., but wasteful recrystallizations from hot ligroin were necessary to yield the pure substance as prismatic rods with melting point 24.5° to 25°C. and refractive index, n_D^{21}, 1.4790. Calc. for $C_6H_{10}N_2O_6$: N, 13.6%. Found: N, 13.4, 13.4%.

trans-Cyclohexane-1,2,-diol Dinitrate

The pure *trans* diol, m.p. 104°C., when nitrated as described for the *cis* isomer, gave an 80% yield of an oil which crystallized as small irregular plates,

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m.p. 17° to 19°C. Recrystallization from hot ligroin reduced the yield of pure material to 56% melting at 18.5° to 19°C. Calc. for $C_6H_{10}N_2O_6$: N, 13.6%. Found: N, 13.5, 13.6%.

Decomposition of the Nitroxycyclohexanes in Alkali

In all cases the solvent was 50% aqueous ethanol by weight, or 60 parts of 95% ethanol to 40 parts of water by volume, the mixtures used being free of acidic impurities and dissolved carbon dioxide.

The experiments with the trinitrates were carried out at 20 ± 0.05°C. in 100 cc. volumetric flasks containing 0.001 mole of each nitrate, and zero time was taken as the moment when the addition of 25 cc. of 0.4184 *N* aqueous–alcoholic sodium hydroxide brought the original solution up to the mark. The solution was promptly and thoroughly mixed. After various times 10 cc. aliquots were made acid by adding 25 cc. of 0.045 *N* hydrochloric acid, and the excess was back-titrated with 0.01013 *N* sodium hydroxide to pH 8.0. A Coleman pH meter was used because of the marked color of certain of the solutions (Figs. 1 and 2).

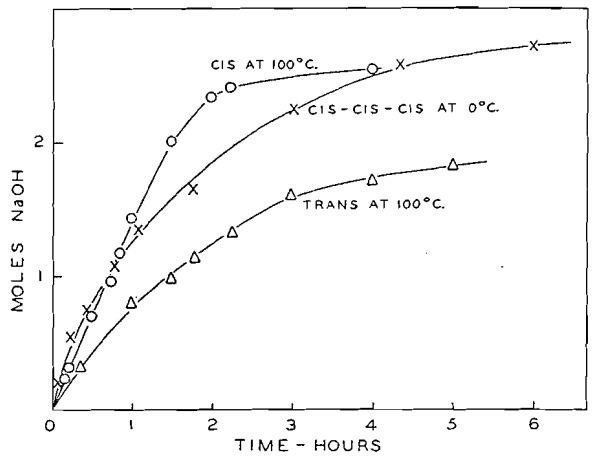

FIG. 1. *Rate of neutralization of 0.105 M sodium hydroxide by 0.01 M solutions of the 1,2-dinitroxycyclohexanes at 100°C., and of the cis-cis-cis-1,2,3-trinitroxy derivative at 0°C. Solvent, 50% aqueous ethanol.*

Since the dinitrates reacted only very slowly at 20°C., they were examined at 100°C. The initial solution of 100 cc. was promptly divided into 10 cc. aliquots, each of which was contained in a 4 oz. bottle fitted with a screw top and a rubber gasket. The bottles were then heated in a steam oven for various times, were cooled, and the contents titrated as before. Blanks run without the nitrate showed that the glass of the bottles neutralized up to 3.7 cc. of the 0.01 *N* alkali as the time of heating was extended to five hours, but the corresponding plot, a reversed S in shape, was used to correct the results (Fig. 1).

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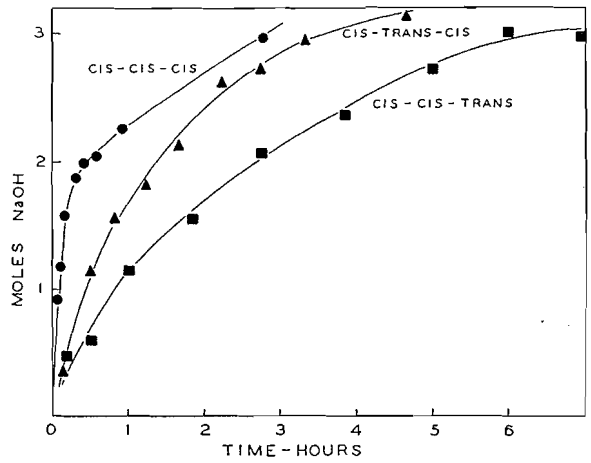

FIG. 2. *Rate of neutralization of 0.105 M sodium hydroxide by 0.01 M solutions of the 1,2,3-trinitroxycyclohexanes at 20°C. Solvent, 50% aqueous ethanol.*

After the titration to pH 8, each aliquot was diluted to 100 cc. and examined for color and nitrite content. The latter was determined by adding 1 cc. of Miller's (20) dimethylaniline – hydrochloric acid reagent to 25 cc. of the solution and estimating the depth of color produced by the yellow nitroso derivative four hours later. A photoelectric colorimeter with a blue filter was used, and the details of the technique were as described elsewhere (9). The blanks consisted of other 25 cc. volumes of each original solution adjusted to approximately the same pH with 1 cc. of 5 *N* hydrochloric acid instead of with 1 cc. of Miller's reagent. Known, accurate dilutions of pure 0.028 *M* sodium nitrite were used to establish the calibration plot and a plot of log per cent transmission of light against the concentration of nitrite was linear within the range studied, as was expected (9). Figs. 3 and 4 summarize the results.

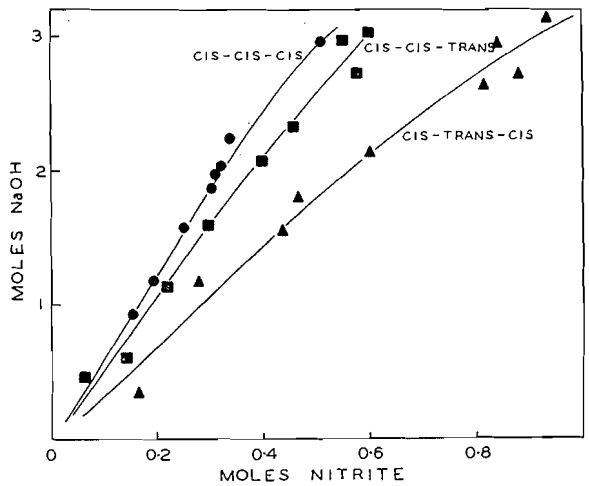

FIG. 3. *Plots of moles nitrite formed against moles of sodium hydroxide neutralized by the solutions of the 1,2,3-trinitroxycyclohexanes at 20°C.*

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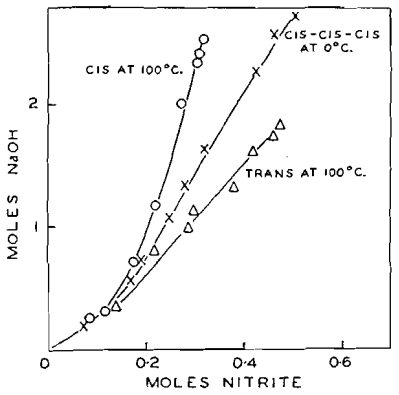

FIG. 4. *Plots of moles nitrite formed against moles of sodium hydroxide neutralized by the solutions of the 1,2-dinitroxycyclohexanes at 100°C., and of the cis-cis-cis-trinitroxy derivative at 0°C.*

The remainder of each neutralized, diluted aliquot was then examined for its content of yellow color, the photoelectric calorimeter being used with a blue filter against distilled water as the standard. As the nature of the coloring material was unknown, it was necessary to assume that the amount was proportional to the intensity of color, and the plots in Fig. 5 were based on this assumption. No determinations were made with the cyclohexanediol dinitrates, both of which yielded solutions whose yellow-brown colors were much less intense than those from the trinitrates. As the intensity varied with the pH, a 10 cc. aliquot of the completely hydrolyzed *cis-cis-trans*-trinitrate was diluted to 100 cc. and acidified, when it became nearly colorless. The pH was then varied from 2.2 to 9.4 by the cautious addition of increments of concentrated sodium hydroxide, the over-all volume change being less than

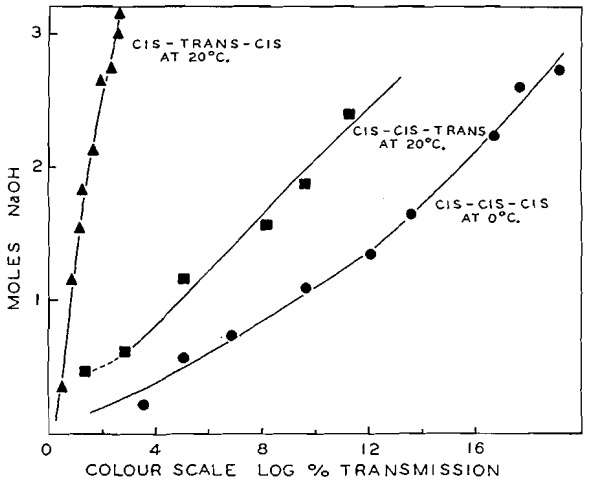

FIG. 5. *Plots of moles sodium hydroxide neutralized against intensity of color produced in the solutions of the cis-trans-cis and cis-cis-trans-1,2,3-trinitroxycyclohexanes at 20°C., and of the cis-cis-cis isomer at 0°C.*

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5%. A plot of the pH against the log per cent transmission of light formed a smooth curve slightly convex to the pH axis and showed that the action of pH was reversible within the limits cited.

Sensitivity to Impact

These tests were made on the Rotter Impact Machine, in which a blow caused by a steel ball falling from a variable height was communicated to the sample resting on a steel anvil. The minimum height required to produce detonations in 50% of the runs was found by trial and was compared with the corresponding heights for nitroglycerine and for trinitrotoluene, which were standard substances. The results are in Table I.

TABLE I

EXPLOSIVE PROPERTIES OF THE DI-AND TRINITROXYCYCLOHEXANES*

Substance	M.p., °C.	Drop test,** cm.	Ignition test		Bergmann–Junk test,† mgm. NO/gm.
			Fumes, °C.	Ignition, °C.***	
Dinitrates					
cis	24.5	*A* (300)		....	....
		B 60	170	....	0.27
trans	19	*A* 85			0.67
		B 72	165	185	
Trinitrates					
cis-cis-cis††	74.5	*A* 55			
		B 60	155	180	0.95
		C 60	170	182	
cis-cis-trans†††		*A* 40			....
(an oil)		*B* 34	155		3.5
		C 38	163	172	
cis-trans-cis	88.5	*A* 85			....
		B 85	155	....	8.6

* *Samples used in Tests A were retested four months later (Series B). Samples prepared four years later by Mr. N. S. Whittall were used for Tests C.*

** *Height of fall of steel ball required to produce detonation. Nitroglycerine, 8 cm.; trinitrotoluene, 100 cm.*

*** *Definite but mild explosions.*

† *After 20 hr. at 106°C. and atmospheric pressure. From data in Fig. 6.*

†† *A 6-gm. sample gave 1.23 times the power of trinitrotoluene in the ballistic mortar test.*

††† *A 6-gm. sample 1.28 times as powerful as T.N.T. in the ballistic mortar test.*

Thermal Stability

The Bergmann-Junk-Mayrhofer (18, 19) method was used, the 0.1 gm. samples being heated at 106 ± 1°C. for various times and the liberated oxides of nitrogen absorbed in 10 cc. of 5% potassium iodide. The equivalents of iodine liberated per mole of sample were estimated with 0.01 *N* sodium thiosulphate and were plotted against the time of heating (Fig. 6). Table I contains the results after heating for 20 hr., expressed as mgm. nitric oxide per gram sample.

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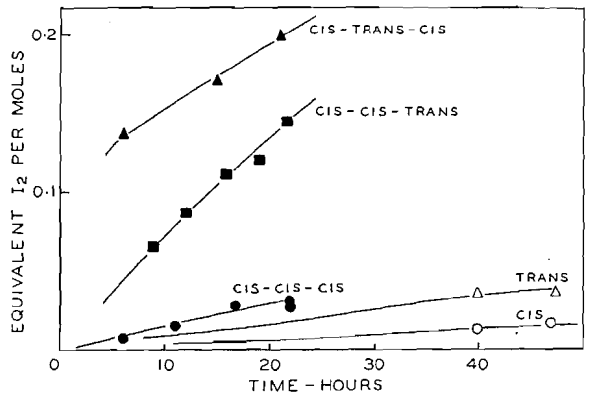

FIG. 6. *Rates of evolution of oxides of nitrogen, expressed as equivalents of iodine per mole, from the 1,2,3-trinitroxy and 1,2-dinitroxycyclohexanes when kept at 106°C.*

Results and Discussion

None of the five nitrates liberated an appreciable amount of acid when kept at room temperature in water, but all could be decomposed at convenient rates when dissolved in an excess of 0.105 *N* sodium hydroxide in 50% aqueous ethanol. The reactions were followed by noting the rate of disappearance of alkali, the rate of formation of nitrite, and the rate at which a yellow color developed in the solutions.

It is obvious from Fig. 1 that the *cis*-dinitrate (circles) neutralized more than the theoretical 2 moles of alkali, and reacted more rapidly than the *trans*-isomer (triangles); also that the rate for the *cis-cis-cis*-trinitrate at 0°C. (crosses) was comparable to that of the *cis*-dinitrate at 100°C. Multiplication of adjacent nitrate groups therefore greatly increased the over-all reactivity toward alkali. Results for the trinitrates at 20°C. (Fig. 2) showed that the *cis-cis-cis* isomer rapidly consumed nearly 2 moles of alkali and that the rate then diminished rather abruptly. Since the plot at 0°C. (Fig. 1) had no similar break, it appeared likely that the saponification proceeded by two reactions whose activation energies were different. The plot at 0°C. for the *cis-cis-cis*-trinitrate and that for the *cis-cis-trans* isomer at 20°C. happened to be almost superposable at all times up to five hours. By analogy with the results in Fig. 1, it was expected that the *cis-trans-cis*-trinitrate would be least reactive toward alkali, but this position was taken by the *cis-cis-trans* isomer (squares). The initial point on the *cis-cis-trans* plots in Figs. 2, 3, and 5 appeared displaced in the direction of a greater consumption of alkali, although the reaction of the original trinitrate toward water was neutral. An unknown, readily saponified impurity or a small amount of an *aci*-modification of the kind encountered by Gand (8) in ethyl nitrate, might have been present in this uncrystallized trinitrate, but the proper explanation was not determined.

The unexpected position of the *cis-trans-cis*-trinitrate in Fig. 2 was perhaps related to the superior amount of nitrite which this isomer produced (Fig. 3), and in this case the *cis-cis-trans*-trinitrate occupied the intermediate position.

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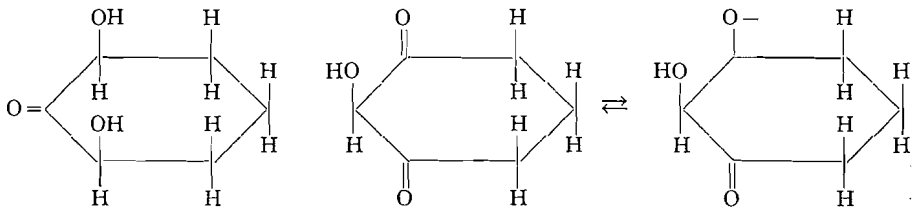
Although these plots at 20°C. appeared to be linear, the mechanics of nitrite formation were probably complex because the data for the *cis-cis-cis* isomer at 0°C. clearly indicated a more extensive initial reaction (Fig. 4, crosses). The same type of plot was given by the *cis*-dinitrate at 100°C., and possibly by the *trans* isomer, which definitely produced more nitrite per mole of sodium hydroxide consumed. Since the plot for the *trans*-dinitrate at 100°C. was accurately superposable on that for the *cis-trans-cis*-trinitrate at 20°C., the mechanism of nitrite formation was probably independent of temperature and identical for both of these *trans* compounds.

It was noted that the color assumed by the alkaline solutions of the nitrates ranged in intensity from slight yellow-brown for the dinitrates at 100°C. to a clear, very deep yellow for the *cis-cis-cis*-trinitrate at 20°C. Fig. 5 shows that the intensity of color imparted by this trinitrate, even at 0°C., exceeded those given by the other two isomers at 20°C., and that the *cis-cis-trans*-trinitrate was once more in the intermediate position. These intensity measurements were all made at pH 8 because the depth of color decreased in a reversible fashion with pH. The assumption that the intensity of color was proportional to the amount of the color-producing substances led to the conclusion that the *cis-trans-cis*-trinitrate, which produced most nitrite and presumably the greatest amount of alkali-sensitive carbonyl compounds, nevertheless gave the smallest yield of colored products. The production of about 0.9 mole of nitrite from the three nitrate groups in the *cis-trans-cis* isomer might, however, have resulted in a 90% yield of a monoketone such as (IV), which would remain nearly colorless in alkaline solution. On the other hand, the 0.5 mole of nitrite released by the *cis-cis-cis*-trinitrate might correspond to the formation of 25% of a diketone of type (V), which would probably behave as an indicator yielding a colored charged particle (VI) in the higher pH range (14). A further breakdown of a diketone would also explain the high consumption of alkali by the *cis-cis-cis*-trinitrate (Fig. 2). These speculations are at present entirely unsupported by experimental evidence.



IV. V. Colorless VI. Colored

Submission of the five nitrates to a temperature of 106°C., as in the standard Bergmann–Junk test for the thermal stability of explosives, liberated oxides of nitrogen that were estimated as equivalents of iodine per mole of sample (Fig. 6). The *cis-trans-cis*-trinitrate proved to be the least stable, and was also distinguished by the failure of the plot to pass near the origin of the co-ordinates. The amounts of the oxides liberated thermally were in the same sense as the production of nitrite in the saponifications, both for the trinitrates

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and for the much more stable *trans* and *cis* dinitrate. Table I, Column 5, expresses the decompositions after 20 hr. in the customary way as mgm. nitrous oxide per gm. sample. The ignition test (Table I) revealed little difference between the nitrates, but sensitivity to detonation by shock was definitely greater for the *cis-cis-cis*-trinitrate and *cis*-dinitrate than for the corresponding *trans* compounds. These results paralleled the rate and amount of alkali consumed by the nitrates (Figs. 1 and 2) and not the amount of nitrite formed during saponification. The *cis-cis-trans*-trinitrate, however, consumed less alkali than its isomers but was much more sensitive to shock. Although this trinitrate was an uncrystallized raceme, the unexpectedly high sensitivity could hardly be attributed to impurities or to the occlusion of gas, because a sample prepared four years later by another worker gave a concordant result. The explanation of this anomaly remained obscure. Since both the *cis* and *trans* dinitrates were molten when tested for sensitivity, the results must be attributed to their difference in molecular shape rather than to difference in crystal habit. The same inference might possibly be drawn for the all-*cis* and all-*trans* trinitrates, because their respective sensitivities duplicated those of the *cis* and *trans* dinitrates within the observational error.

As already mentioned, crystalline nitroglycerine of the "stable" type was more sensitive to detonation by shock than the "labile" isomer. Analogy with the present work suggests that the respective conformations would be *cis-cis-cis* and *cis-trans-cis*, but de Kreuk's arguments reversed this assignment. The superior over-all reactivity of the *cis-cis-cis*-cyclohexanetriol trinitrate toward alkali was unexpected in the light of the general chemical behavior of halide, acetyl, or sulphonyl substituents (24), and the mechanisms underlying sensitivity and thermal stability obviously depended in different ways on *cis-trans* configurations. It was unfortunate that the comparative inaccessibility of the *cis-cis-trans*, and the great inaccessibility of the *cis-trans-cis*, cyclohexane-1,2,3-triols prevented a closer study of these problems.

Acknowledgments

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AN IMPROVED SYNTHESIS OF *CIS-CIS-TRANS*-CYCLOHEXANE-1,2,3-TRIOL[1]

By C. J. Gogek,[2] R. Y. Moir,[3] J. A. McRae,[3] and C. B. Purves[4]

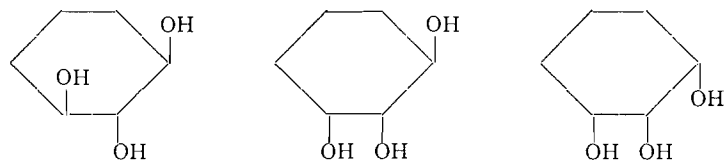
Abstract

Cyclohexene-3-ol acetate was readily made from cyclohexene and when oxidized, preferably with performic acid, gave 20 to 25% yields of partly acylated *cis-cis-trans*-cyclohexane-1,2,3-triol, but only 1 to 2% of the *cis-trans-cis* isomer. The structures of the three cyclohexane-1,2,3-triols were deduced from the theory of the Walden Inversion.

Introduction

In a previous article (9) it was shown that *cis-cis-cis*-cyclohexane-1,2,3-triol (γ-pyrogallitol) was readily obtained in about 60% yield by the high-pressure hydrogenation of pyrogallol, but that this method gave unsatisfactory amounts of the *cis-cis-trans* and *cis-trans-cis* isomers (β- and α-pyrogallitols). Moreover, the separation of these isomers by fractional crystallization from the preponderating *cis-cis-cis* form was tedious and wasteful. The object of the present work was to employ cyclohexene as a starting material for an independent synthesis of the less accessible isomers.

Lindemann and de Lange (23) obtained and carefully characterized all three of the possible cyclohexane-1,2,3-triols from the hydrogenation of pyrogallol; two of these isomers had previously been made from cyclohexene and accurately described by Brunel (8), and the third had been made by Senderens and Aboulenc (34). Assignment of the correct stereochemical structure to each of the isomers proved difficult. Since the triol with structure II is the only one



I II III

which is resolvable, Lindemann and de Lange (23) converted each of the triols into its *l*-menthylurethane in an attempt to find the resolvable form. The α-triol and the γ-triol each gave single products, while the β-triol gave an oil whose failure to crystallize was thought to be due to the presence of diastereoisomers. Hence they assigned structure II to the β-triol. Posternak and Ravenna (31) by attacking each of the isomers with micro-organisms which oxidized

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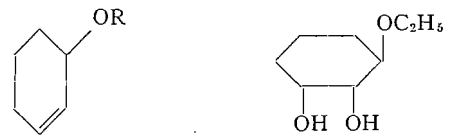
cis glycols in preference to *trans* glycols, were able to show that the α-isomer, m.p. 108°C., had structure I, that the β-isomer, m.p. 124°C., had structure II and was resolvable into optical isomers, and that the γ-isomer, m.p. 148°C., had structure III. This assignment of structures was confirmed, both by Posternak and Ravenna (31) and by Christian, Gogek, and Purves (9), by measuring the rate at which each of the triols reacted with lead tetraacetate.

It is also possible to deduce the structures of the triols from Brunel's syntheses by means of recent developments in the theory of the Walden Inversion. This in part was done by Posternak and Ravenna; a more complete analysis is now given. The following rules, which are based upon the theory and which have been repeatedly verified by experiment, are employed: (1) oxidation of an olefin with potassium permanganate gives a *cis* glycol (3, 5, 32); (2) dealkylation of an alkyl ether with hydrobromic acid does not cause inversion of configuration (16, 19, 21, 24, 30); (3) when a nucleophilic reagent attacks an ethylene oxide ring, the carbon of the ring which retains the oxygen atom is not inverted, but the carbon of the ring which is attacked by the reagent is inverted (2, 3, 29). When Brunel (8) oxidized 3-ethoxycyclohexene (IV*a*) with potassium permanganate and treated the resulting syrupy glycol (V) with hydrobromic acid, he obtained only the β-cyclohexane-1,2,3-triol, m.p. 124°C., so that the β-triol must have two neighboring hydroxyl groups in the *cis* position to each other (Rules 1 and 2). Brunel formed also from 3-ethoxycyclohexene (IV*a*) the oxide VI, probably as a mixture of stereoisomers. When the oxide was heated with water, mixed ethoxydiols were produced, and when



IV*a*: R = C_2H_5
IV*b*: R = OH
IV*c*: R = CH_3
IV*d*: R = $COCH_3$

V VI

these ethoxydiols were heated with hydrobromic acid, both the α-triol, m.p. 108°C., and the β-triol, m.p. 124°C., were obtained. Each of these triols must have a pair of neighboring hydroxyl groups in the *trans* position to each other (Rules 2 and 3). Therefore the β-triol which contains a pair of neighbors in the *cis* position, and a pair in the *trans* position, must be II; the α-triol must be I, and the γ-triol, not formed in the reactions, must be III. Further, one might conclude that the ethoxydiol of Brunel, and the 3-ethoxycyclohexane-1, 2-diol, m.p. 28°C., of Hofmann and Damm (18), made by the permanganate oxidation of 3-ethoxycyclohexene, must have structure V. It may be added that substantially the same analysis of the situation was first made by one of us (27) in 1944, independently of any of the other determinations of structure already mentioned.

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Two exceptions are known to the third rule (that the ethylene oxide ring is opened with one inversion of configuration). The first, involving the acid hydrolysis of 1-phenylcyclohexene oxide (5) is a striking confirmation of the mechanism proposed by Kadesch (1, 20) for the 'abnormal', acid-catalyzed reactions of certain oxides which can have an intermediate carbonium ion stabilized by resonance. The second (28), involving the two-step conversion of 2-acetyl-6-trityl-3:4-anhydro-α-methygalactoside into a galactose derivative, that is, with an over-all retention of configuration, is an equally striking illustration of Winstein's 'neighbor' mechanism (40). Ordinarily after an oxide ring has been opened by inversion, subsequent reactions of the resulting groups take place without inversion of configuration because of the presence of a neighboring group in the *trans* position, but in this example from the work of Oldham and Robertson (28) neither neighboring group can participate, one because it is in the *cis* position with respect to the attacked center, the other because it is already tied up in a cyclic acetal ring. Thus two successive inversions occur with over-all retention of configuration. Neither of these exceptional reactions disturbs in any way the application of the rule to simple oxides such as those under discussion in this paper.

A modification of Brunel's synthesis of the α- and β-triols was first investigated as a method of producing these triols in quantity. The starting material, 3-methoxycyclohexene (IV*c*) had been made and characterized by Brunel (7) and during the course of our work was also made by Berlande (4), but it is much more conveniently prepared in quantity by the action of sodium methylate upon cyclohexene dibromide—a method used by Hofmann and Damm (18) for the production of 3-ethoxycyclohexene (IV*a*). Oxidation of the 3-methoxycyclohexene with peracetic acid by the method of Scanlan and Swern (32) gave a syrupy mixture of the 3-methoxycyclohexane-*trans*-1,2-diols, and this mixture when treated with hydrobromic acid yielded a mixture of the α-cyclohexanetriol (I) and the β-cyclohexanetriol (II) in almost equal amounts, but in low yield. Although disappointing from the preparative point of view, this synthesis served to confirm the structure of the 3-methoxycyclohexene made by the method of Hofmann and Damm. Since olefins are oxidized to *trans* glycols by peracids (5), it also confirmed the structure of the γ-triol (III) by a method more direct than the triol synthesis of Brunel.

Better results were obtained by synthetic routes which employed 3-acetoxycyclohexene (IV*d*) as an intermediate. A methylene group in the allylic position in cyclohexene is vulnerable to attack by such reagents as lead tetraacetate (11), selenium dioxide in acetic anhydride (15), chromic anhydride in acetic acid (37), diazonium compounds (38), oxygen in the presence of osmium (39) or in the presence of ultraviolet light (12, 14), mercuric acetate (6, 36), and *N*-bromosuccinimide (41). Farmer and Sundralingam (14) and Kötz and Richter (22) both used cyclohexene hydroperoxide (IV*b*) as an intermediate in the synthesis of mixtures of the cyclohexanetriols; Farmer and Sundralingam isolated the pure β-triol (II) from the mixture obtained by them. However, the first two methods seemed more practical to us. Criegee's yield

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of 21% of 3-acetoxycyclohexene (IV*d*), from the oxidation of cyclohexene with lead tetraacetate (11), was confirmed, but for larger-scale work, Guillemonat's oxidation with selenium dioxide (15) was found preferable even although his yield of 45% could not be reproduced. Three preparations made according to his instructions each gave close to 19% of the uncrystallized but redistilled acetoxycyclohexene, together with 0.4% of cyclohexenone, whereas Guillemonat's recovery of the latter was 10%. Saponification of the acetate gave a 68% yield of 3-hydroxycyclohexene, with the correct boiling point. No previous value for the yield was found in the literature.

The hydroxylation of the 3-acetoxycyclohexene was carried out by three methods, the first of which employed tertiary-butyl peroxide with selenium dioxide as a catalyst (33); the second, hydrogen peroxide in sulphuric and glacial acetic acids (25), and the third, hydrogen peroxide in formic acid (35). In each instance acyl groups were removed from the distilled but uncrystallized product by saponification, and the resulting mixture of crude triols was separated by fractional crystallization of the tribenzoates. The yields of the pure *cis-cis-trans*-cyclohexanetriol (II) tribenzoate were 24.6%, 22.9%, and 20 to 25% for the three methods of preparation, but the corresponding figures for the *cis-trans-cis* tribenzoate (of the α-triol) were only 2%, 0.5%, and 1%. Although for convenience the performic acid method was preferred, the results strongly suggest that the factor dominating the mode of *trans* addition to the double bond was not the conditions of the hydroxylation with peroxide but rather the presence of the acetoxy group. This group appeared in the product overwhelmingly in the *cis* relationship to the adjacent hydroxyl group and in consequence the synthesis offers a reasonably satisfactory preparation for the *cis-cis-trans*-, but not for the *cis-trans-cis*-cyclohexanetriol.

Experimental

Materials

Cyclohexene, boiling correctly at 82° to 84°C., was prepared by Coleman and Johnstone's procedure (10). The selenium dioxide was a high grade sample generously given by Canadian Copper Refineries Ltd., Montreal.

3-Cyclohexenol Acetate

Guillemonat's procedure (15) was closely followed, the quantities used being 820 gm. of cyclohexene (10 moles), 500 gm. of acetic acid, 300 gm. of acetic anhydride, and 389.5 gm. of finely powdered selenium dioxide (3.5 moles). Steam distillation of the product recovered 140 gm. of cyclohexene and 92.4 gm. of 3-cyclohexenol acetate boiling at 81° to 83°C. at 25 mm. pressure.

When heated at 200°C. and 25 mm. pressure, the black still-residue yielded a brown distillate from which an additional 132 gm. of pure cyclohexenol acetate was eventually recovered, thereby raising the total yield to 224.4 gm. or 19.3% of theory. The same crude distillate on extraction with 40% aqueous sodium bisulphite yielded 3.1 gm. (0.4%) of 2-cyclohexenone with the correct

boiling point of 65° to 67°C. at 24 mm. pressure. Guillemonat's yield was 10%. Cautious treatment of the final still-residue with concentrated nitric acid recovered almost all of the selenium dioxide used.

The acetate was saponified by shaking with an equivalent amount of aqueous barium hydroxide for one hour, the product being extracted from the liquors with benzene. A 68% yield of material boiling at 60° to 62°C. at 12 mm. was obtained. Guillemonat's product boiled at 67°C. at 15 mm. pressure.

Cyclohexene-1,2,3-triols from 3-Cyclohexenol Acetate

(*a*) By Seguin's method (33). The acetate (79.7 gm. or 0.57 mole) and selenium dioxide (2.3 gm.) were added to a solution of 0.58 mole of hydrogen peroxide in 275 cc. of tertiary butyl alcohol (17, 26). After a few minutes' shaking, all of the oxide dissolved and the solution was kept at 6°C. for six days. Distillation *in vacuo* first removed the butyl alcohol, then 22.7 gm. of unchanged cyclohexenol acetate and 31.3 gm. of a light yellow gum containing a trace of red selenium. The viscous black still-residue contained carboxylic acids. The gum, which boiled at 120° to 130°C. at 0.05 mm. pressure, was saponified at room temperature with 10.1 gm. of potassium hydroxide in 125 cc. of methanol and the alkali was subsequently removed as the chloride. Evaporation and distillation of the mother liquor at 0.2 mm. pressure yielded 24.8 gm. (44%, based on unrecovered cyclohexenol acetate) of crude, semi-solid cyclohexanetriols. Benzoylation of this product gave 63.0 gm. of crude tribenzoates which were separated by fractional crystallization (9) into 45.4 gm. (24.6%) of the pure *cis-cis-trans* form, m.p. 182°C., and 3.7 gm. (2%) of the *cis-trans-cis* isomer melting correctly at 140°C. The mother liquors yielded further small amounts in a less pure condition.

(*b*) By the method of Meerwein, Schoeller, Schwenk, and Borgwardt (25). A solution containing 44.7 gm. of hydrogen peroxide (30%, 0.395 mole), 44.7 gm. of glacial acetic acid and 4.6 gm. of concentrated sulphuric acid, was added to 50 gm. (0.36 mole) of 3-cyclohexenol acetate during one hour. The mixture became homogeneous after being stirred at 10° to 15°C. for five hours, and after 56 hr. at this temperature was kept at 40° to 50°C. for three hours. Two layers appeared when the solution was neutralized exactly with sodium hydroxide, and the upper layer was combined with a benzene extract of the lower aqueous phase. Evaporation of the aqueous phase to dryness, followed by extraction of the residue with acetone, eliminated inorganic salts. The benzene and acetone extracts were then combined and on fractional distillation gave 3.1 gm. of unchanged cyclohexenol acetate and 29 gm. of a light yellow gum boiling at 120° to 127°C. (0.05 mm. pressure). Saponification of this gum gave a brown, salt-free residue of which 13.7 gm. was volatile at 130° to 132°C. (0.08 mm. pressure). When benzoylated, this fraction eventually yielded 34.8 gm. of pure *cis-cis-trans*-cyclohexanetriol tribenzoate (m.p. and mixed m.p. correct at 183°C.) and 0.8 gm. of the *cis-trans-cis* isomer, m.p. 140°C. The over-all yields of the tribenzoates were 22.9% and 0.5%, respectively.

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(*c*) By the method of Swern, Billen, Findley, and Scanlan (35). Hydrogen peroxide, 58.1 gm. (30%, 0.502 mole), was added during 15 min. to a mechanically stirred mixture of cyclohexenol acetate (70 gm., 0.50 mole) and 150 cc. of 87% formic acid. Initial cooling was used so that the temperature did not rise above 55°C., and after two or three hours heat was applied to maintain this temperature for a further 16 hr. The solution was then brown in color and had deposited a small amount of a dark resin. The residue left after removal of solvents yielded 53.2 gm. of a pale yellow distillate, boiling at 120° to 135°C. at 0.05 mm. pressure. Hydrolysis of this product with boiling water to remove formate followed by saponification with methanolic caustic potash to remove acetate groups, left 21.6 gm. of redistilled cyclohexanetriols. Benzoylation and fractional crystallization then recovered 45.6 gm. (20.0%) of the pure *cis-cis-trans*-tribenzoate and 2.5 gm. (1.1%) of the pure *cis-trans-cis* isomer. The crude acetate–formate from a second experiment employing the same amounts of reactants but in which the hydroxylation was for 24 hr. at room temperature, was hydrolyzed in one operation by heating for 90 min. at 50°C. with 3 cc. of concentrated sulphuric acid in 150 cc. of ethanol and 25 cc. of water. After recovery, the 36.3 gm. of crude distilled triols were shaken mechanically with ethyl acetate for an hour to extract 17.5 gm. (25%) of a yellow oil that boiled at 120° to 135°C. (0.15 mm.) and dissolved in benzene and ethanol but not in water. Although this oil was not examined in detail, the formation of a bright red precipitate with 2,4-dinitrophenylhydrazine indicated that it contained a carbonyl group. The remaining 18.6 gm. of the crude distilled triols yielded 11.5 gm. of pure *cis-cis-trans*-cyclohexanetriol (m.p. 125°C. and isolated as such) and a further 17.4 gm. of the pure tribenzoate, the total yield being 24.6%. Two grams of the pure *cis-trans-cis*-tribenzoate (0.9%) were also recovered.

3-Methoxycyclohexene and Cyclohexadiene

The method was that described by Hofmann and Damm (18) for 3-ethoxycyclohexene. Sodium, 71.3 gm., was dissolved in absolute methanol, 900 cc., and crude cyclohexene dibromide, 307 gm., was added. The mixture was refluxed for 10 hr., most of the methanol was distilled away, and the residue diluted with water, 2000 cc. Repeated extraction of the aqueous mixture with ether, followed by distillation of the dried ethereal extract gave 48.0 gm. of crude methoxycyclohexene. Further amounts of the crude product were obtained by repeated fractional distillation of the methanol distillate, so that the average over-all yield was 60%. When several of the crude preparations were carefully fractionated together, a very pure sample of 3-methoxycyclohexene, 278.4 gm., of b.p. 138.7°-138.8°C. (corr.) at 757 mm. (corr.) was obtained. Berlande (4) reported a b.p. of 139°C., and Brunel (7) a b.p. of 139.8°C. for 3-methoxycyclohexene. Cyclohexadiene was recovered in about 7% yield by diluting the lowest-boiling methanol fractions with water, followed by distillation of the insoluble oil. It was conveniently identified and preserved by converting it to the addition product with maleic anhydride, whose m.p. of 147°-147.5°C. agreed with that reported by Diels and Alder (13).

Hydroxylation of 3-Methoxycyclohexene

An adaptation of Scanlan and Swern's method (32) was used for the hydroxylation.

Glacial acetic acid, 250 cc., and 30% hydrogen peroxide, 70 cc., were thoroughly stirred and kept for one hour at 80° to 85°C. in order to form peracetic acid. After cooling the solution to 50°C., 42.7 cc. of methoxycyclohexene were added slowly from a dropping funnel, so that the temperature did not exceed 72°C., and the mixture was then kept at 65° to 70°C. for 1.75 hr. Reduction of the excess peroxide with magnesium metal and a little iron, followed by evaporation of the solution *in vacuo*, left a residue which was thoroughly extracted with ethyl acetate. Distillation of this extract yielded crude 3-methoxy-*trans*-cyclohexanediols as an almost colorless viscous oil boiling at 84° to 98°C. (0.025 mm. pressure). The yield of 17.4 gm. (about 30%) was probably diminished by the presence of inorganic salt during the distillation.

The dealkylation of this product was as described by Brunel (8) for the corresponding ethoxy compound; 9.9 gm. were kept with 11 cc. of hydrobromic acid (saturated with hydrogen bromide at 0°C.) in a sealed glass tube at 60°C. for 20 min. After recovery, the liquid was diluted with water, neutralized with sodium bicarbonate and evaporated to dryness. Distillation of an ethanol extract of the residue yielded 4.8 gm. (about 50%) of partly solid cyclohexanetriols boiling at 95° to 120°C. at 0.04 mm. A small amount, 0.6 gm., of crude *cis-trans-cis*-cyclohexanetriol separated when this mixture was diluted with acetone. Benzoylation of the residue, and fractional crystallization of the product (9) yielded 2.9 gm. each of the crude *cis-cis-trans*- (m.p. 153° to 180°C.) and *cis-trans-cis*-tribenzoates (m.p. 122° to 128°C.). Small amounts of both isomers were subsequently isolated with correct melting and mixed melting points (184° and 142°C., respectively) by tedious fractional recrystallizations. Both crude tribenzoates were recovered in an over-all yield of about 3% from the methoxycyclohexene and of about 10% from the methoxycyclohexanediols.

Acknowledgment

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THE BENZOATE AND THE METHYL ETHER OF 4-HYDROXYCYCLOHEXENE[1]

By C. J. Gogek,[2] R. Y. Moir,[3] and C. B. Purves[4]

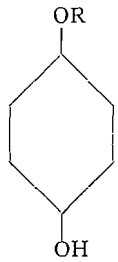
Abstract

Satisfactory preparations, from hydroquinone and its monomethyl ether respectively, were devised for the above compounds which were thought to be new. The methyl ether of 4-hydroxycyclohexene was an oil, n_D^{20} 1.4566, boiling at 136°C.; the uncrystallized benzoate had n_D, 1.5360 and b.p. 149°C. at 12 mm. pressure.

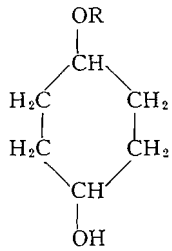
Introduction

The original objective of the work was to study the *cis-trans* isomerism of the four cyclohexane-1,2,4-triols, members of which have been prepared in crude form by Senderens and Aboulenc (7) and by Zelinsky and Titowa (9). Circumstances, however, made it necessary to discontinue the research after preparing 4-hydroxycyclohexene, its methyl ether, and its benzoate (structures III), any of which would yield one pair or another of the desired triols by a directed *cis* or *trans* hydroxylation of the double bond.

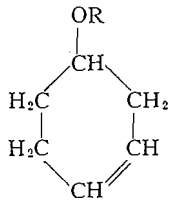
The high pressure hydrogenation of hydroquinone (I, R = H) over a Raney nickel catalyst gave up to 96% yields of crude, crystalline cyclohexane-1, 4-diol (II, R = H, quinitol), the *cis-trans* isomers of which have been studied on several occasions (1, 2, 4, 5). Distillation of the quinitol over a little concentrated sulphuric acid (6) yielded the known substance 4-hydroxycyclohexene (III, R = H), the new monobenzoate of which was then readily prepared



I (R = H or CH_3)



II (R = H or CH_3)



III (R = H, CH_3, or COC_6H_5)

Helfer's (3) methylation of hydroquinone gave a 40 to 44% yield of the crystalline monoether (I, R = CH_3), which on hydrogenation (3, 8) gave 66 to 83% yields of the methoxycyclohexanols (II). Dehydration of the latter resulted in the new compound (III, R = CH_3) in 58% yield.

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The molar refractivities found for 4-methoxycyclohexene (III, R = CH_3) and for cyclohexene-4-ol benzoate (III, R = COC_6H_5) were higher than expected. Our later experience with this general class of compounds has shown that they autoxidize at an unusually fast rate, so that the refractive indices here reported may be slightly higher than the correct values.

Experimental

Benzoate of 4-Hydroxycyclohexene

A solution, 1100 cc., of pure hydroquinone, 525 gm., in ethanol was hydrogenated over 80 gm. of Raney nickel catalyst at 170°C. and 3000 p.s.i., or substantially as recommended by Coops, Dienske, and Aten (2). The product, boiling correctly at 140° to 143°C. at 8 mm., crystallized at once to 527.5 gm. (96%) of the mixed *cis* and *trans*-cyclohexane-1,4-diols. A 527.5 gm. sample of the diols, heated with 2 cc. of 65% sulphuric acid in a bath at 190° to 200°C. (6) yielded a distillate containing water, cyclohexadiene, and 168 gm. (38%) of crude 4-hydroxycyclohexene boiling at 154° to 157°C. Redistillation gave the pure substance with the correct boiling point of 164° to 165°C.

A cold solution of 87.2 gm. (0.89 mole) of the 4-hydroxycyclohexene in 200 cc. of pyridine was mixed with 128 gm. (0.91 mole) of benzoyl chloride diluted with 350 cc. of chloroform. The product, recovered after the mixture had remained for 16 hr. at room temperature, was twice distilled at 12 mm. pressure through a Vigreux column. Cyclohexene-4-ol benzoate was a colorless oil boiling at 149° to 150°C. (12 mm.); d_4^{20}, 1.083 and n_D^{20}, 1.5360. Found: C, 77.3%, H, 6.9%; mol. refraction, 58.23. Calcd. for $C_{13}H_{14}O_2$: C, 77.2%; H, 7.0%; mol. refraction, 57.64.

The benzoate was insoluble in water but soluble in benzene, alcohol, acetone, and chloroform. It decolorized dilute solutions of bromine in carbon tetrachloride, and of aqueous potassium permanganate, instantly.

4-Methoxycyclohexene

Hydroquinone, 660 gm., was methylated in two batches at room temperature with 574 cc. of technical dimethyl sulphate in presence of 600 gm. of sodium hydroxide and 3600 cc. of water (3). *p*-Dimethoxybenzene, 130.8 gm., was separated by filtration, and, after recovery, the *p*-methoxyphenol remained as a light brown oil boiling at 118° to 130°C. at 8 mm. pressure. The distillate rapidly solidified to crystals melting at 55° to 57°C.; yield, 330.6 gm. or 44%. Helfer (3) obtained a 55% yield of material melting at 53°C. The high pressure hydrogenation of the *p*-methoxyphenol, 771.8 gm., with 100 gm. of Raney nickel catalyst was as described by Van Duzee and Adkins (8) and proceeded rapidly at 180° to 190°C. An 83% yield (665.7 gm.) of crude 4-methoxycyclohexanol boiling in the range 85° to 120° (7 mm. pressure) was obtained.

A total of 603.6 gm. of this crude product was distilled at 205°C. in three batches, each containing about 2 cc. of 50% sulphuric acid (6). Redistillation yielded first a mixture (91 gm.) of water with cyclohexadienes and then 257 gm.

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of pure 4-methoxycyclohexene boiling at 135.5° to 136.5°C. (760 mm.). Redistillation of the still residue with an additional 2 cc. of 50% sulphuric acid produced an additional 42.0 gm. of pure material and increased the yield to 58%.

4-Methoxycyclohexene was a colorless oil with d_4^{20}, 0.9009 and n_D^{20}, 1.4566. Found: C, 74.7%; H, 10.4%; mol. refraction, 33.89. Calcd. for $C_7H_{12}O$: C, 74.9%. H, 10.8%; mol. refraction, 33.54. The compound was soluble in organic liquids but not in water, and instantly decolorized bromine in carbon tetrachloride, or dilute aqueous potassium permanganate.

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THE ROLE OF ALPHA-KETOLS IN THE LOW-SUGAR REDOX RECIPE FOR LOW TEMPERATURE EMULSION COPOLYMERIZATION[1]

By R. J. Orr and H. Leverne Williams

Abstract

It was found that the induced decomposition of peroxy compounds could lead to faster rates of polymerization or practical rates of polymerization at lower temperatures. In Germany polymerization recipes were developed containing a peroxy compound in the oil phase, a reducer in the aqueous phase and a metal carrier. This idea was transferred to America after the war and became the basis of the present recipes used in the production of cold rubbers. As reducers the most commonly used appear to be digested *d*-glucose or an excess of ferrous iron but recently the polyamines and other amine compounds have been found to be quite effective. The mixture of amine and sugar was better than either alone. It has been shown that this mixture will function in the presence of reactive monomers such as acrylonitrile. The role of such reducers is of considerable interest so that further studies were undertaken. The results obtained may be illustrated by acetoin. As the amount of acetoin is increased in the recipe the amount of ferrous iron required for maximal conversion in a given time is decreased. This is because at higher than the optimal amounts, although the reaction rate is still increasing, the catalyst system is rapidly exhausted so that the reaction dies at a lower conversion. The data can be explained by assuming formation of free radicals by the induced decomposition of the peroxide either by the acetoin, the ferrous iron, or a complex between the iron and acetoin. This free radical then initiates polymerization. The acetoin free radical residue can induce the further decomposition of the peroxide or possibly can reduce ferric iron to ferrous. Other compounds yield similar results.

Introduction

Some of the earliest studies of activated polymerization reactions are those of Stewart (49,50,51,52,53) in which redox catalysts composed of a polymerization initiator, a heavy metal, and a phosphate or polyphosphate such as pyrophosphate or fructose diphosphate, an organic acid, or a polyhydroxy compound such as dextrose. E. I. du Pont de Nemours and Co. patented similar systems (44).

The German work developed the desirable combination of an oil soluble peroxy compound and a water soluble reducer in combination with a heavy metal carrier to a high degree. These results were summarized by Weidlein (63) who mentioned the system benzoyl peroxide – ferrous fatty acids – sorbose – sodium pyrophosphate. Later several publications appeared in Germany (17, 18,19,20,21,31,33) describing their earlier work and several in the United States describing the studies there which were stimulated by the earlier report (63).

Wall and Swoboda (62) attempted to formulate the reactions of such a system. Some credence to their postulate could be given when such highly

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insoluble peroxides as benzoyl peroxide were used and when the study of Marvel *et al.* (35) showed that a water soluble peroxide such as hydrogen peroxide disappeared from the medium prior to polymerization. However, the work published by Fordham and Williams (5,6,7,8,9), by Kharasch *et al.* (22,23) and by Kolthoff *et al.* (24,28,30) strongly suggested that the most probable locus of initial free radical formation was in the aqueous phase.

Sugars or similar materials have been used as reductant in reduction activation (31,44,49,50,51,54). The use of three parts of dextrose has been mentioned in many papers (32,39,47,58,59,61) and the use of about one part in many others (4,11,20,29,33,39,46,47,48,58,64). Sorbose (10,13,14, 19,20,62,63), dihydroxyacetone (20,26,27,30,33), ascorbic acid (31,33) invert sugar (60), lactose (60), fructose (25,60), and scylloinosose (30) have also been mentioned. Longer lists of materials tested were published (10,12, 18,29,36,37). These lists include many of the above compounds also. The use of amines, sugars, and ferrous iron mixed has been shown to be a versatile and effective system (4,48).

Studies of the role of enediols or alpha ketols in emulsion polymerization have been largely confined to comparisons between effective materials (4,12, 18,19,20,30,31,33,36,37,39,44,49,50,51,60). The general concept in these papers would appear to be that the sugar is a reductant whose prime purpose is to reduce the ferric iron to ferrous. The most extensive description of the reactions has been that of Kolthoff and Medalia (25,38). The mechanism suggested included induced decomposition of the peroxide by ferrous iron and by the sugar and also reaction of the free radicals produced by either process with the sugar to produce another radical. In subsequent publications the advantages of dihydroxyacetone (26) and ferrous sulphide (27) as reductants were indicated but significantly the differences in the relative effectiveness of sugars at 30° and 0°C. was discussed (29). Fryling *et al.* also compared a number of sugars (10) at 15°C. They concluded that an enediol equilibrium permitted the use of these materials in a low iron recipe. Kharasch *et al.* (23) concluded that ferric iron was not reduced by the sugar, that a free radical was formed by reaction of a free radical with the sugar, and that the sugar free radical reduced the ferric iron.

Generally speaking the concept which guided the present study was that the sugar was the reductant when complexed with iron. Further, an investigation of the role of enediols or alpha ketols in emulsion copolymerization might lead to a better understanding of the mechanism of redox with the aim of reducing or eliminating entirely the amount of ferrous iron or enediol added. This iron, if any remained in the polymer, was suspected to be the cause of degradation of the polymer (43) and the glucose caused fermentation of the latex and instability. The polyamines promised to be a replacement for the sugar and most of the iron so that the investigation of the role of the enediols was not carried beyond that stage where the mechanisms seemed at least plausible.

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Experimental Techniques

Polymerizations were conducted in 8 oz. screw cap bottles, the caps of which were pierced and fitted with self sealing and oil resistant gaskets so that samples would be inserted or withdrawn by a syringe and needle. To the bottles was added the soap and electrolytes dissolved in most of the water and methanol (when used). Most of the styrene and all of the MTM was then added. The bottles were flushed of oxygen by adding more than the desired weight of butadiene and allowing the excess to evaporate, driving out the air. The bottles were securely capped when the correct weight was reached and inserted in a constant temperature bath where they were rotated end over end until cooled. The activator was than added and after a few minutes the catalyst in the rest of the styrene thereby starting the reaction. After the desired period of time the stopping agent was added and the degree of conversion determined by measuring the amount of rubber formed from the monomers. The stopping agent was a 7.5% dispersion of ditertiary butyl hydroquinone in the emulsifier used (15% solution). Investigations were carried out at 5°C. and −18°C. The recipes used are shown in Table I.

TABLE I

POLYMERIZATION RECIPES

	I	II
Monomers		
Butadiene	72 parts	70 parts
Styrene	28	30
Aqueous phase		
Water	180	157
Dresinate 214 (Hercules Powder Co.)	4.7	–
Potassium fatty acid soap flakes (Swift and Co.)	–	5.1
Daxad 11 (Dewey and Almy Chem. Co.)	0.10	0.10
Methanol (du Pont Synthetic)	–	46
KCl	0.25	–
K_2SO_4	–	0.2
Modifier		
MTM (Phillips Petroleum Co.)	0.24	0.24
Activator		
$FeSO_4/K_4P_2O_7$ ratio	1:1	–
$FeSO_4/K_4P_2O_7/As_2O_3$	–	1:1:1
Catalyst		
CHP, cumene hydroperoxide (Hercules Powder Co.)	0.10	–
DIP, diisopropylbenzene monohydroperoxide (Hercules)	0.10	0.15
Polymerization temperature	+5°C.	−18°C.

The activator was made by mixing solutions of the ingredients and aging the resultant suspension 30 min. at 60°C. in a bottle with nitrogen atmosphere. The amount of activator was varied as indicated in each experiment, i.e. by the amount of ferrous sulphate used, the other ingredients remaining in equimolar ratio. Greater detail will be found in two earlier papers (41,42) and others from this laboratory (4, 39, 48).

The α-ketol under investigation was added by injection into the bottle. Most were water soluble and were added in aqueous solution the water being withheld from the initial charge. Benzoin, which was oil soluble, was added in styrene solution, the styrene being withheld from the initial charge.

Experimental Results

Acetoin in Polymerization Systems

The first step in the investigation was to investigate the effect of α-ketols using initiating systems of varying concentration. Acetoin, one of the simplest α-ketols, was chosen for this phase of the work. A typical example of what happened when acetoin was added to a system containing insufficient ferrous iron is shown in Table II.

TABLE II

EFFECT OF ACETOIN ON LOW IRON RECIPE* AT 5°C.

Acetoin (parts)	% Conversion at 17 hr.	
	(*a*)	(*b*)
0	16.9	4.5
0.2	32.0	21.1
0.4	43.2	36.5
0.6	47.0	–
0.8	52.6	47.5
1.0	48.9	46.9

* *Recipe 1, $FeSO_4$. $7H_2O$ 0.10 part, cumene hydroperoxide 0.10 part.*

Thus, for a 17 hr. reaction cycle the polymer yield had reached its maximum at 0.8 part acetoin. The results in column (*a*) were obtained using only experimental precautions already outlined. For column (*b*) all solutions were heated to 60°C. and nitrogen than bubbled through to remove oxygen dissolved in the various components of the recipe. It may be seen that the point at which the maximum was reached did not alter and for this reason the experimental precautions previously outlined for the removal of oxygen were considered sufficient. To make the reason for this maximum yield clearer, time-conversion studies were made at points below and above the optimal acetoin content with the results shown in Fig. 1. It may be seen that as the acetoin content increased, the initial rate increased but the conversion time relationship departs from linearity and after a given time no further reaction takes place. It is this effect, normally known as "dying," that causes the polymer yield to be less when larger amounts of reducers are used.

The optimal acetoin content was determined as a function of ferrous iron content, hydroperoxide content, and hydroperoxide type. The data thus determined are shown in Table III and Fig. 2.

It is obvious that the optimal acetoin content diminishes with increasing ferrous iron content and differs for different polymerization temperatures and hydroperoxide catalysts.

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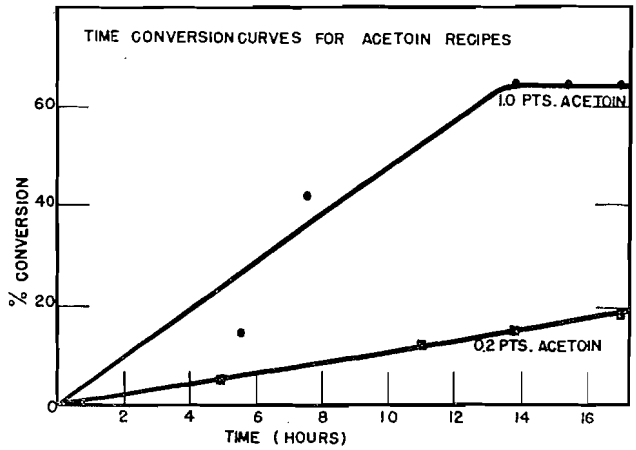

FIG. 1. *Time conversion curves with acetoin in recipe.*

TABLE III

OPTIMAL ACETOIN CONTENT RELATIONSHIPS

Temp., °C.	Ferrous iron content (part)	Optimal acetoin content (part)	Hydroperoxide content (part)	Hydroperoxide type
5	0.07	1.0	0.10	CHP
	0.10	0.8	0.10	"
	0.14	0.4	0.10	"
	0.18	0.0	0.10	"
	0.07	0.4	0.05	"
	0.06	0.4	0.10	DIP
	0.08	0.4	0.10	"
	0.16	0.0	0.10	"
−18	0.10	0.8	0.15	"
	0.15	0.0	0.15	"

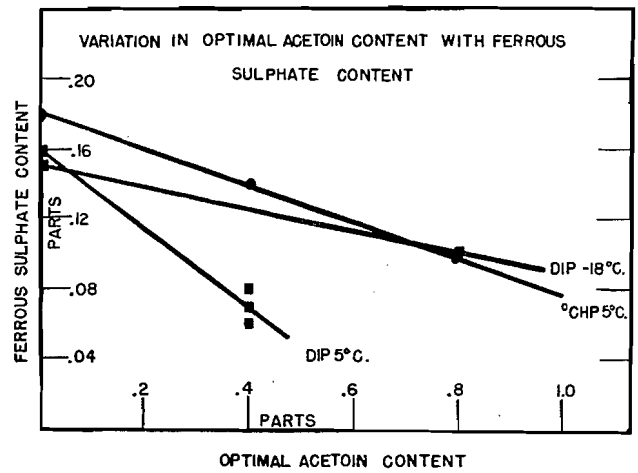

FIG. 2. *Optimal acetoin concentration versus iron concentration in recipe.*

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Investigation of Various α-Ketols

An explanation of the role of α-ketols has recently been advanced (23) on studies made of solution polymerization. The α-ketol (DH) and the initiating free radical (RO)· may undergo the following reaction:

$$RO\cdot + DH \rightarrow ROH + D\cdot \qquad I$$

Here D· rather than DH represents the species effective in reducing as illustrated in the following equation.

$$D\cdot + Fe^{+++} \rightarrow D^{+} + Fe^{++}. \qquad II$$

Reasoning on this basis, the rate of reaction II will depend on the steady state concentration of D· which in turn will be dependent on the absolute rate constant of reaction I. Thus, if acetoin and the RO· generated from CHP react more slowly in I than acetoin and the RO· generated from DIP, the steady state concentration of D· must be much smaller when CHP is used as the hydroperoxide than when DIP is used. For this reason acetoin will tend to appear a much weaker reducing agent in the presence of CHP than it is with DIP.

The slope of the ferrous iron optimal acetoin content relationship may be adopted as a measure of the over-all efficiency of an α-ketol in emulsion polymerization. It represents the sum of two terms, one due to reaction I and the other due to reaction II. This quantity, which may be defined as the reduction coefficient, for various metal–hydroperoxide–ketol combinations may be tabulated. Various α-ketols were evaluated in the presence of CHP and 0.14 part $FeSO_4.7H_2O$. Knowing this optimal α-ketol content at this ferrous iron content and assuming that the ferrous iron content at or above which α-ketols at all concentrations lowered the polymer yield was constant, it was possible to calculate the slope of the corresponding ferrous iron optimal α-ketol content relationship. In Table IV are compiled the slopes which were determined for various α-ketols under various conditions.

TABLE IV

A SUMMARY OF REDUCTION COEFFICIENTS

α-Ketol	Hydroperoxide	Temp., °C.	Reduction coefficient (moles Fe^{++}/mole α-ketol)
Acetoin	DIP	5	0.070
Acetoin	CHP	5	0.024
Acetoin	DIP	−18	0.006
Tartaric acid	CHP	5	0.017
Lactic acid	CHP	5	0.001
Gluconic acid	CHP	5	0.050
Benzoin	CHP	5	0.040
Arabinose	CHP	5	0.027
Galactose	CHP	5	0.035
Sorbose	CHP	5	0.036
Dextrose	CHP	5	0.035

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As was pointed out, the reduction coefficient of acetoin increased markedly upon changing from CHP to DIP. Also of interest is the large decrease of the reduction coefficient with decreasing temperature. This would seem to restrict the usefulness of α-ketols in subzero polymerizations. As a change from one α-ketol to another is made, the reduction coefficient undergoes changes of a fairly large magnitude. Sugars containing six carbon atoms, such as dextrose, sorbose, and galactose show the same reducing effects regardless of their internal configuration. Arabinose, possessing only five carbon atoms, shows distinctly lower reduction coefficient. This may be attributed to the extra hydroxyl groups and is supported by the experience with hydroxy acids in which the reduction coefficient steadily rises from a low with lactic acid through tartaric acid with gluconic acid representing the most promising reducer tested. An oil soluble α-ketol benzoin, showed surprisingly good results considering that all reaction must take place either along an oil water interface or in the soap micelles.

Rates of Polymerization with Various α-Ketols

It was observed that somewhat different yields were obtained using the various α-ketols. A summary of the results is shown in Table V. The results shown are the optimal for the various experiments.

TABLE V

OPTIMAL CONVERSION FOR VARIOUS CONCENTRATIONS OF α-KETOL

α-Ketol	Moles $FeSO_4.7H_2O$/ 100 gm. monomer $\times 10^4$	Moles α-ketol/100 gm. monomer $\times 10^3$	% Conversion (17 hr.)
Acetoin	2.5	11.4	46.6
Acetoin	3.6	9.1	52.6
Acetoin	5.0	4.6	74.1
Acetoin	6.1	0	91.1
Tartaric acid	5.0	6.6	70.8
Lactic acid	4.0	41.0	41.7
Gluconic acid	5.0	2.0	47.5
Benzoin	5.0	2.8	31.3
Arabinose	5.0	4.0	76.2
Galactose	5.0	3.3	69.9
Sorbose	5.0	3.1	73.2
Dextrose	5.0	3.3	80.0

Thus it is evident that as the iron content is decreased with a corresponding increase in the α-ketol content, the conversion is lowered. This may be due to the greater concentration of D· free radicals which act as retarders of polymerization through combination with other free radicals. Some of the hydroxy acids are the most active in this respect although tartaric acid seems to be an exception. Sugars, in general, yield quite rapid rates of conversion. Acetoin is intermediate in this respect. Benzoin seems to be a strong retarder possibly because all free radicals produced from benzoin are near the locus of initiation of the polymerization reaction and receive ample opportunity for recombin-

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ation with the growing polymer chain. It may be that the tendency of the different α-ketols to complex with ferrous iron have a decided effect on the polymer yield. This type of reaction has been observed (3) but as yet no study of its contribution to the polymerization in emulsion has been made.

Discussion

On plotting of the data in Table III it is evident that there is a linear relationship between the initial ferrous iron content and the amount of acetoin necessary to bring about a maximum in the polymer yield (Fig. 2). The slope of this relationship should be dependent on the relative ease of the reaction

$$Fe^{+++} + \alpha\text{-ketol} \rightarrow Fe^{++} + \text{oxidation products}$$

i.e. where the α-ketol used is a powerful reducing agent, only a small amount of α-ketol would be necessary to compensate for a relatively large reduction in the initial ferrous iron content. Hence a greater slope will be shown in this α-ketol ferrous iron relationship for stronger reducing agent than for weaker reducing agents. This, however, does not describe the experimental data, for when DIP was substituted for CHP, the slope increased markedly, indicating that it was not alone dependent on the α-ketol type. Indeed this observation appears to invalidate the explanation of the role of reducers in redox polymerization, i.e. as reducers of ferric iron. Rather the iron–sugar complex is the primary reducer and the sugar free radical may reduce ferric ion to ferrous subsequently and incidentally.

That sugars may form a complex with iron has been indicated by several publications (3,4,25,55,56,57). On the other hand the digestion (10) of dextrose may result in many compounds such as fructose, acids, and oxidation products (12). Any of the products may be capable of forming complexes with iron which may in fact behave like antioxidants through the mechanism postulated by Kolthoff (25) and formulated by Kharasch (23). For instance sugars retard the autoxidation of ascorbic acid (15,16) whereas iron catalyzes the autoxidation.

The work of Embree *et al.* (4) strongly suggests that sugars are also able to form complexes with amines which complexes are still powerful reductants in the virtual absence of iron but are not destroyed by cyanoethylation reaction with acrylonitrile (4,64). That amines and sugars may form complexes has been indicated (34,40,45).

In the iron–hydroperoxide catalyst activator systems the sugar or other alpha-ketol, combined in complex form with iron, acts as the reductant for part or all of the induced decomposition of the cumene hydroperoxide. It seems likely that ferric complexes with sugar are formed readily and are active reducers. When ferrous iron is used there is the additional possibility of active reduction of the hydroperoxide by the ferrous iron. The reductant such as acetoin, dextrose, etc., has a ferrous iron sparing action.

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The other mechanism is to complex polyamines in such a manner that the complex is still an active reductant for cumene hydroperoxide but is not susceptible to the destruction by the cyanoethylation reaction when acrylonitrile is present. Thus the amine–sugar combinations form very effective activators even for butadiene–acrylonitrile copolymerization reactions. The nature of this complex is not readily understood. An alternative explanation, namely, that the polyamine can replace the ferrous iron in the sugar complex does not seem quite as probable since iron has amazing specificity of action. However, slow dissociation of the amine sugar complex to yield the free amine is possible.

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THE PAPILIONACEOUS ALKALOIDS

XIV. CONCERNING SPATHULATINE AND NONALUPINE[1]

By Léo Marion

Abstract

The two alkaloids nonalupine and spathulatine reported in the literature have been found to be identical and to consist of the monohydrochloride of pusilline, $C_{15}H_{23}N_2$. On heating *in vacuo* the hydrochloride undergoes disproportionation, giving rise to the free base and the dihydrochloride. The peculiar reactions of spathulatine are explained by the fact that they simply liberated the base from its salt. Pusilline forms a dipicrate containing an additional mole of picric acid, which accounts for the necessity of using a solution of that acid for its recrystallization.

Spathulatine was first described by Couch (1) who found it in a plant first thought to be *Lupinus spathulatus* Rydb., but the identification of the species was subsequently questioned and the plant assumed to have been *L. marianus* Rydb. (2). Later, in an investigation of *L. sericeus* Pursh, the same author again reported the presence of spathulatine and a new, neutral alkaloid that he designated nonalupine (2). The latter has also been found by Couch in *L. andersonii* Wats. (3). Both alkaloids have high melting points and have been assigned widely different empirical formulae, i.e., $C_{33}H_{64}O_5N_4$ (spathulatine) and $C_{15}H_{24}ON_2$ (nonalupine). The empirical formula of spathulatine, unusual in the papilionaceous alkaloids, and the anomalous neutrality of nonalupine, which according to its assigned formula contains two nitrogen atoms and only one oxygen, rendered a further study of these bases interesting. Such an investigation was undertaken with quantities of material kindly provided by Dr. James F. Couch.

Nonalupine has been described as forming a hydrate, $C_{15}H_{24}ON_2.2H_2O$, melting at 91.5—92.5°, which after drying at 110° softened at 219° and melted at 235°(2). The sample of nonalupine received from Dr. Couch melted at 87—90°. In order to purify it, it was distilled *in vacuo*, but was found under those conditions to be fractionated into a low-boiling oil and a solid subliming at a higher temperature. The oil gave rise to a crystalline monoperchlorate identical with the monoperchlorate of pusilline (4). Nonalupine picrate when recrystallized from methanol containing picric acid melted at 183.5—185.5°. Although it had not been possible earlier (4) to prepare a crystalline picrate from pusilline by using the calculated quantity of picric acid, this has now been done successfully by employing an excess of picric acid. Pusilline picrate proved to be identical with nonalupine picrate. This fact and an examination of the reported analytical figures of nonalupine suggested that this alkaloid might not be a base but a base hydrochloride, which would account for its high

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melting point. Indeed, this has been found to be so, and the sublimate described above has been shown to be the dihydrochloride of pusilline, identical with the salt prepared by neutralizing pusilline with hydrochloric acid.

Since pusilline is an oil and its dihydrochloride a high melting solid, nonalupine which is a crystalline substance cannot be a simple mixture of the two. Nonalupine, without previous distillation, was therefore recrystallized from acetone. It consisted of a beautifully crystalline solid that proved to be pusilline monohydrochloride monohydrate, identical with a specimen prepared by titrating pusilline with methanolic hydrochloric acid to a phenolphthalein end point. Hence, nonalupine is not a base but pusilline monohydrochloride, and it is noteworthy that this salt on heating *in vacuo* undergoes disproportionation giving rise to pusilline and its dihydrochloride.

The recorded melting point of the picrate of spathulatine was almost the same as that of nonalupine and when recrystallized both salts were found to be identical. Therefore, spathulatine picrate is pusilline picrate. A comparison of the reported analytical figures of spathulatine with those of nonalupine (2) shows that the nitrogen content is about the same. Furthermore, the melting points of the two compounds are the same (spathulatine, m.p. 233—234° and nonalupine, m.p. 235°). Unfortunately, Dr. Couch's samples do not include one of spathulatine itself so that a direct comparison cannot be made, but it is highly probable that the substance is identical with nonalupine and hence that it consists of pusilline monohydrochloride monohydrate.

Spathulatine is said to be decomposed by boiling hydrochloric acid to an isomer of spartyrine isolated as its perchlorate (2). The recorded melting point of this perchlorate is the same as that of pusilline perchlorate (4) and the reported analytical figures are in good agreement with those required for this salt. It seems obvious that no reaction took place and that in the process of isolation of the product the base was simply liberated from its hydrochloride and converted to its perchlorate.

There remained to explain the peculiar potassium iodide addition complex of spathulatine. Couch's specimen of this compound was recrystallized several times from boiling acetone and thus separated from what proved to be an excess of potassium iodide. The final crystalline product that separated from the acetone solution consisted of pusilline monohydriodide. This salt has been shown to be the product of an ionic interchange between pusilline monohydrochloride and potassium iodide and to be identical with the hydriodide prepared by titrating pusilline with hydriodic acid. The identity of the so-called complex with pusilline monohydriodide as well as its method of formation supplies the proof that spathulatine is pusilline monohydrochloride and that it is, therefore, identical with nonalupine. Consequently both the names spathulatine and nonalupine should be deleted from the literature.

The close similarity between the properties of pusilline and those of sparteine was pointed out earlier (4). Although the analytical figures obtained with

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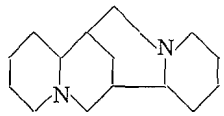
the base and its various salts are not all in complete agreement with theory, the best empirical formula derivable from these is $C_{15}H_{28}N_2$. No double bond appears to be present since pusilline in dilute hydrochloric acid solution does not absorb any hydrogen in the presence of Adams' catalyst, and this seems to confirm the assigned hydrogen content. Further, since pusilline contains one N-methyl group (4) and its infrared absorption spectrum does not reveal the presence of any NH group, it must contain one ring less than sparteine (I) and its most probable structure appears to be II.



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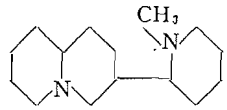

II

Experimental[2]

Nonalupine

The sample supplied by Dr. Couch was a light brown crystalline substance, m.p. 87—90°. When a portion (1.00 gm.) was distilled *in vacuo*, two fractions were obtained: an oil, b.p. 140—145°/0.12 mm., wt. 0.35 gm., and a white solid that sublimed at 160—180°/0.12 mm., wt. 0.63 gm. The oily fraction when redistilled boiled at 95—100°/0.2 mm., and consisted of a colorless liquid. It was dissolved in methanol and the solution made just acid to Congo red with 65% perchloric acid. A crystalline perchlorate that separated after a few drops of acid had been added had all dissolved when the neutral point was reached. Addition of ether brought down an amorphous perchlorate that could not be induced to crystallize. On the assumption that the amorphous salt was a diperchlorate while the crystalline salt that had first separated was a monoperchlorate, the ether was evaporated and two drops of ammonium hydroxide were added to the residual solution. A crystalline salt separated immediately which was recrystallized from methanol. It consisted of long flat needles, m.p. 217°. In admixture with pusilline perchlorate (4) the melting point was unchanged. Calcd for $C_{15}H_{28}N_2.HClO_4$: C, 53.49; H. 8.62%. Found: C, 53.63; H, 8.78%.

Some of the base recovered from the perchlorate was distilled *in vacuo* and analyzed. Calcd for $C_{15}H_{28}N_2$: C, 76.20; H, 11.94; N, 11.85%. Found: C, 76.71, 76.60; H, 10.62, 10. 81; N, 12.04, 12.35%.

The solid fraction that sublimed at 160—180°/0.12 mm. (see above) was recrystallized twice from boiling ethyl acetate from which it separated as closely packed clusters of fine needles. It began to sinter at 262° and melted at 270—273°. An aqueous solution of a small quantity of the substance containing a drop of nitric acid produced a white precipitate on the addition of a little silver nitrate. It was dried *in vacuo* at 100° prior to analysis. Calcd for $C_{15}H_{28}N_2.2HCl$: C, 58.24; H, 9.78; N, 9.06; Cl, 22.92%. Found: C, 58.01;

[2]*All melting points are corrected.*

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H, 9.53; N, 9.30, 9.44; Cl, 22.10, 21.66%. This salt was difficult to crystallize and separated only on long standing. The analytical results indicate that it was not quite pure.

This dihydrochloride was dissolved in methanol and added to a methanolic solution of picric acid. A lemon-yellow picrate separated which was recrystallized from a methanolic solution of picric acid.[3] It separated as clusters of small yellow prismatic needles, m.p. 183.5—185.5°. A sample of Couch's nonalupine picrate after recrystallization from a methanolic solution of picric acid melted at 183.5—185.5° either alone or in admixture with the above picrate.

A small quantity of freshly distilled pusilline was dissolved in methanol and the solution made just acid to Congo red by the addition of methanolic hydrochloric acid. The resulting solution was evaporated to dryness, the residue redissolved in methanol and again evaporated. The residue was dissolved in boiling ethyl acetate from which the salt crystallized slowly on standing as small warts. It began to sinter at 260° and melted at 269—271° either alone or in admixture with the sublimate above.

Pusilline Picrate

A small sample of pusilline (4) was dissolved in methanol and added to a solution of an excess of picric acid in methanol. A picrate separated which after recrystallization from a solution of picric acid in methanol, consisted of clusters of pale yellow prismatic needles, m.p. 183.5—185.5°, either alone or in admixture with nonalupine picrate. Calcd for $C_{15}H_{28}N_2.3C_6H_3O_7N_3$: C, 42.91; H, 4.04; N, 16.68%. Found: C, 42.89, 42.66; N, 3.54, 3.50; N, 16.52%. The analysis shows that an additional mole of picric acid is present over that required for a dipicrate, which accounts for the necessity of an excess of picric acid to bring about crystallization.

Pusilline Monohydrochloride

In order to determine the nature of nonalupine itself, a quantity was recrystallized without previous distillation. It was dissolved in acetone, the solution boiled with a little charcoal and filtered. The filtrate when concentrated and cooled deposited beautiful colorless prismatic needles which melted at 88—90°, resolidified, began to fuse at 220° and melted at 235.5—236.5°. The melting point of nonalupine is given as 235° after softening at 219°. Calcd for $C_{15}H_{28}N_2.HCl.H_2O$: C, 61.93; H. 10.74; N, 9.63%. Found: C, 62.27, 62.41; H, 10.11, 9.98; N, 9.41, 9.56%.

A quantity of freshly distilled pusilline was dissolved in methanol and titrated with methanolic hydrochloric acid to a phenolphthalein end point. The solution was evaporated to dryness on the steam bath, the residue dissolved in methanol and the resulting solution again evaporated to dryness. The crystalline residue was dissolved in boiling acetone from which the salt separated as colorless prismatic needles. Like "nonalupine" it melted at 88—

[3]*This picrate does not recrystallize from pure methanol and requires the presence of excess picric acid to form crystals.*

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90°, resolidified and melted again at 235.5–236.5° after beginning to fuse at 220°. Mixture of the two did not alter these constants.

Pusilline Monohydriodide

A sample of spathulatine – potassium iodide compound obtained from Dr. Couch was boiled with acetone. A portion did not dissolve and was filtered off. The insoluble material proved to be potassium iodide. The filtrate was concentrated to a small volume and allowed to cool. Colorless prismatic needles separated that melted at 252.5° after sintering at 250.5°. Calcd for $C_{15}H_{28}N_2$. HI: C, 49.44; H, 8.02; N, 7.69%. Found: C, 49.62; H, 7.79; N, 7.62%.

Pusilline monohydrochloride was dissolved in methanol and added to a solution of potassium iodide in methanol. After boiling for five minutes the solution was evaporated to dryness and the residue boiled with acetone. The mixture was filtered hot to remove the insoluble excess potassium iodide and the filtrate evaporated to dryness. The residue was again boiled with acetone, the solution filtered and concentrated on the steam bath. On cooling it deposited colorless prismatic needles, m.p. 252.5°, either alone or in admixture with Couch's recrystallized "spathulatine – potassium iodide compound."

Pusilline hydriodide was also prepared by titration of a methanolic solution of pusilline with methanolic hydriodic acid to a phenolphthalein end point. The salt, after recrystallization from acetone, melted at 252.5°, either alone or in admixture with the salt prepared by the action of potassium iodide on pusilline monohydrochloride.

Furthermore, a quantity of "spathulatine – potassium iodide complex" was decomposed with aqueous potassium hydroxide and the recovered base converted to the monoperchlorate, m.p. 217° either before or after mixture with pusilline monoperchlorate.

Spathulatine Picrate

A quantity of this salt supplied by Dr. Couch was recrystallized twice from a methanolic solution of picric acid. It was obtained as small clusters of lemon-yellow prismatic needles, m.p. 183.5–185.5°. Mixing with pusilline picrate or nonalupine picrate failed to depress the melting point. Calcd for $C_{15}H_{28}N_2 \cdot 3C_6H_3O_7N_3$: C, 42.91; H, 4.04%; Found: C, 43.12; H, 3.81%.

Acknowledgment

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THE BIOGENESIS OF ALKALOIDS

III. A STUDY OF HYOSCYAMINE BIOSYNTHESIS USING ISOTOPIC PUTRESCINE[1]

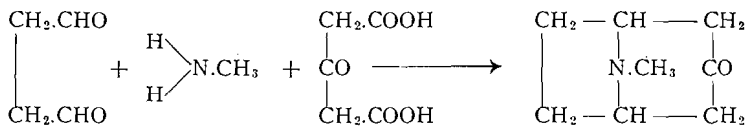
By D. G. M. Diaper,[2] Sam Kirkwood,[3] and Léo Marion

Abstract

Putrescine-1: 4-C^{14} was fed to mature *Datura stramonium* in an investigation of the biosynthesis of *l*-hyoscyamine. Although C^{14} was metabolized by the plant, no radioactivity was found in the isolated alkaloid; the mechanism of biosynthesis of the tropane nucleus is discussed in the light of published work and of this observation.

Introduction

A theory of biogenesis of the tropane nucleus from ornithine was first developed by Robinson (18, 19) after an *in vitro* synthesis of tropinone from succindialdehyde, methylamine, and acetone-dicarboxylic acid.



Degradation of arginine, proline, and ornithine to succindialdehyde or γ-aminobutyraldehyde and its related carbinolamine are plausible intermediate steps in the synthesis of the tropane system. Another plausible intermediate is putrescine, 1: 4-diaminobutane, also closely related to this group of amino acids.

Cromwell (6, 7) has collected evidence that points to putrescine acting as a precursor of *l*-hyoscyamine in *Atropa belladonna* and *Datura stramonium*. Minor increases in percentage of alkaloid in stem and leaf were reported following injection of putrescine through stem stumps. Additional evidence was demonstration of the presence of a diamine oxidase (capable of converting putrescine to succindialdehyde) and of small amounts of putrescine in *A. belladonna*.

James (11), working with detached leaves and using statistical methods of evaluation, considers that significant increase in yield of *l*-hyoscyamine followed feeding of ornithine or arginine to *A. belladonna*. He has failed to demonstrate enzymic degradation of ornithine to putrescine by tissue preparations of *A. belladonna* (12) but has prepared a polyphenolase from this plant that causes oxidation of ornithine to α-keto-δ-aminovaleric acid (13).

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It seems most probable, therefore, that the ornithine–arginine system of amino acids acts as a precursor of the tropane alkaloids. There is, however, conflicting evidence for each of two possible metabolic routes from amino acid to alkaloid.

In the present work, the role of putrescine in biosynthesis of hyoscyamine in *D. stramonium* has been investigated by a tracer technique. Putrescine-1:4-C^{14} was synthesized by standard methods and administered to mature *D. stramonium*; the alkaloid was isolated by a carrier technique.

Experimental

Putrescine-1:4-C^{14}

Several synthetic routes to putrescine were explored with a view to selection of that most easily employable in microsynthesis with compounds containing C^{14}. One unsatisfactory route was based upon reduction of γ-phthalimidobutyronitrile (15) which, in our hands, gave poor yields of putrescine upon reduction with sodium and ethanol. When the nitrile (1.02 gm.) in ethanol (3 cc.) in the presence of ammonia (1.0 cc., sp. gr., 0.88) was hydrogenated at 1500 lb. and 100° over Raney nickel, a 91% yield of putrescine was obtained; phthalimide was the other major product. This route was abandoned because synthesis of γ-phthalimidobutyronitrile containing C^{14} would involve separation of small quantities of liquid intermediates (2).

The route adopted involved hydrogenation of succinonitrile; the latter being obtained from potassium cyanide-C^{14} by a method similar to that of Kushner and Weinhouse (16). Potassium cyanide-C^{14} was made from barium carbonate-C^{14} by fusion with sodium azide (1). Difficulties encountered by us in this preparation were similar to those already reported (10) but unexpected difficulty was encountered in evaporating to dryness aqueous solutions containing potassium cyanide. To avoid loss of cyanide by alkaline hydrolysis and by volatilization of hydrogen cyanide, it was necessary to neutralize excess of potassium hydroxide with (nonradioactive) hydrogen cyanide, basify with ammonia, and concentrate *in vacuo* over calcium chloride. Presence of the anion of a mineral acid in the ammoniacal solution reduced the pH (by buffering) and considerable loss of cyanide was experienced.

To a residue of potassium cyanide-C^{14} (obtained from 1.288 mgm. of barium carbonate at a radioactive level of 4.2×10^7 counts per minute) were added 0.615 gm. of potassium cyanide, a trace of potassium iodide (9), 1.0 cc. of water and 3.0 cc. of ethanol. Ethylene dibromide (1.61 gm., 1.18 equiv.) was added and the mixture was boiled, under reflux, for 75 min. After addition of water (100 cc.) and removal of unchanged ethylene dibromide with the aid of ether, the mixture was treated with sulphuric acid (5 *N*, 20 cc.) and, after 30 min. at room temperature to hydrolyze isocyanides, succinonitrile was isolated by continuous extraction with chloroform. Evaporation of the extract gave a crystalline residue (222 mgm.) of succinonitrile which was not further purified.

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A solution of succinonitrile-C^{14} (222 mgm.) in ethanol (2 cc.) containing Raney nickel was cooled and an equal volume of liquid ammonia was added. The vessel was quickly sealed in a bomb and hydrogenation of the nitrile was performed at 100° and 1200 p.s.i. (4). The reaction mixture was added to 500 cc. of dilute hydrochloric acid and, after filtration, putrescine-1:4-C^{14} was precipitated as the *reineckate* (362 mgm., at a radioactive level of 3.8×10^6 counts per minute.) Calc. for $C_{12}H_{30}O_2N_{14}S_8Cr_2$: N, 25.7%. Found: N, 26.0%. It was found that the reineckate is a useful solid derivative of this base. It is quantitatively precipitated from aqueous solution by ammonium reineckate and this gravimetric estimation method is unaffected by ammonium chloride at 60 gm. per liter. Putrescine can thus be sharply separated from ammonia. The reineckate is soluble in acetone. Recovery of putrescine from this derivative was accomplished by the method of Kapfhammer and Bischoff (14) or more conveniently by heating with strong potassium hydroxide solution and trapping the vapors in hydrochloric acid.

Cultivation of Datura stramonium and Feeding Experiments

Seeds of *D. stramonium* were sown in boxes in a greenhouse at the beginning of October. In mid-December the seedlings were transferred to beakers of a hydroponic nutrient solution and feeding experiments with putrescine hydrochloride were performed on the mature plants in the following April, May, and June. The nutrient solution employed contained potassium nitrate, 500 mgm. per liter; calcium nitrate, 1180 mgm. per liter; magnesium sulphate, 495 mgm. per liter; potassium dihydrogen phosphate, 136 mgm. per liter; ferric tartrate, 48 mgm. per liter; and traces of micronutrients (Mn, B, Cu, Zn). Light was excluded from the beakers of solution to minimize growth of algae on the roots.

Four feeding experiments were performed, each in total darkness to eliminate photosynthesis and consequent randomization of C^{14} in the alkaloid (8). In two of the experiments the putrescine hydrochloride was administered, in dilute solution in distilled water, through the roots; in the other two experiments the solution was administered to the wilted plant by uptake through a cut stem. A single healthy plant with flower buds was used for each feeding experiment.

Isolation of Alkaloid

To establish the presence of *l*-hyoscyamine in the plants the alkaloid was isolated as follows: Aerial parts of two plants were oven-dried at 110° and powdered (24 gm.). Following continuous extraction with methanol and evaporation of the extract, the gummy residue was shaken with sulphuric acid (0.5 *N*, 200 ml., in three portions). Extraction with a mixture of chloroform (20 cc.) and ether (80 cc.) was used to free this aqueous extract from suspended gum and the basic material was liberated by ammonia. After extraction with three portions (totalling 300 ml.) of a similar chloroform–ether mixture, the extract was dried and evaporated, finally using suction at 100°. To the residue

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of crude alkaloid (25 mgm.) was added dilute hydrochloric acid and 40 mgm. of gold chloride. A black oil separated. Extraction of this black oil with boiling water gave two crops of dark yellow crystals, totalling 16.5 mgm. Recrystallization afforded yellow plates, m.p., 160.5-161.5° undepressed in admixture with authentic hyoscyamine aurichloride. Isolation of the alkaloid as aurichloride (17) was found preferable to isolation as picrate (6) as the latter compound could be obtained only in a poor yield and crude state.

After a feeding experiment, the root, which contains hyoscine (3) and aerial parts were extracted separately. Hyoscyamine (60-200 mgm.) as carrier was added to each extract. Isolation of the alkaloid was performed along the lines above, but samples of each fraction were counted in a "Nucleometer".

Samples were evaporated on aluminum dishes and counted as layers of finite thickness. Self-absorption corrections were applied, but reproducibility of counts was no better than 30%. Alkaloid aurichloride samples were recrystallized before counting as an infinitely thick layer.

Results

For location of radioactivity in treated plants, see Table I in which all figures represent total activity in the fraction described.

TABLE I

LOCATION OF RADIOACTIVITY

Experiment	Radioactivity administered (counts per min.)	Duration	Portion studied	Radioactivity found (counts per min.)			
				Residue (chiefly cellulose)	Fatty material	Water-soluble nonbasic material	Alkaloid aurichloride
1*	71,000	1 week	Root	3650	90	6450	None
			Shoots	None	None	300	None
2*	530,000	41 hr.	Root	10,300	2200	72,000	12
			Shoots	None	110	1500	None
3†	100,000	24 hr.	Root	1100	400	790	20
			Shoots	4300	1810	21,000	None
4†	100,000	9 days	Root	None	110	380	None
			Shoots	2090	350	8000	10

* *Uptake through the root.*
† *Uptake through the stem.*

Uptake of C^{14} was followed from day to day in Experiment I, showing that selective disappearance of radioactivity from the solution was occurring. Concentrations of radioactivity in the solution in the first three days were 650, 320, and 140 counts per ml.

Recovery of C^{14} not absorbed was 960 counts per minute in Experiment 1; 100,000 in 2; 48,000 in 3; and 13,000 in 4.

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The possibility of "water-soluble nonbasic material" containing C^{14} as putrescine was investigated by taking this stem extract from Experiment 3, basifying with sodium hydroxide, and extracting with ether. The ratio of C^{14} in the ethereal and aqueous solutions was 1: 1.4.

Discussion

C^{14} detected in the *l*-hyoscyamine isolated was negligible in comparison with the amount of C^{14} administered. Those counts observed were probably due to impurity. These experiments do not lend support to the postulate of Cromwell (7) that putrescine is an intermediate in the biosynthesis of *l*-hyoscyamine in *D. stramonium*. On the other hand, positive evidence, in an investigation of this nature, is far more valuable than negative evidence.

If these experiments be interpreted to dismiss all consideration of putrescine as a precursor of *l*-hyoscyamine, and if the diamine oxidase of Cromwell (7) be accepted, there is doubt whether synthesis of the tropane skeleton from succindialdehyde occurs. To this must be added the fact that Cromwell was unable to demonstrate the presence of methylamine in *A. belladonna* or *D. stramonium*. On the other hand, the Robinson tropinone synthesis (20) and the demonstration by Schöpf and Lehmann (21) that it proceeds best at physiological pH are highly suggestive. Feeding experiments with labelled succindialdehyde and methylamine would be useful.

The present experiments are irrelevant to the possible route of *l*-hyoscyamine biosynthesis from ornithine through α-keto-δ-aminovaleric acid (12).

If an authentic tracer-containing intermediate in hyoscyamine synthesis were fed to a virile plant, it is reasonable to assume that the absolute amount of tracer in the alkaloid would rise quickly to a maximum and then decrease asymptotically to zero. We have no means of knowing the time-scale of this hypothetical curve, but the spread of experiment duration (24 hr. to 9 days) means that, if the putrescine hypothesis is to be retained, alkaloid turnover must be either very fast or very slow. It may be mentioned that *D. stramonium* does not survive in darkness for much more than a week.

It is difficult to know whether the conditions of the experiments (darkness, withdrawal of supplies of salts, administration of unusual ions) could sufficiently disturb the metabolism to arrest alkaloid synthesis. This is considered, however, to be unlikely.

The fate of C^{14} in the plants was consistently extensive incorporation into both methanol-soluble and methanol-insoluble fractions. Although purification of fats and cellulose was not attempted, it seems likely that both contained C^{14}. Much of the radioactivity appeared in the water-soluble nonbasic fraction; this contains sugars. It is possible to visualize a metabolic route for putrescine that leads through succinate into the tricarboxylic acid cycle and thence to carbohydrate and lipid synthesis (5).

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The question of the presence of unchanged putrescine in the water-soluble nonbasic fraction must be left open. It is a stronger base than ammonia and would not appear in the alkaloid fraction; on the other hand, the value of the experiment using sodium hydroxide and ether cannot be assessed without knowledge of the amount of putrescine present and its partition coefficient. In any case, under the conditions of administration of a solution through a cut stem, some material must inevitably adhere to the surface without entering the plant vascular system at all.

Selective removal of C^{14} from the solution during root uptake experiments can be explained by metabolism of putrescine by the bacteria and algae unavoidably present on the roots. It is, however, considered likely that the radioactivity in the plant was derived from putrescine itself, rather than from uptake of any metabolites produced by microorganisms from the base. This objection is inapplicable to stem-feeding experiments.

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HYDROLYSIS AND POLYMERIZATION OF CYCLIC DIMETHYLETHYLENE OXALATES[1]

By L. G. Ripley and R. W. Watson

Abstract

Macrocrystalline cyclic oxalates (2,3-dimethyl-5-6-*p*-dioxanediones) were prepared by vacuum distillation of the polymeric mixture formed on heating ethyl oxalate, and 1, 2-dimethylethylene glycol with an ester-interchange catalyst. Monomeric dimethylethylene oxalate polymerizes less readily than propylene oxalate, and only at an elevated temperature in the presence of a catalyst. Dimethyl substitution therefore confers marked stability on the six-membered ring. Hydrolysis reaches 50% completion almost instantaneously, followed by a slow first order reaction resulting in complete cleavage of the monobasic acid in about one month at room temperature. Hydrolysis constants for the *levo-* and *meso-* oxalates are 0.069 and 0.076 days^{-1} respectively. The crystalline monomers do not possess sharp melting points and represent stereoisomeric mixtures which display optical activity in solution.

Reversible polymerization is a well known characteristic of six-membered cyclic esters (1). The unsubstituted esters, e.g. δ-valerolactone (6), the lactone of hydroxyethylglycolic acid (7), and ethylene oxalate (1) polymerize spontaneously at room temperature. As a general rule the presence of substituent groups markedly affects ring stability. The substituted six-membered esters, e.g. the lactone of 2,3,4-trimethyl-*l*-arabonic acid (5), propylene oxalate (1), and α-*n*-propyl-δ-valerolactone (2) require either heat or catalysts or both to effect polymerization. Carothers *et al.* (2) have noted that ease of polymerization is related to susceptibility to hydrolysis. The present investigation explores the relation between hydrolysis and polymerization in the previously uninvestigated dimethylethylene oxalates.

Immediate titration with 0.01 *N* sodium hydroxide of aliquots of freshly prepared aqueous solutions of the *levo-* and *meso*-oxalates showed 50-52% of the calculated total acidity. It appears therefore that 50% of the linkages in the dimethyl-substituted monomers are readily hydrolyzed. This anomaly may be explained by assuming rapid ring opening, followed by slow hydrolysis of the hydroxy acid. As shown in Fig. 1 hydrolytic cleavage of the monobasic acid is complete in about one month at room temperature. Hydrolysis constants of the *levo-* and *meso*-oxalates in this slow latter phase, determined from aliquots of aqueous solutions (see experimental section), were 0.069 and 0.076 days^{-1} respectively.

Both dimethylethylene oxalates polymerize less rapidly than propylene oxalate (1). Repeated vacuum sublimation of the pure dimethyl monomers at temperatures just below their melting ranges failed to effect any apparent change in properties. Both the *levo-* and *meso*-monomers remained unchanged after storage under anhydrous conditions for more than one year. However,

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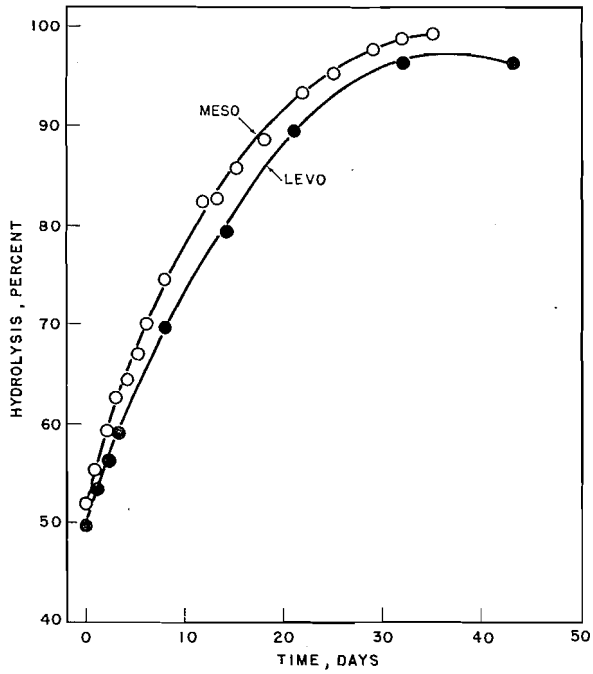

FIG. 1. *Hydrolysis of meso- and levo-oxalates.*

when either was heated with a trace of potassium carbonate at 110°C. under deoxygenated nitrogen, amorphous polyesters were formed in about one day. The highest polymer obtained under these conditions from the *meso*-oxalate was a hard resin, while the corresponding product from the *levo*-monomer was a viscous balsam. The inherent viscosities (4) in 2% acetone solution of these polymers are plotted against time of formation in Fig. 2. The reaction forming the *meso*-polyester is more rapid, and assuming an average value for $K_{eqv.}$ (10, 11, 13) the molecular weight indicates the formation of an ω-polyester. During polymerization there is a loss in weight of less than 2%.

The comparison between ease of polymerization and hydrolysis in the oxalate series is shown in Table I. The fundamental observation (2) that ease of polymerization is related to susceptibility to hydrolysis may be explained by assuming that traces of water initiate polymerization. More rarely two six-membered rings may coalesce (3) but ordinarily the first step in chain formation is assumed to be hydrolytic ring opening to form the hydroxy acid. The hydroxyl group of the acid may then react with another ring to form the linear dimer (2).

The depression in the rate of polymerization of cyclic oxalates with increasing methyl substitution may be explained through the comparatively low reactivity of secondary hydroxyl groups. Adjacent methyl groups introduce steric effects as well as changes in bond strength. In the compounds under investigation,

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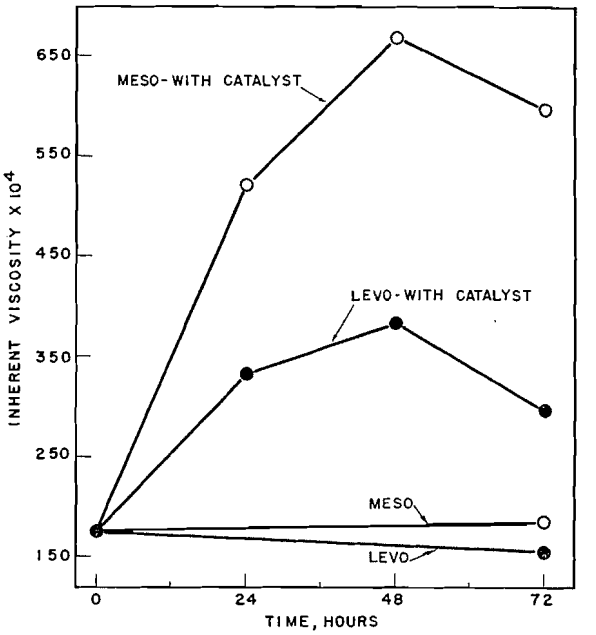

FIG. 2. *Inherent viscosity vs. time of formation of polyesters from cyclic monomers.*

TABLE I

COMPARISON BETWEEN POLYMERIZATION AND HYDROLYSIS OF CYCLIC OXALATES

Monomer	Polymerization	Hydrolysis
Ethylene oxalate (1)	Spontaneous at room temperature	Instantaneous with warm dilute alkali
Monomethylethylene oxalate (1)	When heated to 140°C. for eight hours	No data available
Dimethylethylene oxalate	Only when heated to 110° C. in presence of catalyst	50% hydrolysis instantaneous: complete in 30-35 days

rapid hydrolysis of the cyclic monomer and slow hydrolysis of the hydroxy acid are correlated with a depressed rate of polymerization. The methyl-substituted lactones investigated by Hollo (7) showed rates of hydrolysis depressed below those of corresponding unsubstituted compounds, but in every instance the methyl group was in a different position on a dissimilar ring. At present it is difficult to offer an explanation for the extremely rapid hydrolytic ring opening in the dimethylethylene oxalates.

Experimental

levo-2, 3-Butanediol, obtained from the fermentation of wheat by *Bacillus polymyxa* (9) was redistilled to $n_D^{25} = 1.4310$, $[\alpha]_D^{25} = -12.76$. *meso*-2, 3-Butane-

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diol, produced by *Aerobacter aerogenes*, was redistilled to $n_D^{25} = 1.4340$, $[\alpha]_D^{25} = +1.78$ (12). Eastman ethyl oxalate, $n_D^{22.5} = 1.4089$, was used without further purification.

levo-Dimethylethylene Oxalate

The method of preparation has been previously described (14). Approximately 50 gm. of the cyclic monomer purified by repeated vacuum sublimation, had the following properties:

Calc. for $C_6H_8O_4$: C, 50.00; H, 5.55. Found: C, 50.29, 50.45; H, 5.37, 5.56. Melting range, 97.1° to 100.5°C.*; $\alpha_D^{25} = +9.14$ ($c = 3.61$ in chloroform); +23.31 ($c = 5.15$ in ethyl acetate); +24.58 ($c = 5.29$ in acetone). Molecular weight (theoretical), 144; observed values (Rast), 139, 145, 145.

meso-Dimethylethylene Oxalate

The *meso*-cyclic oxalate was prepared by the method described for the *levo*-monomer (14). The Rast molecular weight was 154 (observed values: 150,151, 156, 157, 158: theoretical, 144). Calc. for $C_6H_8O_4$: C, 50.00, H, 5.55. Found, C, 50.22, 50.42; H, 5.35, 5.42. Melting range, 78.4°-80.4°C.: $\alpha_D^{25} = -0.465$ ($c = 2.68$ in acetone).

To determine the hydrolysis constant, 0.50 gm. of the cyclic monomer was dissolved in 5 ml. of redistilled reagent acetone. The acetone solution was added to carbon dioxide-free distilled water in a 500 ml. volumetric flask, made to volume, mechanically stirred, and maintained at 25.0° ± 0.2°C. in a water bath. At intervals a 10 ml. aliquot was removed and titrated with a 0.01 *N* sodium hydroxide to the phenolphthalein end point.

Polymerization of 0.2 gm. samples of the monomers, to each of which a trace of anhydrous potassium carbonate was added, were carried out in 10 × 30 mm. test tubes under nitrogen at 110°C.

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* *All temperatures are corrected.*

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CUPRIETHYLENEDIAMINE AS A REAGENT FOR HEMICELLULOSE SEPARATION FROM WHEAT STRAW HOLOCELLULOSE[1]

By V. D. Harwood

Abstract

Wheat straw and wheat straw holocellulose were dispersed in aqueous cuprietheylenediamine solutions and fractionated by graded precipitation with acid and alcohol. From the holocellulose a 25.4% recovery of a hemicellulose containing negligible quantities of hexoses was achieved. The corresponding product from wheat straw was contaminated with both lignin and cellulose but a comparison of the chemical compositions of the two hemicelluloses showed that the acid chlorite used for delignification had caused very little hydrolytic action. The acetate of the hemicellulose from holocellulose was fractionated from chloroform solution by the addition of petroleum ether into a series of fractions and subfractions. Analysis of representative fractions from this series led to the conclusion that the hexoses present were not chemically combined with pentosan. Molecular weights were determined by periodate oxidation, the Signer isothermal distillation method, and from the lowering of the vapor pressure of their chloroform solutions and showed that the hemicellulose molecules were relatively small (mol. wt. $< 10{,}000$). The decreasing ratio of xylose to arabinose in the fractions of lower molecular weight indicated increasing chain branching.

Introduction

Norman (17) has defined hemicelluloses as "alkali-soluble polysaccharides, hydrolyzable by dilute acids to component sugars and sugar acids". This definition includes various mixtures of amorphous polyuronide hemicelluloses and also short chain cellulosans derived from the cellulose micelles. On the basis of this definition it is not surprising to find that the conventional procedure for hemicellulose isolation has usually involved the extraction of the plant material with cold dilute alkali followed by acidification of the extract and subsequent precipitation of the hemicelluloses, with or without the addition of ethanol or other organic solvents.

This general procedure suffered from the rather serious drawback that the hemicelluloses thus isolated were contaminated with alkali-soluble lignin. To surmount this difficulty, plant material has been delignified by either alternate treatments with chloride dioxide or chlorine and organic bases (22, 24, 32) or by the action of acid chlorite (14, 33, 34). The resulting holocellulose is then subjected to milder solvent treatment for the extraction of hemicelluloses (31). Complete delignification of holocellulose can be achieved, however, only with concurrent loss of carbohydrate material (2, 14, 34). The nature of the degradative action of acid chlorite is not yet understood. Using wheat straw holocellulose as a starting material, Adams and Castagne (3) and Bishop and Adams (4) have been able to remove 25.3% and 27.6% of the holocellulose respectively by successive extractions with solvents ranging from cold water to 2% aqueous potassium hydroxide. Although the compositions of these fractions varied considerably, D-xylose, L-arabinose, and D-glucose were found

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in all and D-galactose in many of them. A hexuronic acid was also present. Recent work by Adams (1) in these laboratories has shown that the arabinose molecules are present in side chains.

In the present investigation the problem of hemicellulose isolation was approached by dispersing the holocellulose from wheat straw in cupriethylenediamine and separating it into somewhat impure cellulose and hemicellulose fractions by precipitation of the former with acid. This method has been applied to the fractionation of cotton and flax celluloses by Straus and Levy (28, 29) but is new to the holocellulose field although cuprammonium hydroxide has been used by Haas in increasing concentrations to fractionate the holocelluloses of beech and pine wood (9, 10).

Materials and Methods

Commercial cupriethylenediamine solution which was one molar with respect to copper was obtained in 1 gal. bottles from the Ecusta Paper Corporation, Pisgah Forest, N.C. Deterioration of the reagent was prevented by storing under an atmosphere of nitrogen. Pectin- and extractive-free wheat straw holocellulose that had been isolated by chlorite delignification (2) was provided by G. A. Adams of this laboratory. Pentoses were determined by distillation with 12% hydrochloric acid and the evolved furfural was measured by the bromine oxidation procedure of Hughes and Acree (12). Uronic acid anhydride was determined by the method of Tracy (30); methoxyl by the microprocedure of Clarke (8), and acetyl content by alkali saponification and back titration with standard acid. Lignin was determined by the 72% sulphuric acid procedure of Ritter, Seborg, and Mitchell (23). Reducing sugars were determined by the method of Somogyi (25) and the component sugars of the various polysaccharides, after acid hydrolysis, were separated by paper chromatography. Periodate oxidation by the method of Halsall *et al.* (11), the Signer isothermal distillation method (8), the lowering of the vapor pressure of their solutions (21), and viscosity measurements were used to estimate the approximate molecular weights of individual fractions. Moisture and ash were determined at 110° and 550°C. respectively and, unless otherwise noted, all analyses were on an ash-free, moisture-free basis.

Experimental Procedures and Results

The investigation proceeded along three lines; separation of holocellulose into cellulose and hemicellulose components; application of the same procedure to wheat straw; fractionation of the hemicellulose derived from the holocellulose into subfractions, some of which were used for molecular weight determinations.

Preparation of Cupriethylenediamine Hemicellulose From Holocellulose

Straus and Levy (29) dissolved cellulose to the extent of 1 gm. per 100 ml. of 0.5 *M* cupriethylenediamine but preliminary experiments on wheat straw holocellulose showed that it was soluble at about half this concentration. On

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this basis approximately 100 gm. of wheat straw holocellulose was dispersed in 4.5 liters of 0.5 *M* cupriethylenediamine in an atmosphere of nitrogen and diluted with an equal volume of water. An insoluble material (Fraction I) was recovered by centrifuging and washing with water. This residue and a further quantity of holocellulose were retreated with 4.5 liters of 0.5 *M* cupriethylenediamine and the procedure repeated until eventually 328.6 gm. of holocellulose had been dispersed in 27 liters of 0.25 *M* cupriethylenediamine solution. The whole of Fraction I was then removed by centrifuging. The addition of 1.5 liters of 8 *N* hydrochloric acid to the centrifugate reduced the pH from 12.8 to 11.5 and caused the precipitation of a gelatinous "cellulose" (Fraction II). This product was washed with 50% ethanol, subsequently deashed with 3% hydrochloric acid in 50% ethanol and dried through ethanol and ether on a centrifuge. A second lot of 1.5 liters of 8 *N* hydrochloric acid was added to the 42 liters quantity of centrifugate and acidic washings from the gelatinous "cellulose" precipitate to further reduce the pH to 4.3 and to cause the precipitation of Fraction III, a granular material. Finally the combined 45 liters of washings and centrifugates was neutralized with 8 *N* potassium hydroxide and concentrated *in vacuo* at 40-50°C. to 6.7 liters. To each liter of this solution 4.5 liters of 95% ethanol and 0.4 liters of 4 *N* hydrochloric acid were added to precipitate Fraction IV, a "hemicellulose" that was recovered by centrifuging, washed with 1.5% hydrochloric acid in 75% ethanol, and then dried through ethanol and ether. All four fractions were analyzed for pentosan and uronic acid content. The yields and analytical data are recorded in Table I.

From Wheat Straw

A 16.0 gm. sample of the pectin-free and extractive-free wheat straw was shaken for 16 hr. with 375 ml. water and an equal volume of 1 *M* cupriethylenediamine. An insoluble residue was recovered by centrifuging and washed successively with water, 30 ml. of 8 *N* hydrochloric acid, and finally with ethanol and ether. This residue was termed "lignin". The pH of the centrifugate and washings was reduced to 6.5 and a precipitated "cellulose" fraction recovered. After neutralization with aqueous potassium hydroxide, the 4 liters of washings and centrifugate from the "cellulose" precipitation were concentrated *in vacuo* at 40-50°C. to 625 ml., and 2.5 liters of 95% ethanol was added along with sufficient 8 *N* hydrochloric acid to reduce the pH to 4. A "hemicellulose" fraction was thus obtained. The analyses of these three fractions are given in Table II.

Hydrolysis of Fractions from Wheat Straw and Holocellulose

Three different procedures were used for the hydrolysis of the various fractions described in Tables I and II.

(*a*) A 50 mgm. sample of the hemicellulose from the holocellulose was hydrolyzed by 5 ml. of 0.5% sulphuric acid in a boiling water bath. After a small insoluble residue had been recovered by centrifuging the supernatant liquor was analyzed directly by paper chromatography.

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TABLE I

COMPOSITION OF FRACTIONS PREPARED FROM WHEAT STRAW HOLOCELLULOSE BY CUPRIETHYLENEDIAMINE

Material examined	Dry weight, gm.	Ash, %	Ash-free wt., gm.	Recovery of original, %	Pentosan, *		Uronic acid anhydride	
					%	Gm.	%	Gm.
Holocellulose	306.7	2.1	300.2		29.3	88.0	4.9	14.7
Fraction I	8.6	17.0	7.2	2.4	4.1	0.3	2.7	0.2
Fraction II	184.3	0.6	183.2	61.0	9.7	17.8	2.6	4.8
Fraction III	6.0	1.1	5.9	2.0	41.9	2.5	4.0	0.2
Fraction IV	80.2	4.9	76.3	25.4	82.9	63.3	7.3	5.8
Totals			272.6	90.8		83.9		11.0
Recovery based on holocellulose, %						95.3		74.8

* *Corrected for pentosans liberated from uronic acids.*

TABLE II

COMPOSITION OF FRACTIONS PREPARED FROM WHEAT STRAW BY CUPRIETHYLENEDIAMINE

Material examined	Dry wt., gm.,	Ash, %	Ash-free wt., gm.	Recovery of original, %	Pentosan, *		Uronic acid anhydride		Lignin,	
					%	Gm.	%	Gm.	%	Gm.
Wheat straw	14.91	0.9	14.77		30.0	4.43	6.5	0.96	20.0	2.95
Fraction										
"Lignin"	4.22	1.7	4.15	28.1	11.9	0.49	1.2	0.05	23.7	0.98
"Cellulose"	6.40	1.5	6.30	42.7	25.5	1.61	0.8	0.05	7.9	0.50
"Hemicellulose"	3.22	3.6	3.10	21.0	74.9	2.32	5.3	0.16	12.7	0.39
Totals			13.55	91.8		4.42		0.26		1.87
Recovery based on wheat straw, %						99.8		27.1		63.4

**Corrected for pentosans liberated from uronic acids.*

(*b*) The procedure for the other three fractions from the holocellulose was to treat a 100 mgm. sample with 10 ml. of 0.5% sulphuric acid. When the reducing value of the hydrolyzate reached a constant value, it was removed by centrifuging and the residue rehydrolyzed with 10 ml. of 4% sulphuric acid, at 100°C. At the completion of the second hydrolysis the hydrolyzates were neutralized with barium carbonate, the precipitate removed and washed with warm water, and the solution analyzed by paper chromatography. The residues remaining, which amounted to from 45-80 mgm. were treated with 1.0 ml. of cold 72% sulphuric acid and left for 16 hr. at 5°C. Hydrolysis was completed by adding 37.6 ml. of water and heating in a boiling water bath for four hours.

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Barium carbonate was again used to neutralize the sulphuric acid. Treatment of the concentrated hydrolyzate with a washed culture of resting cells of *Torulopsis utilis* var. *thermophila* (N.R.C. 862) preferentially fermented the glucose. Reducing-power determinations before and after fermentation and paper chromatography of the glucose-free solution led to a complete analysis of the products.

(*c*) An alternate procedure that resulted in a more complete recovery of sugars in the same three holocellulose fractions was to treat 250 mgm. samples overnight with 1.1 ml. of cold 72% sulphuric acid, then to boil under reflux with 45 ml. of water to complete the hydrolysis.

The various fractions which had been prepared from wheat straw were analyzed by Method (*c*) using 1 gm. samples and correspondingly larger amounts of sulphuric acid. Each solution was then made up to 1 liter, a 100 ml. aliquot taken, and neutralized with barium carbonate. After removal and washing of the precipitate, the filtrate and washings were concentrated to 10 ml. and analyzed by paper chromatography.

Analysis of Constituent Sugars in Hydrolyzates

The chromatographic procedure used in these laboratories was developed by Perlin (18) after a consideration of various methods. Xylose, arabinose, and glucose were the only sugars qualitatively detected and quantitatively estimated in the wheat straw (Table III) and holocellulose (Table IV) fractions. These results confirmed the previously established fact (3, 4) that xylose and arabinose are the main constituent sugars of the hemicellulose from wheat straw holocellulose.

Fractionation of Hemicellulose Prepared from Holocellulose

To estimate the molecular weight distribution of the hemicellulose prepared by the cupriethylenediamine procedure, it was necessary to fractionate the product into as many distinct fractions as possible. Trial experiments using water or cupriethylenediamine failed to yield any distinct separations, but acetylation followed by precipitation with petroleum ether from chloroform solution showed more promise.

TABLE III

CONSTITUENT SUGARS OF WHEAT STRAW FRACTIONS
(Based on weight of nonlignin part, by difference)

Constituent sugars	"Lignin"	"Cellulose"	"Hemicellulose"
Anhydroarabinose, %	2.6	6.6	9.7
Anhydroxylose, %	9.7	21.5	65.8
Anhydroglucose, %	76.5	53.5	4.5
Total, %	88.8	81.6	80.0
Xylose: arabinose	3.7: 1.0	3.3: 1.0	6.8: 1.0
Glucose: pentose	6.2: 1.0	1.9: 1.0	1.0: 16.8

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TABLE IV

CONSTITUENT SUGARS OF HOLOCELLULOSE FRACTIONS

Fractions	Hydrolysis method	Anhydrosugars, %			Total, %	Xylose / Arabinose	Glucose / Pentose
		Arabinose	Xylose	Glucose			
I	Complete (*c*)	..	1.4	80.4	81.8	..	57:1.0
II	Graded (*b*)	0.7	10.0	56.1	69.7	14.3:1.0	4.1:1.0
	Complete (*c*)	1.7	8.8	82.9	93.4	5.2:1.0	7.9:1.0
III	Graded (*b*)	3.4	38.9	32.6	74.9	11.4:1.0	1.0:1.3
	Complete (*c*)	2.0	38.7	35.0	75.7	19.4:1.0	1.0:1.2
IV	Complete (*a*)	8.8	71.9		80.7	8.2:1.0	

Acetylation of Hemicellulose

A quantity of hemicellulose equivalent to 20.0 gm., ash- and moisture-free, was dispersed in 354 ml. (400 gm.) of formamide by stirring for 1 to 1.5 hr. at 60 to 70°C. (6). To this suspension were added successively 400 ml. of dry pyridine and 400 ml. of benzene, the latter to maintain the system as a fluid instead of as a gel. Acetic anhydride was added over a period of 1.5 hr. in four lots of 32 ml. and the solution was stirred for 16 hr. The acetate was recovered by pouring the reaction mixture into 6 liters of ice water, followed by stirring to decompose the acetic anhydride. The precipitated acetate was washed with water, 3% hydrochloric acid, more water, then ethanol and yielded 34.7 gm. of dry acetate (38.7% acetyl). To reacetylate, 300 ml. of benzene and an equal volume of pyridine were added to the product which was then heated and stirred at 70°C. for 30 min. The addition of 300 ml. of acetic anhydride and further stirring for 40 hr. at room temperature and for 16 hr. at 50-55°C. completed the reacetylation. The yield was 34.0 gm. (39.6% acetyl).

Fractionation of Hemicellulose Acetate

Almost the total yield of acetate, viz. 33.7 gm., was dissolved in 3400 ml. of chloroform and successive fractions precipitated by the addition of increasing quantities of petroleum ether (b.p. 40-60°C.). Each precipitate was centrifuged and washed with a solvent mixture of the same approximate composition as the supernatant liquor before a final washing with pure petroleum ether. In this manner 18 fractions and a small residue were recovered from the original solution. The optical rotation of all but the first fraction was readily obtained using 1% solutions in chloroform. These solutions were then used for viscosity determinations at 0.5, 0.25, 0.125, and 0.063% concentration in chloroform using an Ostwald–Cannon–Fenske viscometer (A.S.T.M. 50) in a water bath at 25°C. ± 0.02°C. The plots of $\eta\ sp/C$ versus C or of $\ln \eta\ R/C$ versus C were straight lines for all but the first five fractions, where C was expressed in terms of grams per liter of solution. When extrapolated to zero concentration the intrinsic viscosities $[\eta]$ were derived from the graphs.

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Refractionation of Hemicellulose Acetate Fractions

Fraction I was dispersed in chloroform and subfractions 1-6 precipitated from it by successive additions of petroleum ether.Fractions 8 to 11 inclusive were refractionated to determine whether any greater differences might be apparent in their optical rotations and intrinsic viscosities. This was done by dissolving Fraction 8 in chloroform to make a 1% solution and then adding petroleum ether to cause the precipitation of Subfraction 7. To the centrifugate and washings of Subfraction 7, a 3% solution of 9 was added and then more petroleum ether. This was repeated until Fractions 8 to 11 were recovered as Subfractions 7-14. In Table V are tabulated the data on viscosity, rotation, and yield of all fractions and subfractions. On the basis of similar rotations and intrinsic viscosities, Fractions 4 and 5; 6, 7, and Subfraction 7; Subfractions 8-11 were combined to form the composite fractions *A*, *B*, and *C* respectively. Samples of certain representative fractions, viz. 13, 14, 15, 16 and Subfractions 1, 4, and 13 and the composite fractions *A*, *B*, *C*, were deacetylated with a calculated 10% excess of potassium hydroxide in an acetone dispersion of the acetate and hydrolyzed by 0.5% sulphuric acid. Paper chromatography led to the results recorded in Table VI.

Molecular Weight Determinations

Physical Methods

Attempts were made to determine the molecular weights of a few acetates from the lowering of the vapor pressure of their solvents (21). Chloroform, the

TABLE V

PHYSICAL CONSTANTS OF HEMICELLULOSE ACETATE FRACTIONS AND SUBFRACTIONS

Fractions	Weight, gm.	$[\alpha]_D^{20}$ in chloroform	Intrinsic viscosity* $[\eta]$	Subfractions		Weight, gm.	$[\alpha]_D^{20}$ in chloroform	Intrinsic viscosity* $[\eta]$
1	10.04	..	..	From Fraction I	1	1.50	..	..
2	5.65	−104°	0.060		2	3.51	..	..
3	1.55	−109	0.068		3	2.09	..	..
4	1.23	−111	0.054		4	0.91	−110°	..
5	0.99	−108	0.051		5	0.53	−117	..
6	1.53	−114	0.056		6	0.29	−108	..
7	0.78	−112	0.059	From Fractions 8 to 11 inclusive	7	0.90	−108	0.057
8	2.08	−114	0.051		8	0.85	−106	0.049
9	0.67	−114	0.052		9	0.50	−102	0.050
10	0.75	−113	0.048		10	1.18	−109	0.046
11	1.93	−115	0.045		11	0.35	−102	0.047
12	1.82	−111	0.040		12	0.60	−108	0.044
13	1.26	−111	0.033		13	0.45	−114	0.034
14	0.68	−105	0.026		14	0.06	..	..
15	0.74	−100	0.020					
16	0.49	− 81	0.015					
17	0.09	− 81	0.012					
18	0.06	− 58	0.011					
19	1.16							

Total (1 to 19) 33.50 (99.5% recovery)

* *Mean of values from the extrapolations of $\eta sp/C$ and ln $\eta R/C$ vs. C curves.*

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TABLE VI

COMPOSITION OF THE DEACETYLATED HEMICELLULOSE ACETATE FRACTIONS AND SUBFRACTIONS

	Original hemicellulose, %	Constituent anhydrosugars, %			Xylose / Arabinose
		Arabinose	Xylose	Hexoses	
Fractions					
A	6.6	6.7	70.4	....	10.5:1.0
B	9.5	7.3	72.7	....	10.0:1.0
C	8.6	7.0	63.6	....	9.1:1.0
13	3.7	8.4	64.9	....	7.7:1.0
14	2.0	12.0	81.2	....	6.8:1.0
15	2.2	11.4	74.8	....	6.6:1.0
16	1.5	16.9	58.7	6.3	3.5:1.0
Subfractions					
1	4.5	8.7	74.4	....	8.6:1.0
4	2.7	7.1	80.4	....	11.3:1.0
13	1.3	9.5	76.3	....	8.0:1.0

only acetate solvent with a reasonably high vapor pressure at room temperature, was freed of ethanol by passing it through a column of silica gel. Because of either the photolysis of the solvent or the use of highly concentrated solutions in the apparatus, few values could be obtained. A second approach was by Signer's isothermal distillation method (8). Solvent decomposition might also have been the cause of the limited success of this technique since it required chloroform solutions of the acetates and of a reference compound, sucrose octaacetate. Here the likelihood of decomposition of the chloroform was enhanced by the extensive period required for equilibrium to be established.

Chemical Method

Periodate oxidation is the basis of an end-group method for the determination of molecular weights (5). The procedure adopted in the present investigation was to deacetylate sufficient material to yield 150 mgm. samples of each fraction. To each sample, in an actinic glass flask, was added 100 ml. of water and 20 ml. of a solution made by neutralizing 6.0 gm. of periodic acid with 0.1 *N* sodium hydroxide using bromcresol purple as indicator (16). The samples and a blank of the same composition were shaken at 15°C. for two weeks. Aliquots were analyzed for periodate consumed after 2, 3, 4, 6, 9, and 13 days and for formic acid produced after 9 and 13 days only. On the assumption that one mole of formic acid was formed from a nonreducing xylose end-group, and that two moles were liberated from the reducing end, a molecular weight was calculated from the milliequivalents of formic acid formed at the level of maximum oxidation. The latter was reached after nine days when almost one mole of oxygen per mole of anhydroxylose was consumed. In Table VII the molecular weights determined by all three methods are summarized.

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TABLE VII

DEGREES OF POLYMERIZATION OF HEMICELLULOSE ACETATE FRACTIONS

Fraction	Vapor pressure lowering method	Signer method, mean of three values	Mean of physical methods	Periodate oxidation method	Intrinsic viscosity [η]	$Km \times 10^{-3}$	
						Mean of physical methods	Periodate oxidation
A	....	31.5	31.5	41.8	0.052	16.5	12.4
B	22.0	25.8	23.9	45.1	0.057	23.8	12.6
C	21.8	34.3	28.1	56.7	0.048	17.1	8.5
13	....	20.0	20.0	39.2	0.033	16.5	8.4
15	10.9	15.6	13.3	22.4	0.019	14.3	8.5
Subfraction 13	....	19.2	19.2	37.0	0.034	17.7	9.2

Discussion

Numerous investigators (19, 20) have postulated that lignin is chemically combined with carbohydrates in lignified cell walls. As to the linkage involved, the usual suggestions are acetal or ether-like combinations or an ester-like union between an acidic group in the lignin complex and an hydroxyl group of the carbohydrate. A perusal of Table II shows that good recoveries of pentosans and of the components of the original straw were obtained but that considerable losses of uronic acid and lignin were sustained in this fractionation. The loss of uronic acid cannot be explained on the basis of its association with the pentosans (17) which were completely recovered in this case. The uronic acid might, however, be associated or combined with that portion of the lignin or nonpentosan carbohydrate that remained in solution in the cupriethylenediamine left after removal of the "hemicellulose". No direct evidence is available to prove that the lignin in the various fractions is combined with carbohydrate since the two components might simply have been coprecipitated. With holocellulose (Table I) it is evident that the not inconsiderable loss of uronic acid could be related to the incomplete recovery of both pentosan and nonpentosan carbohydrate. Unfortunately, no way could be found to recover carbohydrates from the mixed cupric chloride and ethylenediamine hydrochloride aqueous alcohol solution left after the "hemicellulose" precipitation.

The composition of the carbohydrates of both the straw and its holocellulose show a definite trend from fractions high in glucose and low in pentose, i.e. a ratio of cellulose to hemicellulose greater than one, to fractions that have little or no glucose, i.e. cellulose. During this fractionation into cellulose and hemicellulose, the composition of the pentosans within the fractions was also changing. The low xylose to arabinose ratio in "lignin" changed to a "hemicellulose" with a 7 to 1 ratio and Fraction IV from holocellulose with an 8 to 1 ratio. These trends were discernible even though the analytical data varied considerably because of the use of 72% sulphuric acid as a hydrolytic agent.

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The recovery of sugars based on the original carbohydrate was low, particularly in the graded hydrolyses (*b*) of the holocellulose fractions although the amounts extracted from the paper chromatograms were at least 80% of those placed on the papers. Presumably 72% sulphuric acid either was not completely hydrolyzing the carbohydrate material or was decomposing some of the monosaccharides. The quantities of pentoses found by both methods were approximately the same as the content of pentosans. The higher xylose to arabinose ratio in holocellulose hemicellulose (8: 1) than in the wheat straw "hemicellulose" (7: 1) suggests that in the preparation of the holocellulose by the acid chlorite method about 8% of the arabinose had been removed. The cuprietylenediamine treatment is not expected to remove more arabinose from one product than the other.

From similarities in the characteristics of the fractions and subfractions (Tables V and VI), the hemicellulose acetates may be divided into three main groups.

The first group, consisting of Subfractions 1, 2, and 3, and amounting to 21.1% of the total, is characterized by the formation of turbid suspensions in chloroform that forestall any attempts to determine their optical rotation or viscosity. A fairly high ratio of xylose to arabinose indicates a medium degree of chain branching since recent work of Adams (1) in these laboratories has shown that the arabinose units are only present as branches off a main xylan chain.

The second group contains the main bulk of the fractions from 2 to 13 and also the reprecipitated Subfractions 4 to 14. Within this group (72% of the total) the composite fractions *A*, *B*, and *C* (24.7% of the total acetate) have very similar intrinsic viscosities and optical relations. Their chemical analyses show marked similarities with respect to constituent groups:

Fractions	Methoxyl, %	Uronic acid anhydride, %
A	4.2	5.8
B	4.2	4.2
C	3.1	4.8

and also a lower ratio of xylose to arabinose indicating more chain branching (Table VI).

The remaining fractions tail off to very small quantities with lower rotations, smaller intrinsic viscosities, and ratios of xylose to arabinose concordant with a high degree of chain branching particularly in Fraction 16 where two xylose units in seven would be expected to have an arabinose group attached. Since measurable quantities of glucose and galactose were detected only in Fraction 16, it is highly probable that as much as 98% of the hemicellulose can be isolated free of hexose. No chemical combination of hexose and pentosan is likely to have pre-existed in the holocellulose since in that event the more

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soluble hexose triacetates would be expected in all the fractions. The low yield of sugars from the hydrolyses of these fractions is probably due to incomplete hydrolysis of uronic acid di- and trisaccharides under the conditions of the experiment, rather than to the chromatographic procedure in which recovery was between 87 and 99% in Fractions *A* to *C*.

In Table VII the molecular weights, in the form of degrees of polymerization (D.P.), are recorded for 6 of the 10 hemicellulose acetate fractions. The D.P. of each of the acetates was calculated on the basis of a xylose acetate unit containing 39.6% acetyl, the average for the acetyl content of the whole hemicellulose acetate. Single values only were obtained by the vapor pressure lowering method (21) and by periodate oxidation. The chemical method gave consistently higher values than those obtained by physical methods. Both the results by physical methods and those by periodate oxidation may be related to the mean intrinsic viscosities to arrive at values for Km in the equation

$$\eta sp/C = KmP \qquad (15)$$

where $\eta sp/C$ is the specific viscosity divided by the concentration extrapolated to zero concentration, i.e. the intrinsic viscosity $[\eta]$, P is the degree of polymerization, and Km is the Staudinger constant. The Km figures recorded in the last two columns of Table VII are not constant in view of the differences in chemical composition of the fractions (*cf.* Table VI). Periodate oxidation results, however, do at least show a break in continuity between the Km values of the less branched fractions with 10 to 1 ratios of xylose to arabinose and the more branched fractions with 8 to 1 ratios.

Several investigators (3, 7, 15), when dealing with hemicellulose diacetates, have used Staudinger's Km values of 11×10^{-4} and 5.3×10^{-4} for cellulose triacetate in chloroform solution (26, 27). Husemann (13) in his work on wheat straw xylan established Km values ranging from 4.2 to 6.6×10^{-4} for various derivatives that did not include the diacetate. The variations in Km values obtained in the present investigation confirm the results of other workers and suggest that caution should be used in applying these constants to viscosity data for molecular weight determinations of hemicellulose derivatives.

From viscosity measurements Husemann (13) established that extensive chlorine dioxide treatment caused a 20% chain length degradation in wheat straw xylan as compared to xylan isolated without the use of chlorine dioxide. More than 80% of the latter had a D.P. greater than 145 determined viscometrically, figures far exceeding the percentage and D.P. of the longest chain material in the present investigation, viz. some 20% with a D.P. greater than 55 in the first group. In the second group the D.P. range was from 55 to 37 and the values for the remainder of the acetates fell below 37 down to about 14. A comparison with Husemann's values lead to the conclusion that either the use of acid chlorite, or of cupriethylenediamine, or both, caused more degradation than the use of chlorine dioxide. Such a conclusion is based, of course, on the assumption that the starting materials contained hemicelluloses with the same degrees of polymerization. A study of the degradation of wheat straw holocellulose by acid chlorite is warranted.

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INFLUENCE DE GAZ ETRANGERS SUR LA FLAMME FROIDE DE L'ETHER[1]

LUDOVIC OUELLET ET CYRIAS OUELLET

Sommaire

Utilisant la méthode photo-électrique déjà décrite (4), on a étudié l'influence de l'addition d'hydrogène, d'azote, de vapeur d'eau, d'anhydride carbonique, de formaldéhyde et d'acétaldéhyde sur la flamme froide de l'éther. Les premiers se comportent comme des diluants. La formaldéhyde agit comme un inhibiteur. Le remplacement d'une partie de l'éther par de l'acétaldéhyde ou l'addition des produits d'une réaction précédente prolonge la période d'induction sans altérer la quantité de lumière émise.

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Introduction

Les diverses façons dont les caractéristiques de la flamme froide de l'éther éthylique sont influencées par les variables: température, pression, composition du mélange combustible et diamètre du récipient ont été décrites dans des travaux récents (2, 3, 4). L'addition de gaz étrangers exerce aussi des effets considérables, susceptibles de nous renseigner sur certains aspects du mécanisme de ce phénomène. Quelques expériences effectuées en présence d'oxyde d'azote et de plomb tétraéthyle ont été décrites sommairement (2), mais l'étude détaillée des effets de ces substances reste à faire. Le présent travail contient l'exposé des résultats obtenus avec trois catégories de gaz: (1) les gaz neutres ou simples diluants, dont l'action permet dans certains cas de distinguer entre une réaction thermique et une réaction en chaînes, (2) les inhibiteurs, en particulier les aldéhydes qui sont en même temps des produits intermédiaires de la réaction et finalement, (3) les produits mêmes de la flamme froide, phénomène à la fois autocatalytique et auto-inhibé.

Toutes les expériences mentionnées ici ont été effectuées à 215°C. avec des mélanges d'éther éthylique et d'oxygène en proportions équimoléculaires. On s'est servi de la méthode déjà décrite (4), qui consiste à produire une lueur statique en introduisant brusquement le mélange gazeux dans un récipient en Pyrex maintenu à une température appropriée et à mesurer l'émission lumineuse au moyen d'une cellule photo-électrique et d'un oscillographe cathodique. Les récipients utilisés étaient des tubes de Pyrex de 130 mm. de longueur et de 46 mm. de diamètre. Les oscillogrammes représentés sur les figures portent une échelle de temps en secondes et une échelle d'intensités arbitraire mais uniforme. Autant que possible, les oscillogrammes sont caractérisés par les paramètres commodes suivants: l'émission lumineuse intégrale A, la hauteur h_2 de la dernière crête et sa position t_2 sur l'axe des temps, ainsi que la durée totale approximative t de la lueur.

[1] *Manuscrit reçu le 13 juillet, 1951.*
Contribution du Département de Chimie, Université Laval, Québec. Travail subventionné par le Conseil des Recherches pour la Défense.

Résultats

Addition de gaz neutres

Le Tableau I indique les conditions dans lesquelles ont éte effectuées quelques expériences comportant l'addition d'azote, d'hydrogène, d'anhydride carbonique et de vapeur d'eau.

TABLEAU I

INFLUENCE DE GAZ NEUTRES SUR LES FLAMMES FROIDES DE MÉLANGES ÉQUIMOLÉCULAIRES D'ÉTHER ET D'OXYGÈNE À 215°C. PRESSIONS PARTIELLES P_{Et}, P_{O_2} ET P_G DE L'ÉTHER, DE L'OXYGÈNE ET DU GAZ NEUTRE, ÉMISSION INTÉGRALE A, HAUTEUR h_2 DE LA DERNIÈRE CRÊTE ET DURÉE t DE LA LUEUR

Expérience No.	P_{Et}	P_{O_2}	P_G	A, mm.²	h_2, mm.	t, sec.
	mm. Hg					
N_2						
1032	38	38	9	800	18	0.92
683	38	38	0	980	21	1.02
1031	35	35	7	660	16	0.83
686	35	35	0	925	20	0.96
1179	16	16	16	150	0	0.35
1168	16	16	0	200	2	0.52
1177	21	21	21	410	6	0.87
690	21	21	0	268	8	0.79
1193	28	28	61	800	18	0.87
1044	29	29	0	570	18	0.77
1194	23	23	50	600	12	0.96
1164	24	24	0	420	13	0.71
H_2						
1109	29	29	4.5	645	18	0.77
1091	29	29	0	550	16	0.78
1110	24	24	3.5	530	15	0.82
CO_2						
965	28	28	28	360	10	0.69
688	28	28	0	600	13	0.82
970	24	24	24	280	10	0.75
972	19	19	19	150	0	0.38
961	27	27	27	300	8	0.65
1165	27	27	0	525	12	0.70
H_2O						
1024	28	28	6	450	13	0.78
1025	26	26	6	400	12	0.75
1026	19	19	4	240	10	0.72
1167	18	18	0	270	11	0.75
1028	40	40	9	690	19	0.80
684	40	40	0	1050	24	1.04
1029	44	44	10	840	21	0.92

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On voit les principaux effets de l'azote sur la Figure 1, où les courbes pointillées obtenues en présence de ce gaz sont juxtaposées aux courbes pleines données par des expériences témoins. En aucun cas la période l'induction ne semble affectée de façon appréciable. A pression totale relativement élevée, la présence de 10% d'azote exerce une faible inhibition qui affecte surtout la première crête. Aux pressions plus basses, la seconde crête est fortement inhibée (1177) ou même supprimée (1179) par 33% d'azote, mais la première crête est accentuée, de sorte que l'émission intégrale est peu affectée. Comme le montre la Figure 1, la faible inhibition de l'émission intégrale par 10% d'azote se change en une augmentation nette lorsque la proportion de ce gaz atteint 52%. On voit aussi apparaître un prolongement de la durée totale, effet d'autant plus marqué que l'on opère à une pression plus élevée.

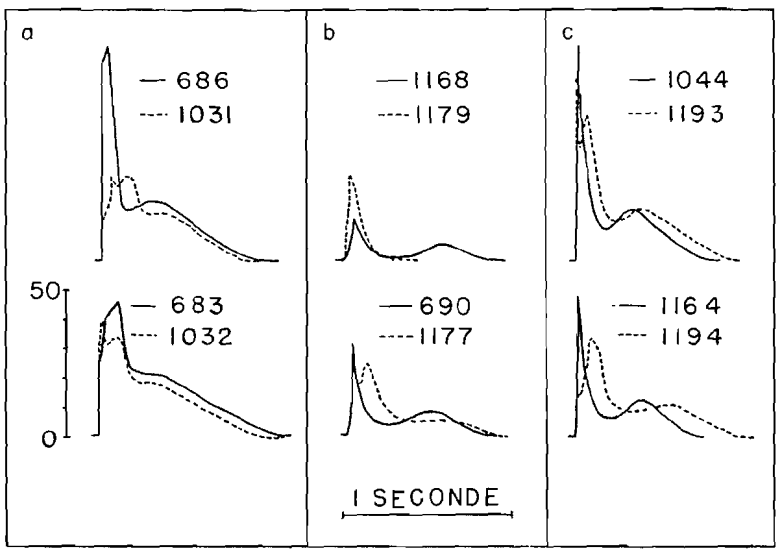

FIG. 1. *Influence de l'addition d'azote sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène. (a). 10% N_2 en volume. (b). 35% N_2. (c). 52% N_2. Les oscillogrammes en traits pointillés obtenus en présence d'azote sont comparés à des oscillogrammes obtenus en l'absence d'azote. Les données apparaissent au Tableau I.*

Quelques expériences en présence de 7% d'hydrogène indiquent que ce gaz se comporte comme un gaz neutre dont les effets (Fig. 2) sont très voisins de ceux de l'azote.

La vapeur d'eau et l'anhydride carbonique exercent aussi une inhibition semblable à celle de l'azote en faibles proportions. L'influence de 33% d'anhydride carbonique est environ le triple de celle de 10% d'eau (Fig. 3); ces deux gaz ont donc des pouvoirs inhibiteurs sensiblement égaux, qui sont d'ailleurs nettement supérieurs à ceux de l'azote et de l'hydrogène.

Addition d'aldéhydes

On sait que la luminescence des flammes froides est attribuée, à cause de son spectre (7), à la fluorescence de la formaldéhyde excitée produite au cours de

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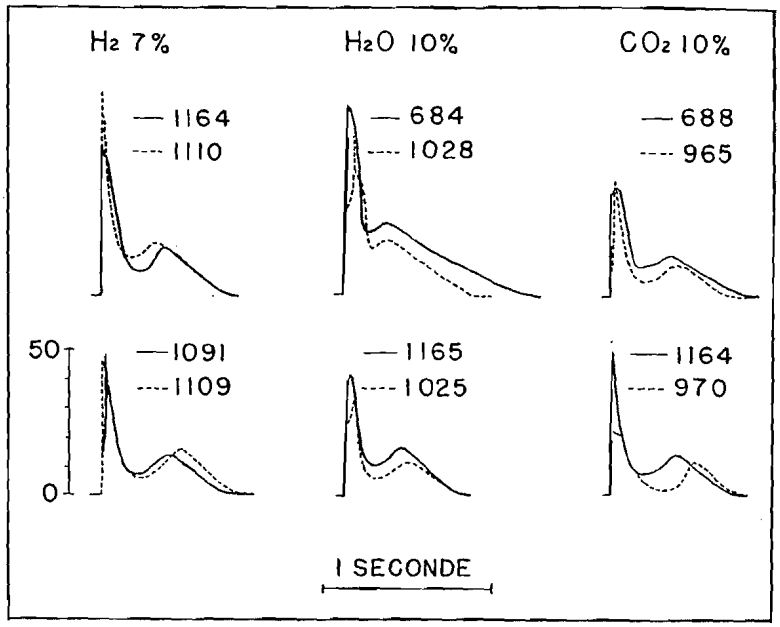

FIG. 2. *Influence de l'addition d'hydrogène, d'eau et d'anhydride carbonique sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène à 215°C. Les oscillogrammes représentés en traits pointillés ont été obtenus en présence de ces gaz étrangers.*

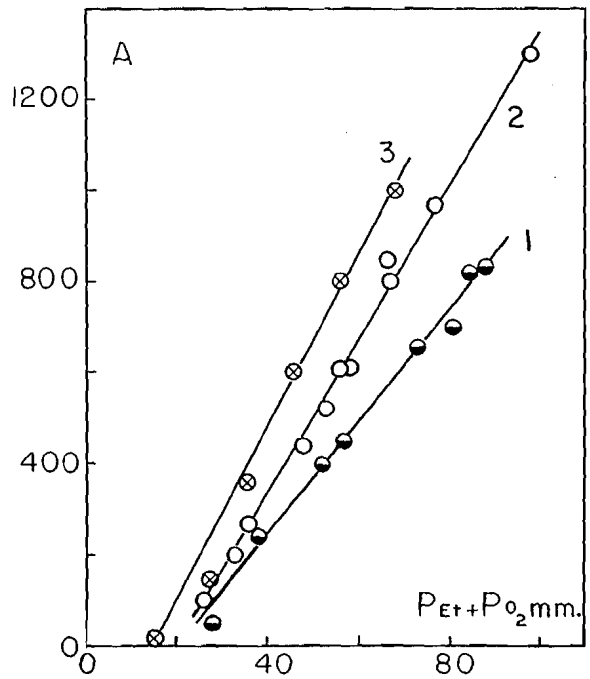

FIG. 3. *Emission intégrale A d'une flamme froide d'un mélange équimoléculaire d'éther et d'oxygène en fonction de la pression d'éther et d'oxygène ($P_{Et} + P_{O_2}$). (1). En présence de 10% de vapeur d'eau, (2). En l'absence de gaz étrangers, (3). En présence de 52% d'azote.*

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la réaction. Cependant, l'oxydation de la formaldéhyde elle-même n'est accompagnée d'aucune émission lumineuse; au contraire, cette substance exerce une action inhibitrice (8) sur les flammes froides. La méthode photo-électrique a permis d'analyser quelques particularités de cette inhibition.

L'addition de formaldéhyde gazeuse, fraîchement préparée par chauffage de la paraformaldéhyde, produit trois effets principaux: prolongement de la période d'induction, inhibition de l'émission et déformation de l'oscillogramme. Le Tableau II contient des renseignements sur les flammes étudiées en présence de ce gaz; on y trouve quelques valeurs approximatives de la période d'induction, que notre dispositif actuel ne permet pas de mesurer avec précision. La Figure 4 montre quelques exemples de flammes inhibées et déformées. Toutes les pulsations sont amorties et retardées; en particulier, la crête initiale n'est plus aiguë et son sommet n'est plus atteint aussi soudainement. Aux pressions suffisamment basses, la dernière crête finit par disparaître (1347), comme dans les cas d'inhibition par les parois (4) ou par les gaz neutres.

TABLEAU II

INFLUENCE D'ALDÉHYDES SUR LES FLAMMES FROIDES DE MÉLANGES ÉQUIMOLÉCULAIRES D'ÉTHER ET D'OXYGÈNE À 215°C. τ EST LA PÉRIODE D'INDUCTION APPROXIMATIVE. LES AUTRES SYMBOLES ONT LA MÊME SIGNIFICATION QU'AU TABLEAU I

Expérience No.	P_{Et}	P_{O_2}	P_G	A, mm.^{2}	t, sec.	τ, sec.
	mm. Hg					
HCHO						
995	37	37	4	570	0.79	1
685	38	38	0	970	1.02	0
994	43	43	5	950	1.00	1
1300	43	43	0	1090	1.03	0
1345	37	37	9	720	1.18	10
1347	27	27	6	320	1.02	10
1348	22	22	5	Aucune réaction		
CH_3CHO						
940	40	40	40	1175	0.94	1
1308	84	42	0	1340	0.90	0
941	36	36	36	910	0.73	1
1309	75	37	0	1110	0.89	0
943	27	27	27	660	0.61	1
1311	54	27	0	640	0.73	0
951	7	7	7	25	0.17	1

L'acétaldéhyde, comme l'éther, donne elle-même naissance à des flammes froides. Elle est d'ailleurs un produit intermédiaire de la flamme froide de l'éther, dans laquelle elle contribue vraisemblablement, comme précurseur, à l'émission lumineuse.

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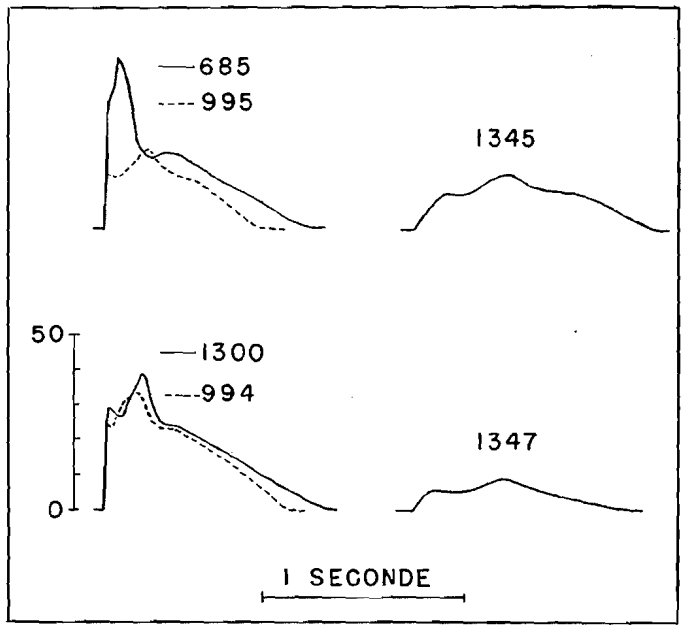

FIG. 4. *Influence de la formaldéhyde sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène à 215°C. Les données apparaissent au Tableau II.*

Comme nous l'avons vu (2), la flamme froide de l'acétaldéhyde a la même allure que celle de l'éther, mais est caractérisée par une durée un peu plus courte et est affectée d'une période d'induction plus longue. L'addition d'acétaldéhyde, distillée deux fois dans le vide, à un mélange d'éther et d'oxygène, impose à la flamme froide une période d'induction de l'ordre d'une seconde, mais ne modifie pas beaucoup la flamme qui apparaît ensuite, comme on peut le constater par l'examen des oscillogrammes de la Figure 5. Il semble que, contrairement à la formaldéhyde, l'acétaldéhyde contribue à l'émission lumineuse, après avoir inhibé une étape antérieure de la réaction. Il est même possible que la flamme de l'éther soit en réalité celle de l'acétaldéhyde, l'éther n'agissant que comme source de ce composé. En effet, si on remplace une partie de l'éther par de l'acétaldéhyde, on obtient des oscillogrammes dont ni la forme (Fig. 5) ni l'émission intégrale (Fig. 6) ne sont sensiblement altérées.

Addition des produits de la réaction

Si, au lieu d'évacuer complètement le récipient à la suite d'une réaction, on y laisse une partie des gaz à une pression partielle de quelques millimètres, l'introduction d'un mélange frais donne lieu à une nouvelle flamme qui est retardée et déformée mais dont l'émission intégrale est à peu près normale. La Figure 7 montre des oscillogrammes normaux et, à leur droite, ceux qui ont été enregistrés dans les mêmes conditions en présence des produits d'une réaction précédente. Les valeurs des périodes l'induction ne sont qu'approximatives.

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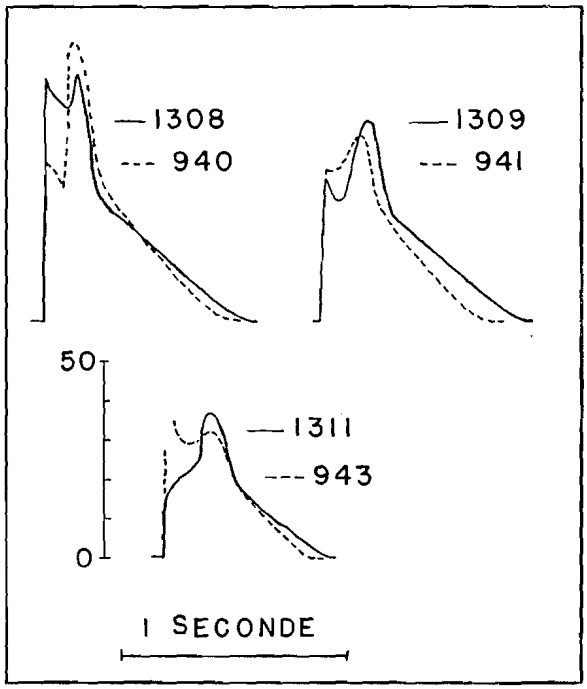

FIG. 5. *Influence de l'acétaldéhyde sur la flamme froide d'un mélange équimoléculaire d'éther et d'oxygène à 215°C. Pour les oscillogrammes en traits pointillés, la moitié de l'éther a été remplacée par de l'acétaldéhyde. Les données apparaissent dans le Tableau II.*

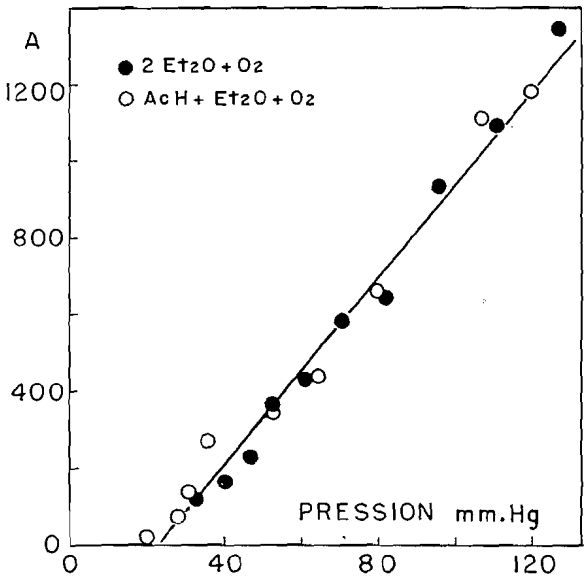

FIG. 6. *Emissions intégrales A de flammes froides à 215°C., à partir de mélanges contenant 33% d'oxygène, avec soit 66% d'éther, soit 33% d'éther et 33% d'acétaldéhyde.*

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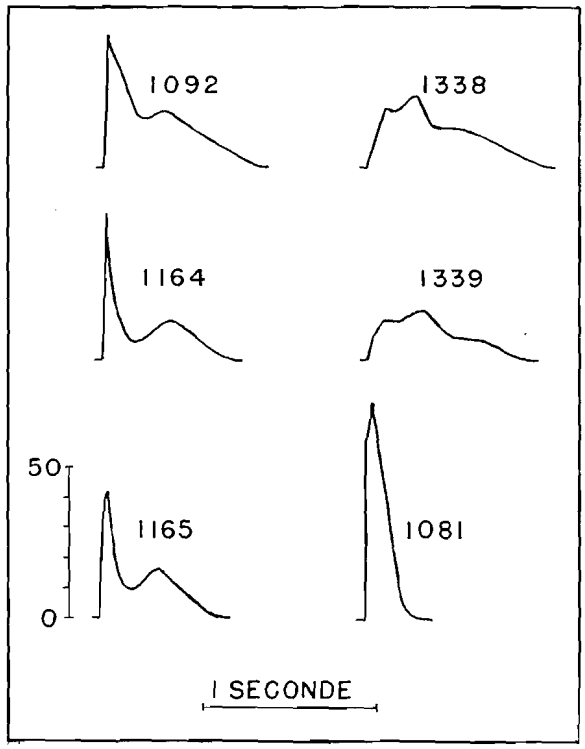

FIG. 7. *Influence des produits de la réaction.*
1338-1339. Les oscillogrammes obtenus en présence des produits de la réaction sont comparés à ceux que l'on obtient sans produits.
1081. Le mélange a été chauffé 20 min. à 166°C. avant d'être introduit dans la chambre à réaction à 215°C.

Un mélange qui avait été maintenu durant 20 min. à 166°C., température à laquelle il n'y a pas de flamme froide, et introduit ensuite dans le récipient à 215°C., a donné la flamme (1081) de la Figure 7, au lieu de la flamme (1165) qui aurait eu lieu dans les conditions normales. On trouvera, au Tableau III, quelques données concernant ces flammes.

TABLEAU III

INFLUENCE DES PRODUITS D'UNE RÉACTION PRÉCÉDENTE À LA PRESSION RÉSIDUELLE *Pr*, SUR LES FLAMMES FROIDES DE MÉLANGES ÉQUIMOLÉCULAIRES D'ÉTHER ET D'OXYGÈNE À 215°C. MÊMES SYMBOLES QU'AUX TABLEAUX I ET II

Expérience No.	P_{Et}	P_{O_2}	Produits	A, mm.²	τ, sec.	Pr, %
	mm. Hg					
1338	32	32	10	620	2	13
1092	32	33	0	800	0.1	0
1339	25	25	7	500	2	12
1164	24	24	0	420	0.1	0
1342	30	30	23	–	20	27
1340	15	15	10	–	300	25
1341	25	25	26	–	300	25
1081	26	26	0	520	0.1	?
1165	26.5	26.5	0	525	0.1	0

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Discussion

La complexité des effets constatés montre qu'il serait prématuré d'étendre les conclusions à des conditions trop éloignées de celles auxquelles on s'en est tenu dans cette étude préliminaire: mélanges equimoléculaires à 215°C. En particulier, les effets opposés de l'azote à 10% et à 50% peuvent être rapprochés des observations de Chamberlain et Walsh (1) sur le renversement de l'influence de ce gaz quand on dépasse certaines valeurs de la pression et de la température.

En ce qui concerne les gaz neutres, il semble que l'on puisse leur attribuer trois actions principales, susceptibles de produire dans certaines conditions des effets opposés.

(*a*) Inhibition du rendement lumineux. Il est possible que cette action s'exerce sur un processus thermique, puisque les pouvoirs inhibiteurs de ces gaz sont, à la précision des mesures près, parallèles à leurs chaleurs moléculaires: H_2, N_2, CO_2, H_2O, (4.4, 4.9, 5.9, 6.6 cal. mole^{-1} degré$^{-1}$). Spence et Townend (5) ont observé un effet du même ordre sur le déplacement de la limite d'inflammation.

(*b*) Exaltation du rendement lumineux aux forts pourcentages (52% N_2), vraisemblablement par protection d'un processus en chaînes qui serait inhibé par la paroi ou par un produit de la réaction. Le coefficient de température de l'émission intégrale étant légèrement négatif (3), une diminution de l'autoéchauffement par addition d'un diluant produirait un effet du même signe, mais probablement trop faible. De plus, cet effet serait plus considérable pour CO_2 que pour N_2, ce qui est contraire à nos observations.

(*c*) Prolongement de la durée (52% N_2 et 33% CO_2). Cet effet est semblable à celui que l'on obtient en augmentant le diamètre du récipient (4), ce qui équivaut à diminuer l'influence relative des parois. Comme la durée est aussi prolongée par un abaissement de la température (3), on pourrait attribuer ce ralentissement à une diminution de l'autoéchauffement temporaire du mélange, dont la capacité calorifique est accrue par l'addition d'un diluant. Mais s'il en était ainsi, l'agrandissement du récipient, avec réduction concommittante du rapport surface/volume, tendrait à favoriser l'auto-échauffement et à abréger la durée, ce qui est contraire à nos résultats. Il est plus probable qu'une réaction en chaînes catalysée par la paroi, et correspondant peut-être à une étape obscure qui sépare les deux crêtes (6), est ralentie par l'addition d'un gaz neutre.

La formaldéhyde diminue le rendement lumineux et ralentit toutes les étapes de la réaction, y compris la période d'induction. En particulier la première crête, généralement aiguë, est arrondie et amortie. Comme cette substance est produite au cours d'une flamme froide normale, elle doit aussi y exercer les mêmes effets inhibiteurs. Si on lui attribue l'amortissement des crêtes qui suivent la première, on peut conclure qu'elle est absente durant la période d'induction, qu'elle aurait pour effet de prolonger, et aussi durant la majeure

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partie de la crête initiale, qui est atteinte très rapidement et reste aiguë dans les flammes normales. Il est remarquable qu'aux très faibles pourcentages d'éther, la flamme froide présente une série de crêtes très aiguës (3), probablement parce que la formaldéhyde n'atteint pas une concentration suffisante. Puisque ces conditions sont justement celles dans lesquelles apparaissent les pulsations les plus nettes, il est difficile d'attribuer ces pulsations à l'influence inhibitrice de la formaldéhyde.

L'acétaldéhyde, bien qu'elle impose à la flamme de l'éther une période d'induction appréciable, contribue à l'émission lumineuse dans une mesure telle que sa substitution partielle à l'éther, molécule pour molécule, passe pour ainsi dire inaperçue. Cette égalité des rendements lumineux porte à croire qu'une molécule d'éther, malgré ses quatre atomes de carbone, ne donne naissance qu'à une molécule d'acétaldéhyde.

En présence des produits de la réaction, on doit s'attendre à retrouver les effets des aldéhydes. On observe la période d'induction prévue, mais il est remarquable que les pulsations soient amorties comme en présence de formaldéhyde tandis que l'émission intégrale reste intacte comme en présence d'acétaldéhyde. Il se peut que la formaldéhyde présente ralentisse la formation de l'acétaldéhyde sans altérer la quantité de ce produit, dont découle l'espèce responsable de l'émission lumineuse.

La flamme intense et brève obtenue à 215°C. après chauffage prolongé à 166°C. doit probablement son caractère à ce que l'étape de la formation des peroxydes est complètement franchie avant le début de la flamme, tandis qu'elle se poursuit ou se répète au cours d'une flamme ordinaire.

Remerciements

Ce travail a été subventionné par le Defence Research Board, auquel nous adressons nos plus vifs remerciements.

Summary

The influence of hydrogen, nitrogen, water vapor, carbon dioxide, formaldehyde, and acetaldehyde on the cool flame of ether has been studied, using the previously described photoelectric method (4). The first gases act like diluents. Formaldehyde is an inhibitor. Replacing a certain amount of ether by acetaldehyde or adding the products of a previous reaction makes the induction period longer but does not change the total amount of light emitted.

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THE RHEOLOGICAL PROPERTIES OF SOME SOAP–OIL SYSTEMS[1]

By G. B. Moses and I. E. Puddington

Abstract

The flow properties of dispersions of sodium, lithium, and aluminum soaps in hydrocarbon oils have been measured over a range of temperature, concentration, and rate of shear using an extrusion plastometer. The variations of residual viscosity and coefficient of thixotropy, with temperature, are similar for all of these soaps. Abrupt changes occur at temperatures that are characteristic of the individual soaps. The variation of thixotropy with concentration is in accord with theoretical predictions, and axial ratios of the solid phase particles, calculated from viscosity data, are in agreement with observed values.

Introduction

Dispersions of soaps, frequently of fairly high chemical purity, in suitable liquid hydrocarbons are commonly used as lubricating greases. One of the most interesting properties of these two phase systems is their behavior under shearing stress. A previous paper (4) discussed calcium soaps in this connection and the present communication is concerned with the properties of dispersions of other soaps.

Experimental

The experimental procedure was similar to that used previously (4). Dispersions were extruded through a metal capillary 2.611 cm. long, with a radius of 0.0368 cm., using compressed nitrogen as a source of variable pressure. A period of one hour was allowed at each temperature for thermal equilibrium to be established before measurements were made. Apparent viscosities were calculated from the Poiseuille equation, and the mean rate of shear was taken as $\frac{4V}{\pi r^3 t}$ where the symbols have their usual meaning. This value of the rate of shear is open to question and $2V$ or $3V$ might be preferable to the $4V$ actually used in the expression. However, with thixotropic systems the conditions of shear in the capillary are not readily ascertained and as the coefficients of thixotropy are used comparatively the value chosen for the rate of shear is not critical.

Graphs relating apparent viscosity and reciprocal of the rate of shear were prepared for each soap concentration at each temperature. These showed linear relations in the high shear range, and from the linear portion of the curve and its extrapolation, the coefficient of thixotropy (θ) and the residual viscosity (η_0) of the system were found.

Different concentrations of soap were prepared by diluting a concentrated sample with the oil used in its preparation, with as gentle agitation as pos-

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sible, to give samples in which the soap particles remained substantially in their original condition. The soap concentrations were determined by exhaustive extraction with petroleum ether and by ashing. Densities of concentrated samples were determined dilatometrically and the values for the diluted samples were calculated from the degree of dilution.

The mean rates of shear used in the measurements varied from 1400 to 250,000 sec.$^{-1}$ and the temperatures varied from 35°C. up to temperatures where the dispersions showed sufficient separation to give results of poor reproducibility or where solution of the soap in the oil was sufficient to reduce the coefficient of thixotropy to a very low value.

Samples of commercial lubricating grease and the oils used during the work were supplied gratuitously by Imperial Oil Limited, to whom grateful acknowledgment is made.

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Sodium Soaps

Dispersions of these soaps are quite stable to heat but have limited usefulness in the presence of moisture. A small amount of water of hydration has been considered essential for their formation (3) although good dispersions can be obtained under anhydrous conditions. It is possible to obtain the individual soap particles in a variety of axial ratios by suitable adjustments in the degree of unsaturation of the fatty acid used in the soap preparation, the type of hydrocarbon oil, and the procedure used in preparing the dispersions (1). When heated, the whole character of these systems changes at a temperature which is characteristic of the soap. When this happens the rheological properties also undergo very substantial changes.

In the present work two types of preparations were used. One was a commercial grease containing 19.7% of soap dispersed in an oil of 335 S.U.S. at 100°F. and a viscosity index of 48. Several samples were prepared from this dispersion by dilution. In the second group of samples U.S.P. grade sodium soaps and the same oil as contained in the commercial sample were used. Five samples were prepared, all containing 15% of soap. Various degrees of unsaturation were obtained by mixing sodium stearate and oleate. The percentages of stearate contained in the various soaps were 100, 75, 50, 25, and 0. The dispersions were made by suspending the dry soap in the oil, heating the mixture to about 120°C., and passing it through the colloid mill. Previous experience showed that this procedure produces dispersions of good uniformity (1).

The length of the soap particles in several of the samples was altered by subjecting the sample to various rates of shear at about room temperature. Samples of the diluted commercial grease were passed through a colloid mill (mean rate of shear about 700,000 sec.$^{-1}$) and allowed to stand for 24 hr. before taking measurements. Part of the sample containing 15% of pure sodium stearate was passed three times through a capillary at a mean rate of shear of 2000 sec.$^{-1}$ and a second portion was passed through the colloid mill. This procedure should produce three fiber lengths in identical concentration.

The results of the viscometric measurements made on these various samples are summarized in Tables I and II where values of the residual viscosities in poises and coefficients of thixotropy in dynes per cm.^{2} at the different temperatures are recorded. The symbols "*l*", "*m*", and "*s*", are used here to indicate samples that are in their original state, samples lightly sheared, and samples highly sheared by passage through the colloid mill, respectively.

TABLE I

RESIDUAL VISCOSITIES AND COEFFICIENTS OF THIXOTROPY FOR DISPERSIONS OF SODIUM SOAPS (COMMERCIAL)

Conc. Vol. %		Temperature, °C.												
		35°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°
19.7 (*l*)	θ	19820	11700	7480	5220	3790	3320	3830	7920	8150	8270	7880	7250	5900
	η_0	7.40	4.20	2.75	1.75	1.20	0.75	0.45	0.25	0.97	1.69	1.22	0.45	0.15
19.7 (*s*)	θ	7300	5350	4350	3600	3000	2900	3300	4900	6500	6950	6850	6300	5600
	η_0	2.90	1.35	0.87	0.57	0.43	0.32	0.25	0.20	0.20	0.41	0.50	0.45	0.30
14 (*l*)	θ	9370	5320	2850	1700	1250	970	1220	2330	3800	3800	3790	2900	1330
	η_0	2.25	1.19	0.84	0.59	0.43	0.31	0.24	0.19	0.21	0.27	0.25	0.21	0.17
14 (*s*)	θ	2830	1820	1580	1390	1340	1320	1590	1730	1760	1800	1720	1600	1350
	η_0	1.91	0.97	0.62	0.45	0.29	0.26	0.41	0.54	0.60	0.83	0.90	0.79	0.43
10 (*l*)	θ	6850	3600	1800	800	400	250	500	1100	2400	3200	3150	3270	900
	η_0	1.56	0.78	0.53	0.37	0.28	0.21	0.16	0.14	0.14	0.15	0.13	0.11	0.09
10 (*s*)	θ	1460	970	810	480	450	430	800	980	1010	1110	1100	1050	1000
	η_0	1.40	0.62	0.42	0.34	0.21	0.17	0.18	0.16	0.22	0.36	0.33	0.23	0.11

NOTE: η_0 = *poises*.
θ = *dynes/cm.*^{2}

TABLE II

RESIDUAL VISCOSITIES AND COEFFICIENTS OF THIXOTROPY FOR DISPERSIONS OF SODIUM SOAPS (PURE)*

Ratio of stearate to oleate		Temperature, °C.												
		35°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°	160°
100–0 (*l*)	θ	45200	28700	21500	15900	10300	6900	4800	3700	3300	4500	7600	5500	2300
	η_0	3.30	1.60	1.04	0.70	0.62	0.55	0.38	0.27	0.30	0.30	0.30	0.32	0.36
100–0 (*m*)	θ	19800	12800	8800	5800	3400	1900	1800	1700	1000	2600	6000	4100	1200
	η_0	3.00	1.41	0.93	0.66	0.46	0.34	0.25	0.21	0.21	0.21	0.22	0.22	0.26
100–0 (*s*)	θ	11780	7750	5350	3350	2000	1170	1120	960	1050	2130	5350	3310	730
	η_0	1.91	1.03	0.73	0.55	0.39	0.28	0.19	0.15	0.13	0.14	0.17	0.19	0.24
75–25 (*l*)	θ	45300	34100	29400	23700	20300	21200	24000	45300	22800	16200	12400	9400	5600
	η_0	5.0	3.45	2.8	2.3	1.7	1.3	0.9	5.2	0.6	0.7	0.6	0.5	0.3
50–50 (*l*)	θ	59200	48000	43800	40000	37500	48500	39400	29200	22200	15900			
	η_0	3.25	2.28	1.71	1.18	0.84	0.65	0.54	0.44	0.35	0.40			
25–75 (*l*)	θ	71200	41100	31300	38100	43700	48700	38400	31100	24600	19700	15300	8750	
	η_0	3.00	2.40	2.00	1.54	1.20	0.85	0.85	0.81	0.75	0.65	0.50	0.30	
0–100 (*l*)	θ	64100	43600	34200	31300	30100	30300	33400	25500	18500	13400			
	η_0	3.65	2.80	2.30	1.93	1.60	1.35	0.95	0.72	0.50	0.45			

* *Concentration of soap 15% by volume in each case.*

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The general behavior of the sodium soap dispersions is similar to that of calcium soap. When examined over a range of temperatures both coefficient of thixotropy and residual viscosity have rather high values at low temperatures and these fall rapidly to a minimum as the temperature is increased. This is followed by a sharp maximum in these quantities with further temperature increases. At higher temperatures the values again fall off as the soap goes into solution. This behavior is shown in Fig. 1, which shows a plot of θ vs. temperature for the commercial grease. The minimum and maximum shown here at 100° and 130°C., respectively, correspond to similar phenomena with

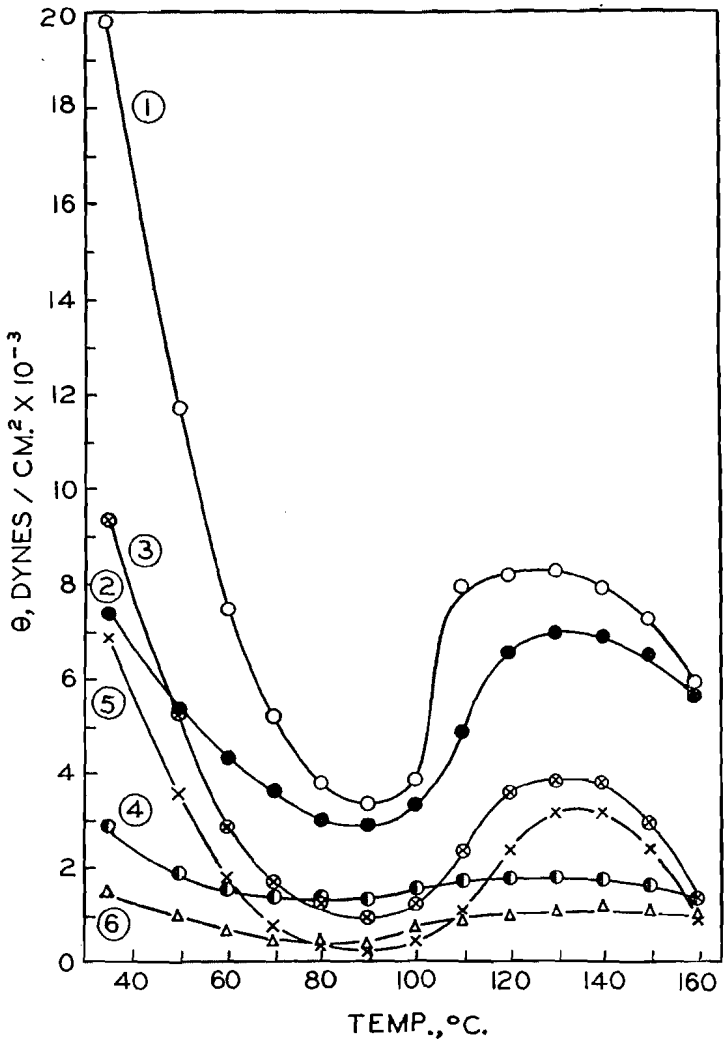

FIG. 1. *Change in the coefficient of thixotropy with temperature at different concentrations and fiber lengths for dispersions of commercial sodium soaps. The graphs represent:*
(1) 19.7% soap, (l); (2) 19.7% soap, (s); (3) 14% soap, (l); (4) 14% soap, (s); (5) 10% soap, (l); (6) 10% soap, (s).

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calcium soap greases at 50° and 65°C. That the degree of unsaturation of the soap has considerable influence on the temperature at which the minimum and maximum occur is shown in Fig. 2 where the soap contains various ratios of oleate to stearate. Here the temperature of minimum thixotropy itself goes through a minimum as one passes from pure sodium oleate to pure sodium stearate. This minimum occurs at a temperature of 60°C. and a molecular ratio of 3 to 1 of oleate to stearate.

It is also noteworthy that mixtures of these two molecules produce higher maxima than either of the pure soaps alone. Finally, a 60°C. spread is found

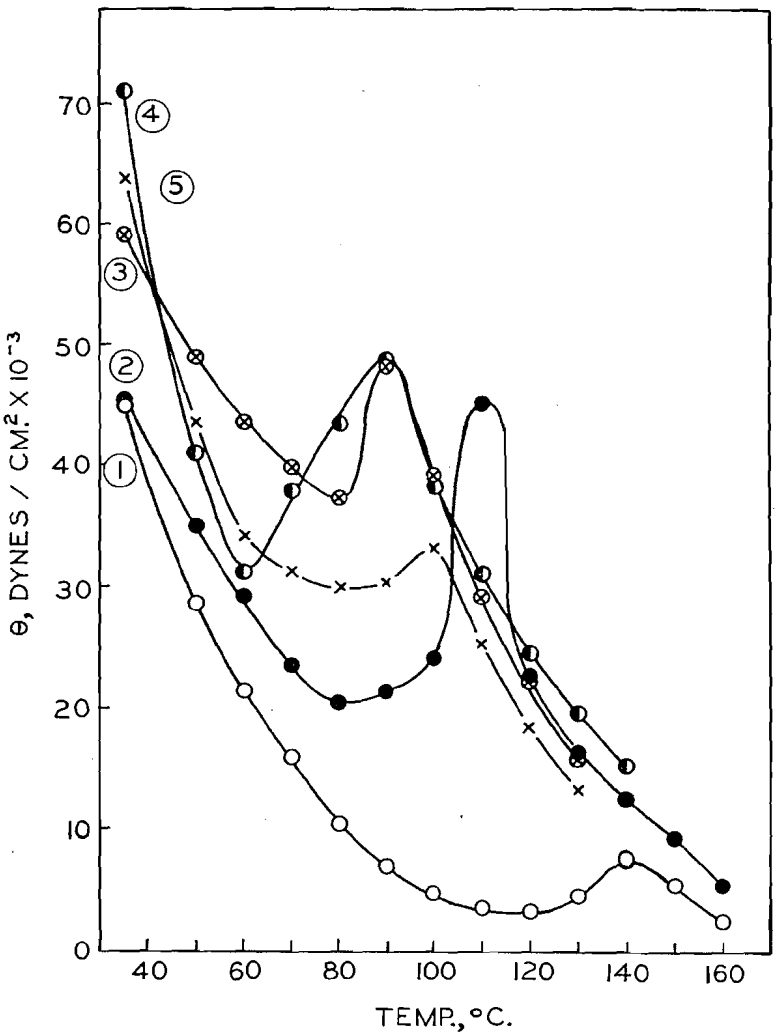

FIG. 2. *Change in the coefficient of thixotropy with temperature for dispersions of mixtures of pure sodium stearate–sodium oleate soaps. The graphs represent: (1) 100% sodium stearate; (2) 75: 25% sodium stearate–sodium oleate; (3) 50: 50% sodium stearate–sodium oleate; (4) 25: 75% sodium stearate–sodium oleate; (5) 100% sodium oleate.*

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in the position of the minimum coefficient of thixotropy as one passes through the composition range. This is of considerable practical importance since, normally, it is not advisable to use grease at temperatures in excess of this minimum. This means that the useful temperature range of the grease may be considerably extended by suitable selection of the soap stocks.

While the temperature at which the minimum and maximum in the coefficient of thixotropy depends only on the soap molecule, the difference between the maximum and minimum values of the coefficient are influenced considerably by the shape of the soap particles. This is shown in Fig. 1 where three concentrations of soap are shown. One group was passed through a colloid mill and the other is in its original form. From microscopic examination, shearing in the cold appears to shorten the fibers only. Since the coefficient of thixotropy depends on the mutual interference of the particles, it is obvious that the effective volume occupied by the longer fibers is more important than the increased number of individual particles produced by the shearing process.

The much smaller temperature coefficient of thixotropy shown in the case of the shorter particles is also of interest. This may be due to the increased flexibility of the longer fibers at the higher temperatures which would make easier separation of mechanical entanglements possible, while the force required to separate a physical contact would remain virtually constant as the temperature is increased. Identical behavior was observed when pure sodium stearate dispersions were treated in the same way.

The curve for residual viscosity vs. temperature is similar in shape to the thixotropy–temperature relation. The initial drop is to be expected since over this temperature range the soap remains comparatively inert and the behavior is similar to that of the oil alone. As the soap absorbs oil at the higher temperatures the liquid phase becomes depleted and the effective soap concentration increases, causing a viscosity increase. A minimum thus appears in the viscosity curve. Eventually, on further increases in temperature, the soap goes into solution in the oil and when this process proceeds to a greater extent than solution of the oil in the soap, a maximum appears in the viscosity curve. With further temperature increases the viscosity of the system falls rapidly.

Lithium Soaps

Dispersions of lithium soaps in oils have recently become of interest on account of their stability at high temperatures and in the presence of moisture. They are usually prepared from a fairly pure grade of lithium stearate by heating the suspension formed in the cold to a temperature in excess of complete solubility (about 200°C.). The soap crystals formed on cooling are considerably smaller than those of sodium stearate. The rheological properties of the dispersions are qualitatively similar to those of sodium and calcium soaps. The only significant difference is the higher temperatures at which the viscosity minimum and maximum occur.

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Experimental data are presented in Table III and in Figs. 3 and 4. These were obtained from a commercial preparation suitably diluted to give the various concentrations. The letters "l" and "s" used in Table III indicate original samples and those passed through the colloid mill, respectively. It is of interest that shearing produced considerably less reduction in thixotropy in the case of lithium stearate dispersions than with sodium stearate of similar concentration. This is apparently due to the greater resistance of the smaller crystals to mechanical breakup by the shearing stress.

TABLE III

RESIDUAL VISCOSITIES AND COEFFICIENTS OF THIXOTROPY FOR DISPERSIONS OF LITHIUM SOAPS

Conc. Vol. %		Temperature, °C.														
		35°	50°	65°	80°	90°	100°	110°	120°	130°	140°	150°	160°	170°	180°	190°
26.9	(*l*) θ	28770	18860	14010	11100	10110	6930	5980	5450	5480	4810	3270	3170	4320	3440	
	η_0	6.9	3.1	1.5	0.9	0.6	0.7	0.7	0.7	0.7	0.7	0.9	0.5	0.6	0.6	
26.9	(*s*) θ	17590	15010	10000	8020	6920	5780	5010	4670	4550	3800	2920	2690	3410	2940	
	η_0	5.15	2.60	1.35	0.84	0.71	0.63	0.62	0.63	0.67	0.74	0.86	1.12	1.34	1.46	
18	(*l*) θ	12300	8950	7010	5680	5250	4200	3990	3700	3800	3530	2950	3820	8650	5200	1700
	η_0	1.15	0.65	0.47	0.38	0.19	0.16	0.15	0.13	0.14	0.13	0.10	0.27	0.65	0.95	0.64
18	(*s*) θ	6470	6010	5400	4710	3970	3260	3040	2860	2920	2580	2360	2440	3750	3910	2870
	η_0	1.36	0.70	0.44	0.28	0.20	0.16	0.15	0.16	0.18	0.24	0.31	0.50	0.90	1.36	0.90
9	(*l*) θ	3470	3123	2847	2793	2320	2050	1975	1890	1712	1660	1294	1090	1800	1780	3460
	η_0	0.80	0.50	0.30	0.20	0.15	0.12	0.09	0.08	0.06	0.06	0.15	0.49	0.52	0.67	0.20
9	(*s*) θ	2940	2400	2000	1560	1420	1310	1280	1230	1260	1210	950	690	930	1020	970
	η_0	0.56	0.26	0.18	0.13	0.10	0.09	0.07	0.06	0.07	0.08	0.10	0.13	0.30	0.41	0.15

Aluminum Soaps

For comparative purposes, results from a single concentration (6%) of pure aluminum distearate in an oil of 893 S.U.S. 100°F. viscosity are shown in Figs. 5 and 6. This dispersion was prepared in the same way as those of lithium stearate. In the case of aluminum soaps the crystals are too small to be resolved microscopically.

The general shape of the residual viscosity and thixotropy curves is similar to those of other soaps. Obviously the usefulness of these dispersions as lubricants is restricted to low temperatures.

Discussion

The explanation advanced for the shape of the residual viscosity vs. temperature curve for sodium stearate is equally applicable to the other soaps. The similar behavior of the coefficient of thixotropy at the lower temperatures is not so readily explained, however. In the particular case of dispersions of calcium soaps where an excess of a third phase (water) is present, the agglomeration of the solid phase which is responsible for the degree of thixotropy, may

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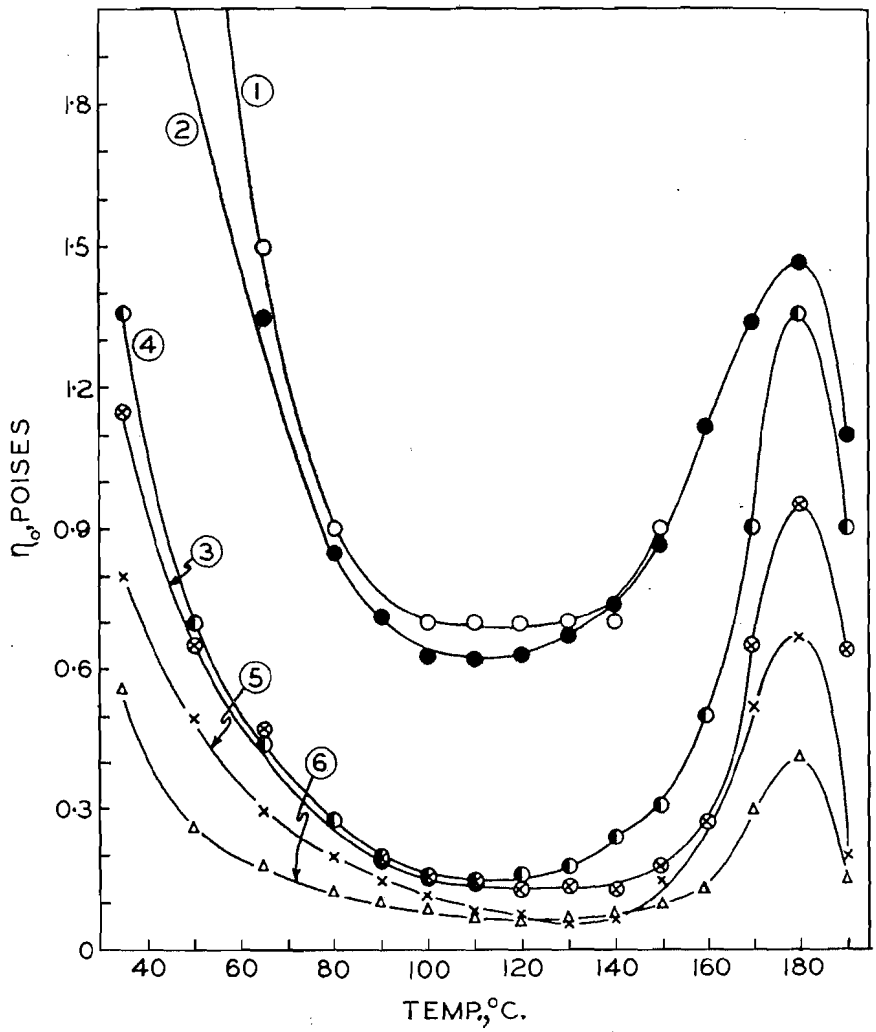

FIG. 3. *Change in residual viscosity with temperature at different concentrations and fiber lengths for dispersions of lithium soaps. The graphs represent: (1) 26.9% soap (l); (2) 26.9% soap, (s); (3) 18% soap, (l); (4) 18% soap, (s); (5) 9% soap, (l); (6) 9% soap, (s).*

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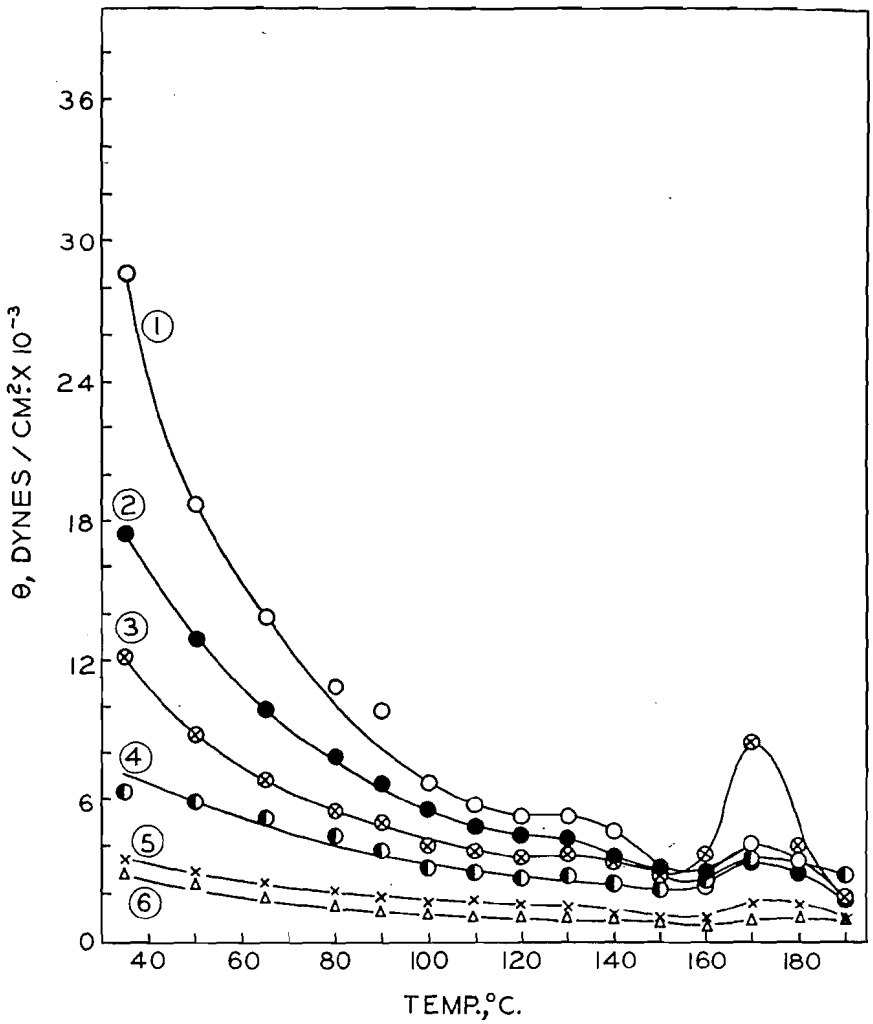

FIG. 4. *Change in the coefficient of thixotropy with temperature at different concentrations and fiber lengths for dispersions of lithium soaps. The graphs represent: (1) 26.9% soap (l); (2) 26.9% soap (s); (3) 18% soap (l); (4) 18% soap (s); (5) 9% soap (l); (6) 9% soap (s).*

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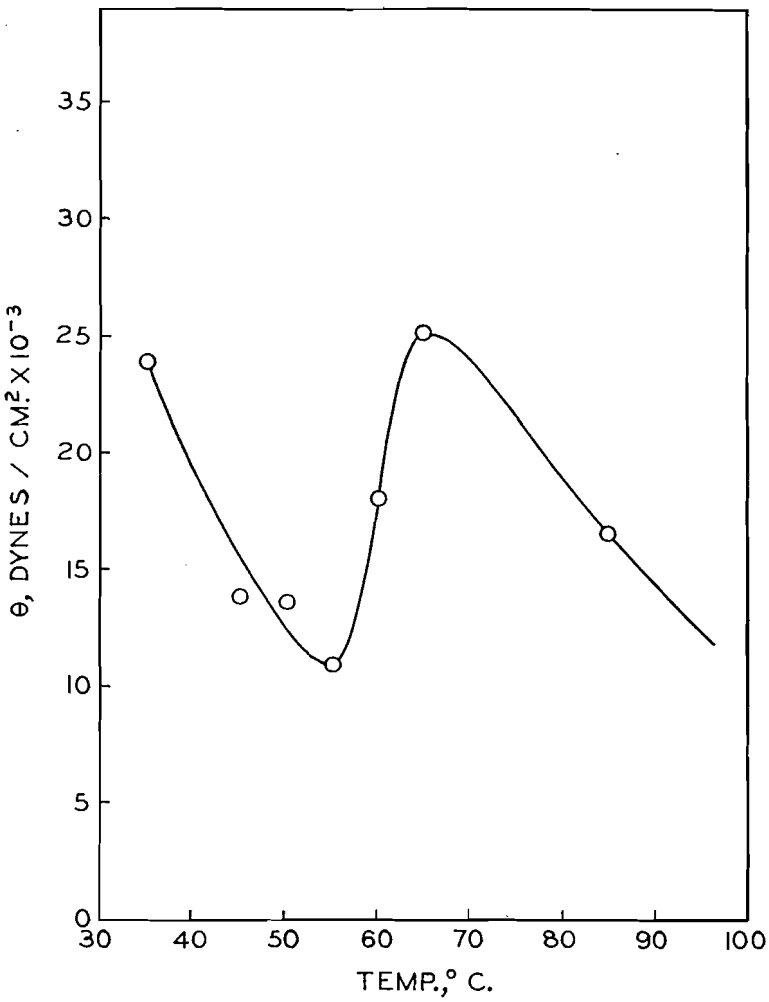

FIG. 5. *Change in coefficient of thixotropy with temperature for dispersion of pure aluminum stearate.*

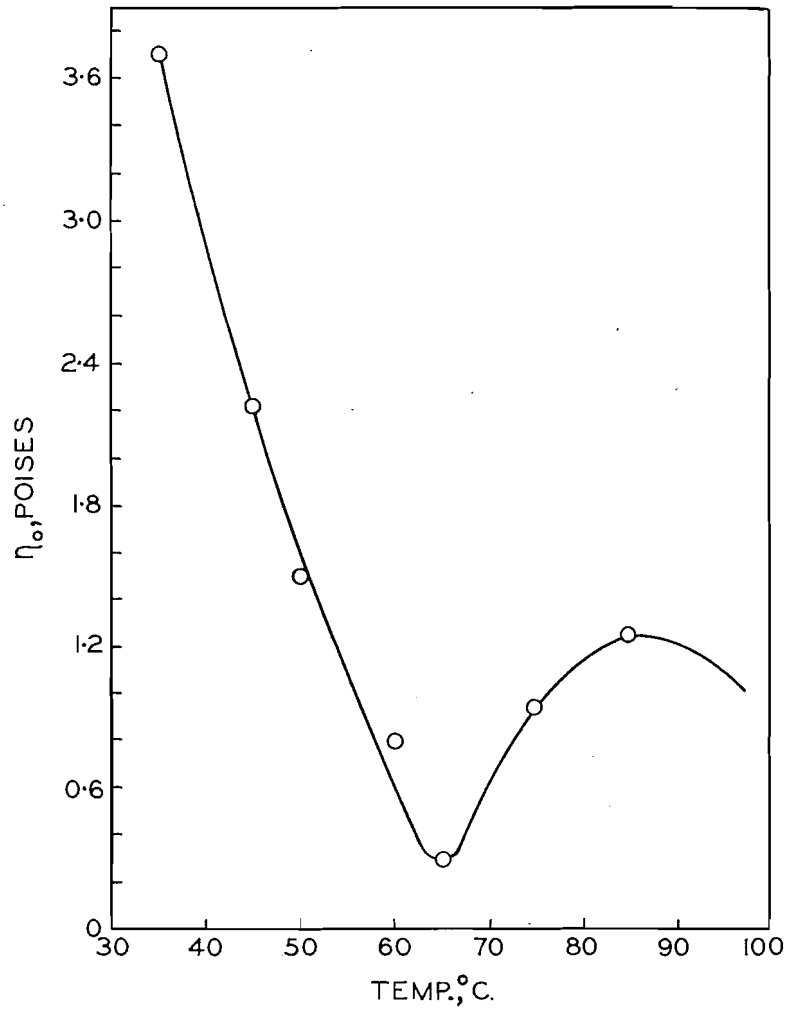

FIG. 6. *Change in residual viscosity with temperature for dispersion of pure aluminum stearate.*

be due to the interfacial surface tension of the two liquids (2). This would be expected to become less with increase in temperature with a consequent drop in thixotropy. Such can not be the case, however, with the three systems under consideration here, since they are substantially anhydrous. Mechanical entanglement of the particles with the consequent formation of strong links seems to be a more likely explanation. In this case the reduction in thixotropy at the higher temperatures is possibly due to greater flexibility of the fibers as the temperature is increased, which allows for much easier breakdown of agglomerates. This hypothesis is supported by the fact that shear sufficiently high to reduce the length of the particles also produces a strong reduction in the degree of thixotropy and also a marked lowering in the temperature coefficient of

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thixotropy. Shorter particles would certainly contribute less to mechanical entanglement but would not reduce the number of interparticle contacts. Were the adhesion due to interparticle friction or interfacial tension, the temperature sensitivity to shape should be less pronounced.

The increase in thixotropy following the initial reduction observed with all the soaps is undoubtedly due to swelling of the soap crystals. The tacky surfaces produced by the swelling causes increased agglomeration which finally passes through a maximum as the soap particles go into solution.

Finally the increasing temperatures of the point of minimum thixotropy and viscosity as one passes from aluminum through calcium, sodium, and lithium stearates appears to be due to the influence of the metallic ion forming the soap and is in the direction of increased electropositivity.

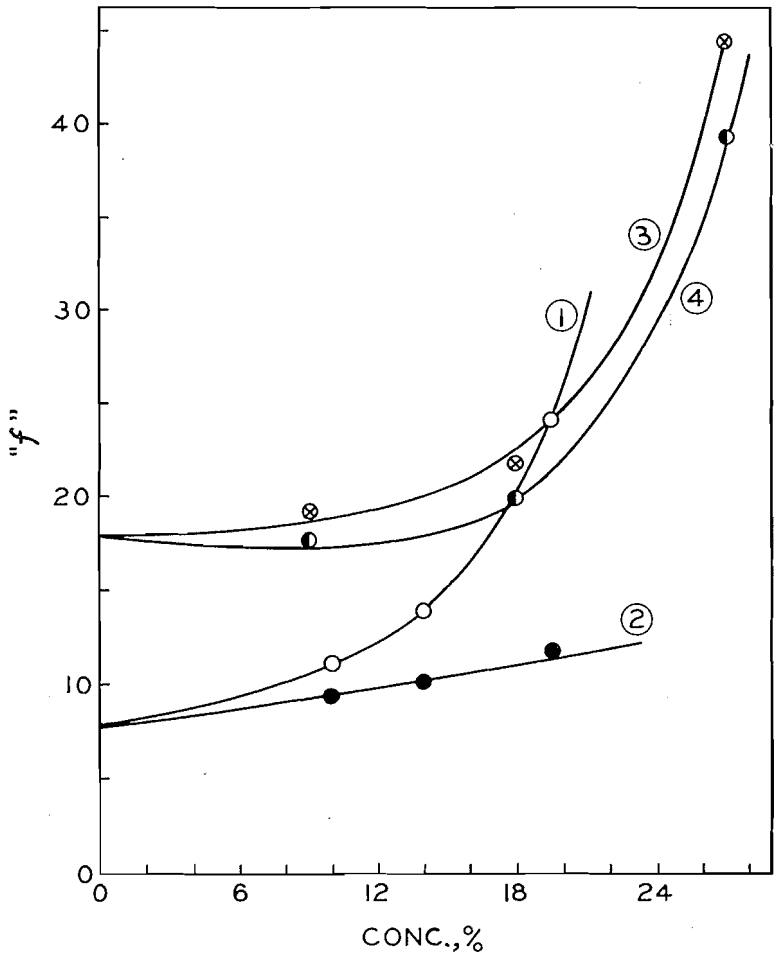

FIG. 7. *Relationship of fiber axial ratio to concentration for some sodium and lithium soap dispersions. The graphs represent: (1) 19.7% commercial sodium soap (l); (2) 19.7% commercial sodium soap (s); (3) 26.9% lithium soap (l); (4) 26.9% lithium soap (s).*

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Attempts have been made previously to get information on the shape of the individual particles of the solid phase by applying the Kuhn equation relating viscosity to volume concentration and shape factor, to the residual viscosity data (4, 5). Results from this work have also been used in this connection with some success. Lithium soap particles gave an extrapolated shape factor of 15 at zero concentration. Sodium soaps at 15% concentration gave a value of 17 for 100% stearate which increased to 23 at 100% oleate, an expected difference. Passage of a sodium stearate – oleate grease through the colloid mill had virtually no effect on the shape factor after extrapolation to zero concentration. The apparent shape at higher concentrations, however, was quite different. Microscopic examination showed progressively less difference in the sheared and unsheared samples as one passed from the higher to the lower concentrations of soap. This would indicate that damage to the soap fibers at a definite

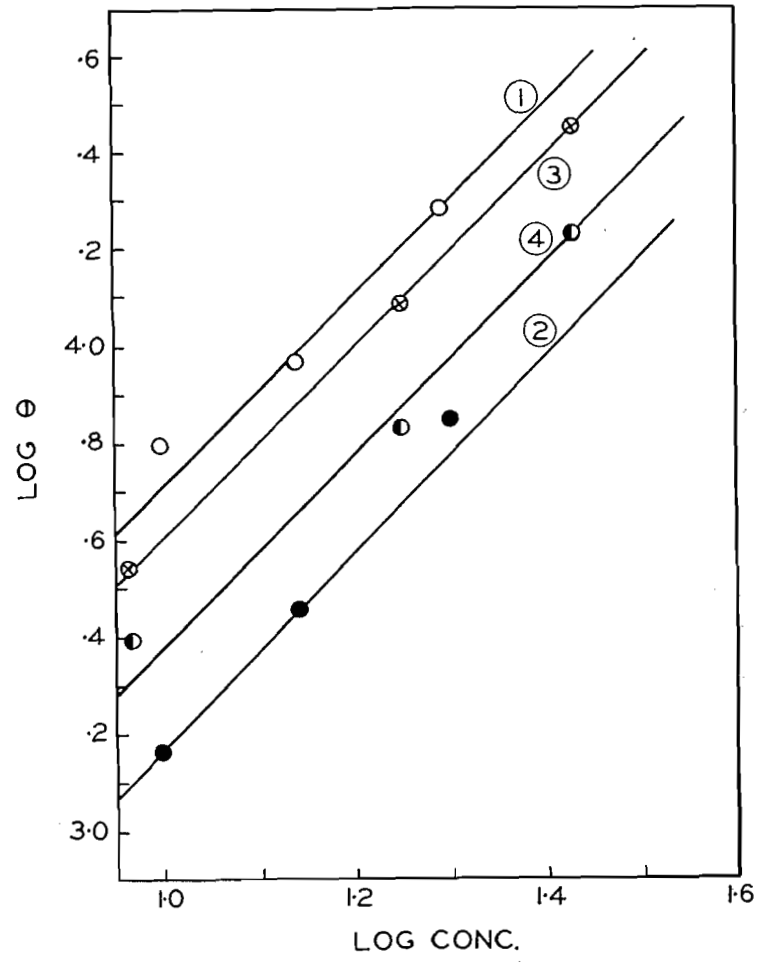

FIG. 8. *Change in coefficient of thixotropy with concentration. The graphs represent: (1) 19.7% commercial sodium soap (l); (2) 19.7% commercial sodium soap (s); (3) 26.9% lithium soap (l); (4) 26.9% lithium soap (s).*

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rate of shear is dependent on the soap concentration, and at low percentage of soap little disintegration of the soap particles occurs. A similar result was obtained with dispersions of lithium stearate. In this case, however, the damage even at high concentrations was slight, owing to the small size of the individual soap particles. These results are shown in Fig. 7. The values quoted above for axial ratios are in agreement with microscopic observations. The "f"values given were calculated from data at 35°C. The calculated axial ratios are substantially independent of temperature, however, below the minimum in the η_0 vs. temperature curve. At higher temperatures the values increase, indicating strong adhesion of the solid particles.

Theory predicts a slope of 2 when the logarithm of the coefficient of thixotropy is plotted against the logarithm of the concentration. The agreement between theoretical and experimental values for these soap systems is shown in Figure 8. All the curves have been drawn with a slope of 2 but a reasonably good fit with the experimental points has been obtained.

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REACTIONS IN DISSOCIATED WATER VAPOR[1]

By R. A. Jones and C. A. Winkler

Abstract

Water vapor dissociated by an electric discharge and passed into a cold trap yielded products which gave off oxygen at temperatures above −120°C. and at room temperature consisted of hydrogen peroxide and water. With products formed under given conditions, the amount of oxygen evolved with warming was proportional to the total amount of product and independent of the warming procedure. The evolution proceeded to completion at −78°C. Water was found at all trap temperatures between −78°C. and −195°C. Hydrogen peroxide was formed only if the trap temperature was below −120°C., and oxygen was evolved only from products formed below −150°C. The yields of water, hydrogen peroxide, and evolved oxygen all increased with decreasing trap temperature. As the volume of reaction chambers inserted between the discharge tube and the trap was increased, the yield of hydrogen peroxide decreased continuously, while the yield of water at first decreased and then increased to a limiting value. Packing a given reaction chamber with glass wool drastically reduced the yield of hydrogen peroxide, but had little effect on the yield of water. Packing the trap itself had only a slight effect on the yields. The results are compared with those obtained by others with the $H–O_2$ system at low temperatures, and a mechanism is proposed to correlate the two systems.

Introduction

When water vapor at low pressures is subjected to the action of a glow discharge of moderate current strength, the primary decomposition products are hydrogen atoms and free hydroxyl radicals (11). If the water vapor is passed continuously through the discharge, the effluent gases have characteristic properties, not all of which can be due to atomic hydrogen alone (3, 7, 18). The possible presence of hydroxyl radicals in these gases has been a matter of controversy. Early workers (18, 7, 8) assumed their presence on the basis of apparently faulty spectroscopic evidence. Subsequently Bonhoeffer and Pearson (2) deduced from spectroscopic data that the hydroxyl radicals disappear so rapidly that no appreciable number could survive outside the discharge. This was contradicted by the results of Oldenberg and his coworkers, who showed with a more refined technique that the hydroxyl absorption spectrum persisted in the discharge tube for at least 0.4 second after the current was interrupted (10, 11, 12). Recently, the assumption has again been made that the water vapor discharge can serve as a source of hydroxyl radicals (9).

Several investigations have shown that the final products of the decomposition are hydrogen, oxygen, water, and hydrogen peroxide in proportions which depend upon experimental conditions, including temperature (4), pressure (16), surface (16), and the presence of catalysts (17). Several mechanisms have been proposed (2, 16, 19) to explain the formation of these final products from the hydrogen atoms and hydroxyl radicals formed initially in the dis-

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charge, but some of the suggestions were based on an incomplete knowledge of the over-all reaction. Rodebush has recently proposed a mechanism which postulated the existence in the active gases of a high concentration of hydroxyl radicals which disappear in the gas phase at ordinary temperatures by an over-all reaction $OH + OH \rightarrow H_2 + O_2$, while at very low temperatures they condense to hydrogen peroxide (14).

This paper reports further investigation of the manner in which the relative yields of the final products depend upon experimental conditions.

Experimental and Results

The apparatus was a conventional flow system (Fig. 1). De-aerated redistilled water was frozen in flask *A* and maintained at 0°C. in an ice-water bath. Water vapor diffused from this flask through the flowmeter chamber *B* and flow-rate control *C* into the discharge tube *D* (22 mm. I. D.). The electrodes were hollow aluminium cylinders (5 cm. × 1.5 cm.) placed 104 cm. apart, while the entrance and exit tubes for water vapor were 89 cm. apart. The discharge tube was cooled by tap water flowing through jacket *E*. High voltage 60 cycle current was supplied to the discharge by a transformer, the output of which could be controlled by a variable transformer in the primary circuit. In all experiments the discharge current was 200 ma. and the discharge potential 1250 v.

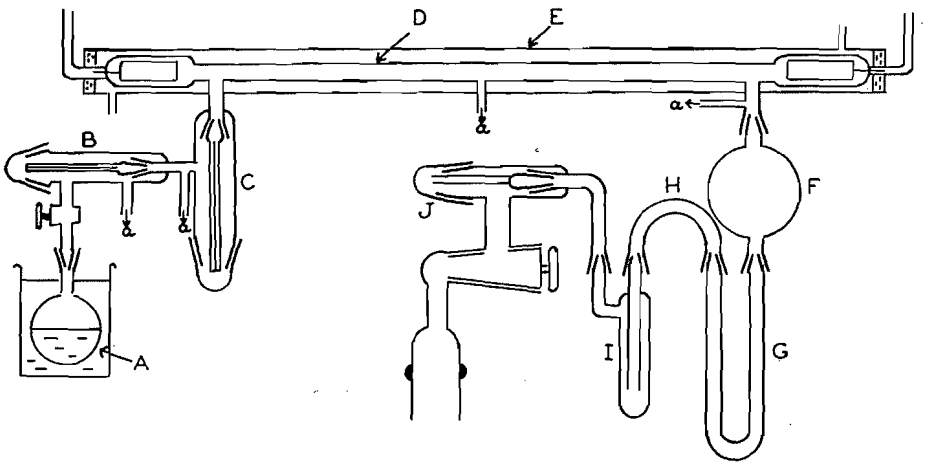

FIG. 1. *Diagram of apparatus.*

From the discharge tube the dissociated water vapor flowed through a short exit tube into reaction chamber *F* and thence into a cold trap *G*. Products not condensed in *G* passed through the connection *H* into a second trap *I* (included to prevent mercury vapor reaching *G* from the diffusion pump) and thence through a second flow-rate contol *J* to the pumping system. This consisted of a high capacity three-stage mercury diffusion pump backed by a Welch "Duo-Seal" mechanical pump.

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The various parts of the reaction chamber and trap assembly were connected by ground glass joints sealed with apiezon "M" grease. This arrangement permitted the insertion of different reaction chambers at *F*, and allowed trap *G* to be detached for product analysis.

By proper choice of flow-restricting tubes in chambers *B*, *C*, and *J*, the system could be operated, within limits, with any desired pressure in the discharge. In all experiments the water input was 15.27 millimoles (mM.) per hour and *J* was adjusted so that the pressure at the mid-point of the discharge tube was 0.1 mm. This procedure ensured that conditions in the discharge were constant for all experiments, regardless of the conditions to which the dissociated water vapor was subjected after leaving the discharge. Gas pressures were measured at points *a* in Fig. 1 by MacLeod gauges kept at 55°C. to prevent condensation of water vapor.

In most experiments, products were collected over a two hour period and the system was filled with dry nitrogen before detaching trap *G* for product analysis.

Gas Evolution from Condensed Product

In a typical experiment in which trap *G* was attached directly to the discharge tube and cooled with liquid nitrogen, the condensed product was obtained as a transparent glassy layer. When the trap was allowed to warm up, this glassy material became white and crystalline, with crystals growing out in rays from a few nuclei. As warming continued, the product melted to give a solution of hydrogen peroxide in water. Violent foaming occurred as the product melted, to produce a gas which was shown by density determination, combustion analysis, and treatment with potassium iodide solution to be oxygen containing about 0.4 mole % of ozone. No measurable amount of hydrogen was found.

In one experiment the trap, containing the product collected during two hours at −195°C., was connected to a manometer. After evacuation, the liquid nitrogen was replaced by isopentane cooled to −150°C. in a Dewar vessel, and the isopentane allowed to warm up slowly, with continuous stirring, while measurements of temperature and gas pressure were made. No oxygen was evolved until the temperature had risen to about −120°C. (Fig. 2). Thereafter the rate of evolution increased rapidly to a value which remained practically constant until evolution ceased. (For convenience, oxygen obtained by warming the cold trap will be designated as evolved oxygen.)

Several experiments were made to investigate the influence of warming procedure upon oxygen evolution. In parallel experiments, products collected in two hours at −195°C. were warmed to room temperature (1) abruptly, by immersing the trap in a water bath, (2) in two stages, by immersion in dry ice – acetone slurry followed by immersion in a water bath, and (3) in five stages, by successive immersion in baths at −78°C., −59°C., −46°C., 0°C.,

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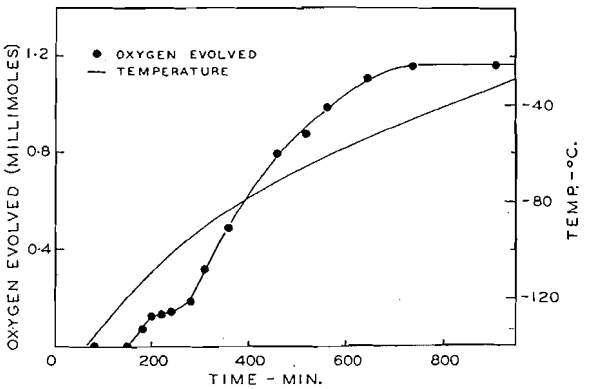

FIG. 2. *Relation between oxygen evolved and time, with increasing temperature.*

and room temperature. In all cases the final total amount of oxygen evolved was substantially the same as that obtained by gradual warming. Other experiments, made under identical conditions but for different lengths of time, so that different total amounts of product were obtained, showed that the yields of evolved oxygen, of hydrogen peroxide, and of water, were all directly proportional to the duration of the experiment.

In a further experiment on oxygen evolution, the cold product collected in four hours at −195°C. was warmed to −78°C. and maintained at that temperature for 24 hr. The results are shown in Fig. 3, in which the amount of oxygen evolved is plotted against time (Curve I) and reciprocal time (Curve II). A reasonable extrapolation of curve II to infinite time gives a value of 2.4 mM. for the amount ultimately evolved at −78°C., i.e. the same as the quantity evolved from comparable amounts of product warmed to room temperature. At the end of the experiment the product (at −78°C.) had become white and crystalline.

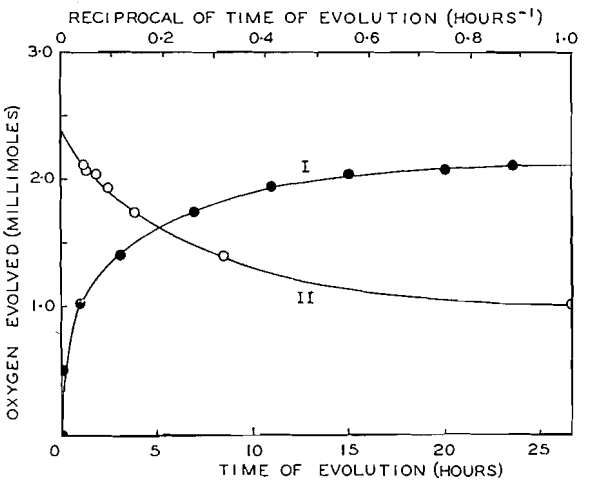

FIG. 3. *Relation between oxygen evolved and time at −78°C.*

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Influence of Trapping Temperature

Earlier work (16, 14) has shown that both water and hydrogen peroxide are obtained at liquid air temperatures but only water is obtained at −78°C. In the present study, product yields were determined as a function of trapping temperature over the intervening range. The trap was attached directly to the discharge tube and was immersed in a vigorously stirred bath of propane or isopentane, which was maintained within 0.2°C. of the desired temperature by pouring small amounts of liquid nitrogen into a test tube suspended in the bath. After each experiment the product was warmed to 0°C., and the evolved oxygen determined manometrically. The trap and residual contents were then weighed, and the hydrogen peroxide content determined by titration with standard potassium permanganate solution. The yield of water was calculated by difference. The amounts of oxygen and hydrogen formed during the experiment were also calculated by difference, from the known total input of water.

The results are given in Table I and Fig. 4. Noteworthy features are: (1) water was obtained at all temperatures; with increasing temperature the amount remained sensibly constant from −195°C. to about −160°C., and then decreased to a lower limit, (2) no peroxide was obtained above −120°C. at which temperature a trace was formed. Below −120°C. the yield increased rapidly until at −195°C. it was 45% by weight of the water input; (3) measurable amounts of oxygen were evolved only from products collected below −150°C.; the yield increased almost linearly with decreasing trap temperature, and at −195°C. amounted to 8.4% of the oxygen input; (4) the amount of molecular oxygen formed during the experiment decreased very rapidly with decreasing temperature, so that at −195°C., 95% of the oxygen input was collected in the trap.

TABLE I

VARIATION OF YIELDS WITH TRAP TEMPERATURE

Trap temperature (°K.)	Yields: mM. per hour					
	H_2O_2	H_2O	Evolved O_2	O_2	H_2	H_2O formed at trap temperature*
193	0	3.84	0	5.72	11.43	0
173	0	4.00	0	5.64	11.27	0.16
153	0.01	4.36	0	5.45	10.90	0.52
138	0.20	5.11	0	4.88	9.96	1.27
123	0.47	5.81	0.03	4.24	8.99	1.91
113	0.97	5.98	0.09	3.59	8.32	1.96
103	1.50	5.93	0.21	2.97	7.84	1.67
93	2.88	5.92	0.41	1.57	6.83	1.26
78	3.74	5.90	0.64	0.31	5.63	0.78

* *Assuming no water to be formed in trap at 193°K. and that, on warming, water and oxygen were formed in the molar ratio 2: 1.*

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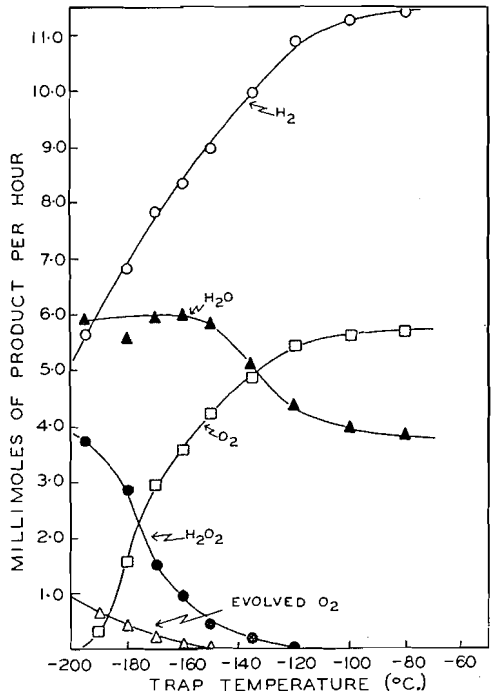

FIG. 4. *Relations between product yields and trapping temperature.*

Influence of Reaction Chamber

In another series of experiments the dissociated water vapor passed through a reaction chamber (*F* in Fig. 1) before entering the cold trap, so that reactions at room temperature proceeded for a time interval determined by the flow rate and the volume of the chamber. Experiments were made at trapping temperatures of −195°C. and −78°C. with four reaction chambers and also with the trap attached directly to the discharge tube (Table II and Fig. 5). Evolved oxygen was not determined. At −78°C., as expected, only water was

TABLE II

YIELDS WITH DIFFERENT REACTION CHAMBERS

	Chamber No. and shape				
	0	1 (Cylindrical)	2 (Spherical)	3 (Cylindrical)	4 (Spherical)
	Yields: mM. per hour				
Volume (ml.)	18	213	1027	1107	5512
Time of passage (sec.)	0.02	0.16	0.70	0.80	3.7
Volume: surface	–	0.088	2.0	0.44	3.6
H_2O_2 at −195°C.	2.79	1.75	1.83	1.22	0.56
H_2O at −195°C.	5.45	4.82	4.76	4.90	5.41
H_2O at −78°C.	3.06	3.04	3.44	4.08	4.85

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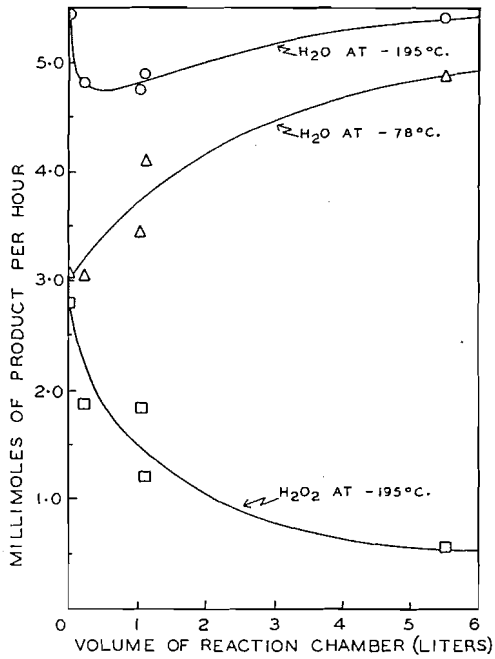

FIG. 5. *Influence of reaction chamber volume on water and hydrogen peroxide yields.*

obtained, in amounts which increased with increasing chamber volume, and apparently approached an upper limit. At −195°C. both hydrogen peroxide and water were obtained. The yield of water, which was always greater than the corresponding yield at −78°C., at first decreased with increasing volume and then increased; it must approach the same upper limit as for −78°C. In contrast, the peroxide yield decreased continuously with volume increase, but was still appreciable with the largest chamber.

Influence of Surface

The difference in the results obtained with chambers (2) and (3) (Table II), which were of comparable volume but different in surface–volume ratio, suggested that surface effects were considerable. This was further investigated by loosely filling chamber (2) with 4.3 gm. of Pyrex wool and determining the amounts of water and peroxide obtained at trap temperatures of −78°C. and −195°C. The results are given in Table III, along with data for otherwise identical experiments with the unpacked sphere. At −195°C. the peroxide yield was drastically reduced by packing, but the yield of water was virtually unaltered. At −78°C. more water was obtained with the packed sphere.

In an experiment to determine the effect of surface in the cold trap itself, Pyrex wool was placed along a 5 cm. section of the inlet arm of the trap, just at the level of the cooling bath. The trap was attached directly to the discharge tube and cooled with liquid nitrogen. Table IV gives the results together with comparable data for the unpacked trap. The yield of water was virtually unaffected, but yields of peroxide and evolved oxygen were reduced.

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TABLE III

EFFECT OF PACKING REACTION CHAMBER (2)

	Yields: mM. per hour		
	At −195°C.		At −78°C.
	H_2O_2	H_2O	H_2O
Unpacked	1.83	4.76	3.44
Packed	0.12	4.73	4.54

TABLE IV

EFFECT OF PACKING TRAP

	Yields, at −195°C. mM. per hour				
	H_2O_2	H_2O	Evolved O_2	O_2 gas	H_2 gas
Unpacked	3.74	5.90	0.64	0.31	5.63
Packed	3.62	5.94	0.48	0.56	5.71
Difference	−0.12	+0.04	−0.16	+0.25	+0.08

Discussion

The final products obtained in these experiments were presumably formed by a four-stage process:

(1) Discharge tube stage, in which the water vapor is partially or completely decomposed into H and OH, with possible subsequent interaction of the active species. Apparently, no detectable amounts of hydrogen peroxide issue from the discharge, since none is collected in a following trap at −78°C. However, a certain amount of water does emerge from the discharge. Examination of the curve showing variation of water yield with trap temperature (Fig. 4) shows that with increasing temperature, the yield of water decreases to a lower limit at about −78°C. It may be reasonably assumed that this residual amount of water, which does not vary with trap temperature, is actually the amount entering the trap, and since in this case the trap was attached directly to the discharge tube, is the amount of water emerging from the discharge in all experiments. This is, of course, equivalent to assuming that no appreciable amount of water is formed in the trap at −78°C.

(2) Reaction chamber stage, in which reactions involving the active species from the discharge tube proceed at room temperature. Results obtained with reaction chambers of increasing volume (Fig. 5) show that these reactions produce water, hydrogen, and oxygen, since a following trap at −78°C. collects only water in amounts which increase with increasing chamber volume. The actual amount of water formed in a given reaction chamber can be calculated by subtracting the yield at −78°C., with the trap attached directly to the

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discharge tube, from the yield at −78°C. with the reaction chamber in question between the discharge and the cold trap. Taking the ultimate yield of water at infinite volume to be 5.5 mM. per hour (Fig. 5), such a calculation shows that 20 weight per cent of the dissociated water vapor leaving the discharge would be converted to water if the reaction were to go to completion at room temperature. Examination of the data for the packed sphere (Table III) reveals that, although in these experiments the reaction had gone almost to completion (shown by the small yield of peroxide and the small increase in yield of water obtained by lowering the trap temperature), only 12 weight per cent of the dissociated water vapor was converted to water. Increasing the surface thus favors the formation of hydrogen and oxygen over the formation of water. Because of this surface effect any quantitative calculation of the rate of disappearance of active species based on the data of Table II would be meaningless. Under some conditions, active species must survive for roughly four seconds, since peroxide was obtained at −195°C. even with the five liter reaction chamber.

(3) Cold trap stage, in which condensable products formed in the reaction chamber or discharge tube are collected, and the active species which have survived passage through the reaction chamber (or have been formed therein), react at a much lower temperature. The nature of the product formed in this stage has not been determined directly, but only by inference from a determination of the products at room temperature.

(4) Warming stage. Above −120°C. the products collected below −150°C. evolve oxygen in amounts proportional to the quantity of product and independent of the temperature of evolution and leave hydrogen peroxide and water in the trap.

By mixing atomic hydrogen and molecular oxygen, Geib and Harteck (6) obtained a product which exhibited the same appearance and behavior as the product found in the present study. Thus, at the temperature of formation, it was glassy and transparent, while at temperatures above −115°C. it gave off oxygen and finally melted to hydrogen peroxide and water. Geib and Harteck suggested that the oxygen was formed by the decomposition of an "abnormal" form of peroxide, $H_2O \rightarrow O$.

Figs. 6 and 7 show respectively the manner in which oxygen: water, and peroxide: water ratios vary with temperature of formation (trap temperature) for the $H–O_2$ system, calculated from the data of Geib and Harteck, and for the dissociated water vapor system (calculated from the data of Table I, excluding the water presumed to have entered the trap as such). Evidently, at a given temperature of formation the products of the two systems have nearly the same composition.*

* *The closeness of the correlation is to some extent fortuitous. According to the data of Geib and Harteck the composition of the product from the $H–O_2$ reaction is dependent on the relative concentrations of H and O_2 and an increase in the H-atom concentration at a given temperature has the same general effect as increasing the temperature. However, the data for this reaction plotted in Figs. 6 and 7 were obtained with a $H_2:O_2$ ratio (1.4) not greatly different from that which would correspond to an equimolar mixture of H and OH (2.0), so that the comparison is by no means without significance.*

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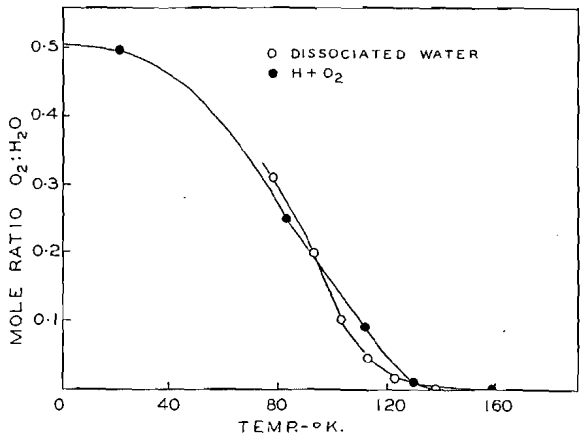

FIG. 6. *Oxygen: water ratio at different temperatures for the H–O_2 reaction (calculated from data of Geib and Harteck), and for the dissociation of water vapor.*

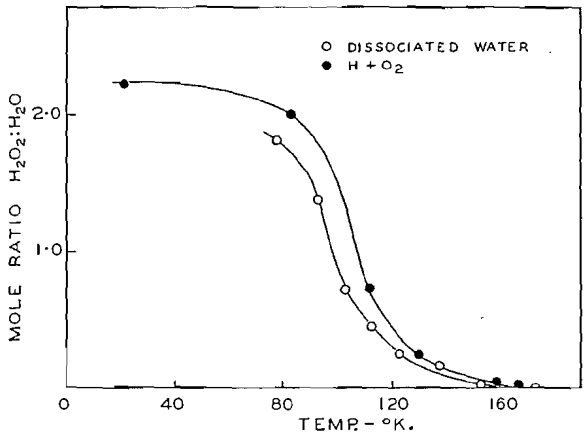

FIG. 7. *Hydrogen peroxide: water ratio at different temperatures for the H–O_2 reaction (calculated from data of Geib and Harteck), and for the dissociation of water vapor.*

The simplest explanation for this correspondence would be that the dissociated water vapor flowing from the discharge tube is actually a mixture of H and O_2, but the experimental evidence against this is strong (11). Therefore it appears that a mixture of H and OH and appropriate mixtures of H and O_2 yield identical products. This means, presumably, that the same mechanism to form the product operates in the two systems, since it is unlikely that two different mechanisms would show the same temperature dependence.

It is possible to suggest a mechanism which correlates the two systems by adaptation and extension of one already proposed by Badin (1) for the low temperature H–O_2 reaction.

It may be represented as shown on the following page. The key unit is an unstable collision complex which exists in two tautomeric (prototropic) forms (*A*) and (*B*) and can be formed by the union of two hydroxyl radicals, or from H and O_2 with the intermediate formation of excited HO_2. Since the reactions

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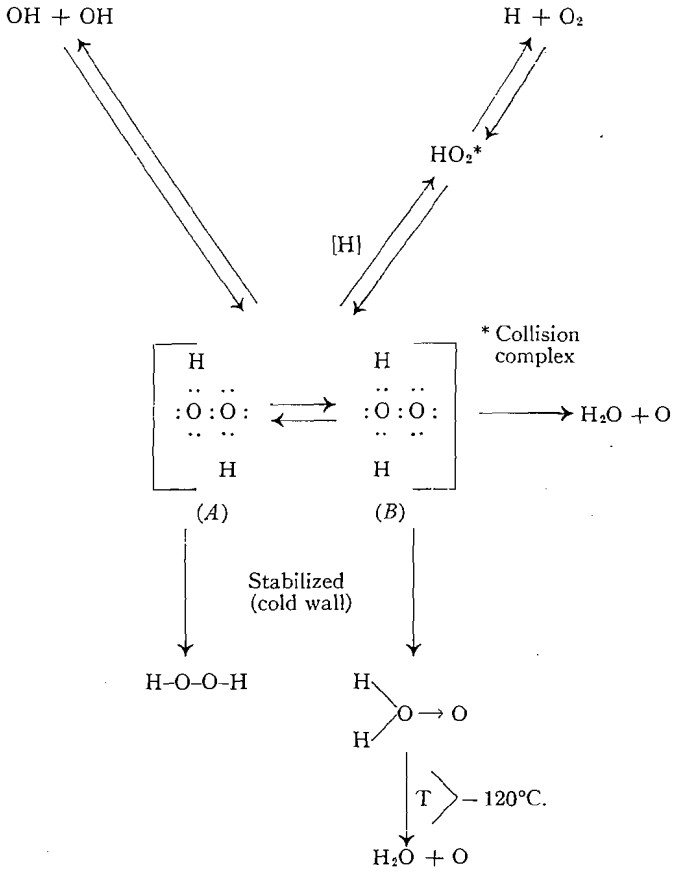
forming this complex are highly exothermic, it has a high energy content and unless it is stabilized it decomposes soon after it is formed. Decomposition may occur in one of three ways: (1) reversibly into two OH radicals, (2) reversibly into 2H and O_2, (3) irreversibly into H_2O and O.* Since H atoms are continuously lost by combination to H_2, the final products, if stabilization does not occur, are H_2, O_2, and H_2O, as observed experimentally.



If, however, the collision complex is stabilized, for instance by collision with a sufficiently cold wall, the reaction takes a different course. Stabilization of (*A*) forms ordinary hydrogen peroxide, whereas stabilization of (*B*) forms the "abnormal" peroxide suggested by Geib and Harteck, which supposedly decomposes above −115°C. to water and oxygen.

The gas-phase equilibrium between (*A*) and (*B*) may be expected to shift with changing temperature. Experimentally, proportionately more oxygen is evolved from products formed at lower temperatures, from which it may be inferred that a decrease in temperature shifts the equilibrium in favor of form (*B*).

* *It has been reported by Rodebush and Wahl (15) and confirmed by the authors, that oxygen atoms do not react with water at liquid oxygen temperatures.*

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Probably the major part of the water formed in the cold trap results from the reaction $H + OH + M \rightarrow H_2O + M$, where M is, in most cases, the cold wall. Column 7, Table I, gives the yields for this reaction, calculated on the basis of the proposed mechanism, i.e. assuming that part of the water is formed by the decomposition of peroxide. With decreasing temperature the yield increases to a maximum at $-160°C.$ and then decreases rapidly again. The initial increase is to be expected because of the increasing efficiency of the reaction as the temperature is lowered. The subsequent decrease may be due to the decrease in concentration of OH that results from increased stabilization of $(HO)_2$ complexes.

Badin (1) has already pointed out that a similar intermediate complex has been postulated by Egerton and Minkoff (5) for the reactions at higher pressures between hydrogen and oxygen. Also, Oldenberg and Rieke, in a study (13) of the kinetics of disappearance of OH in the water vapor discharge, conclude that "OH radicals form collision complexes which have a lifetime much greater than the duration of the bimolecular collision between them".

If the suggested mechanism is valid, the interesting conclusion follows that appropriate mixtures of H and OH, on one hand, and H and O_2 on the other, attain to the same chemical composition, virtually instantaneously, and therefore should exhibit identical chemical behavior. Jackson (7) has, in fact, found that a characteristic action of dissociated water vapor, the oxidation of CO to CO_2, is also displayed by a mixture of H and O_2.

Acknowledgment

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THE REACTION OF NITROGEN ATOMS WITH METHANE AND ETHANE[1]

By H. Blades and C. A. Winkler

Abstract

Methane reacted with nitrogen atoms at temperatures above 300°C. to produce hydrogen cyanide. An activation energy of 11 kcal. and a steric factor of 5×10^{-3} were obtained. The reaction of ethane with nitrogen atoms was studied up to 295°C., with hydrogen cyanide the only product found in measurable amounts. At high temperatures, nitrogen atom consumption was complete in excess ethane, and the hydrogen cyanide production under these conditions, compared with the atom concentration determined by a Wrede gauge, indicated the active species in the nitrogen stream to be only atomic nitrogen. The ethane – nitrogen atom reaction was second order, with an activation energy of 7 ± 1 kcal. and a steric factor between 10^{-1} and 10^{-3}.

The reaction of nitrogen atoms with ethylene has been discussed in previous papers from this laboratory (1, 2). Similar studies have now been made, using methane and ethane, with the results outlined below.

Experimental

The apparatus was similar in all essential respects to that described in the earlier papers. but certain significant changes in procedure were adopted. Commercial nitrogen was passed over copper turnings at about 500°C. to remove oxygen and was metered into the discharge tube after it had passed through a liquid air trap. Hence, unlike the previous study, the present investigation was made with nitrogen containing no water vapor to act as a wall poison in the reaction vessel and trap immediately following it. These were therefore poisoned with phosphoric acid in the conventional way. With one Wrede gauge at the inlet to the reaction vessel and another at the outlet, the effect of temperature on the concentration of nitrogen atoms during their passage through the reaction chamber was determined. At room temperature the atom concentration decreased by about 50% between the inlet and outlet of the chamber but no decrease was detectable at temperatures of 256°C. and 415°C.

Methane (Matheson Co. Inc.) 99% purity, was used as received. Ethane (Pillips Petroleum, 95% pure) was purified by the method described by MacGillvray (3).

Careful manipulation of the reaction products in the absence of moisture prevented, almost entirely, formation of the hydrogen cyanide polymer that was so troublesome in the earlier study with ethylene. The liquid nitrogen trap immediately following the reaction vessel was allowed to warm to room temperature to transfer the condensed hydrocarbons and hydrogen cyanide to a

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small liquid nitrogen trap that could be later weighed. If, during this operation, the hydrogen cyanide was not allowed to melt, it could be transferred by sublimation with little or no loss by polymerization.

The contents of the small trap were fractionated by raising the temperature to −116°C. (frozen ether slurry) and trapping the distillate in another liquid nitrogen trap. The weight of the residue left at −116°C. was determined, after which 5% potassium hydroxide solution was added and the cyanide content determined volumetrically (4). The quantity of distillate was obtained by expanding it into a standard volume and measuring the pressure. This was followed, when desired, with analysis in a Podbielniak still.

Results

Reaction with Methane

The experimental conditions used, and results obtained, in the study with methane are shown in Table I. In these experiments a small quantity of hydrocarbon (identified by combustion) was obtained from the fractionation at −116°C. Calculated as ethane, it represented about 2% of the methane that had reacted. No consideration has been given to it in setting up Table I.

TABLE I

EXPERIMENTAL AND CALCULATED DATA ON THE METHANE – ATOMIC NITROGEN REACTION

Total pressure, mm. Hg	Ratio of methane to atomic nitrogen	Temp., °C.	Flow rate of atomic nitrogen, moles/min.	Flow rate of methane, moles/min.	Rate of HCN production, moles/min.	Collision yield
1.65	0.282	416	9.23×10^{-4}	2.60×10^{-4}	0.43×10^{-4}	1.79×10^{-6}
1.65	0.675	322	"	6.23	0.44	4.71×10^{-7}
1.65	0.668	370	"	6.14	1.13	1.37×10^{-6}
1.68	0.682	397	"	6.30	2.15	2.74×10^{-6}
1.68	0.688	402	"	6.35	1.10	1.37×10^{-6}
1.76	1.00	425	"	9.26	2.14	1.88×10^{-6}
1.68	1.05	344	6.45×10^{-4}	6.77	0.54	7.66×10^{-7}
1.68	1.08	376	"	6.95	0.75	1.13×10^{-6}
1.71	1.08	389	"	6.98	0.74	1.15×10^{-6}
1.70	1.04	401	"	6.70	1.42	2.62×10^{-6}
1.68	1.08	435	"	6.95	1.21	2.24×10^{-6}
1.93	2.17	377	9.23×10^{-4}	20.1	3.22	1.25×10^{-6}
1.93	"	424	"	19.9	5.71	2.46×10^{-6}
1.93	"	446	"	20.0	5.28	2.38×10^{-6}

Collision yields were calculated in the usual way, using values of 3.75Å. and 3.0Å. for the collision diameters of methane and atomic nitrogen respectively.

A plot of log (collision yield) against $\frac{1}{T}$ (Fig. 1) shows that, with the exception of three points, a reasonably good linear relation is obtained. Since there is no definite trend of collision yield with methane – nitrogen atom ratio, the scatter of points is presumably due only to experimental uncertainties.

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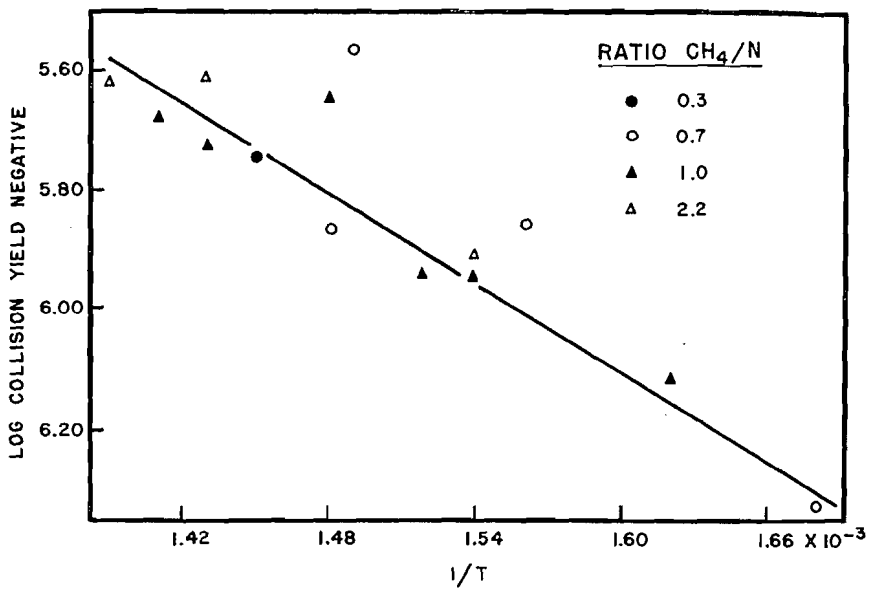

FIG. 1. *Plot of log collision yield versus 1/T for the atomic nitrogen – methane reaction.*

From the line of Fig. 1, an activation energy of 11 kcal. and a steric factor of 5×10^{-3} may be evaluated.

Reaction with Ethane

With this system, a material balance was readily obtained by the procedure outlined previously. The only substances trapped in identifiable amounts were hydrogen cyanide and unreacted ethane, and these two fractions accounted, within experimental error (2-3%) for all the ethane passed into the system. Podbielniak distillation of the volatile fraction obtained at −116°C. showed no trace of any other material than ethane, while the weight and volumetric estimations of hydrogen cyanide in the residue agreed within the uncertainty of the titration. The vapor pressure and melting point (approximate) also corresponded with the values for hydrogen cyanide.

In Table II are recorded some data obtained with relatively large mole ratios of ethane to atomic nitrogen (Wrede gauge measurements). Under these conditions, the reaction appeared to proceed to complete consumption of nitrogen atoms, since the rate of production of hydrogen cyanide was independent of temperature. In the last column of the table are recorded the nitrogen atom concentrations estimated from the hydrogen cyanide production. The close correspondence between these values and the atom concentrations determined with the Wrede gauge would seem to leave little doubt that the chemical activity in "active nitrogen" derives only from its atomic nitrogen content.

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TABLE II

REACTION BETWEEN ETHANE AND NITROGEN ATOMS, WITH ETHANE IN EXCESS

Temp., °C.	Nitrogen atom* conc., % (Wrede gauge)	Av. mole ratio, $\frac{\text{ethane}}{\text{atomic nitrogen}}$	Flow rate of ethane, mole/min.	Rate of HCN production, moles/min.	Nitrogen atom conc., % (HCN prod.)
176	12 ± 2	2.7	1.71×10^{-3}	6.9×10^{-4}	10 ± 0.3
194	"	"	1.73	6.4	"
208	"	"	1.74	6.6	"
285	"	"	1.72	6.4	"
260	14 ± 1.5	3.4	1.72	5.1	14 ± 0.3
250	9 ± 1.5	2.0	1.70	9.6	7.7 ± 0.3
285	"	"	1.77	8.9	"

* *Each value is the mean of six consecutive gauge readings and the uncertainty given is the average deviation of these readings.*

In Table III are recorded further data for the reaction, obtained under conditions of temperature and reactant concentrations such that "clean-up" of nitrogen atoms did not occur.

TABLE III

RATE OF PRODUCTION OF HYDROGEN CYANIDE FROM THE ETHANE – NITROGEN ATOM REACTION UNDER VARIOUS REACTION CONDITIONS

Pressure, mm. Hg	Ratio ethane to atomic nitrogen	Temp., °C.	Flow rate of atomic nitrogen, moles/min.	Flow rate of ethane, moles/min.	Rate of HCN production, moles/min.	k_2 calculated by Equation (1)	k_2 calculated by Equation (2)
1.52	0.256	127	9.23×10^{-4}	2.36×10^{-4}	1.36×10^{-4}	3.09×10^{5}	7.86×10^{5}
1.62	0.256	202	9.23	2.36	2.45	8.85	30.1
1.55	0.264	230	9.23	2.44	2.96	14.5	57.0
1.55	0.262	243	9.23	2.42	2.85	14.4	54.6
1.35	0.492	106	9.23	4.54	1.65	2.48	5.31
1.35	0.549	168	9.23	5.06	3.64	8.05	24.5
1.27	0.560	243	9.23	5.17	5.98	29.3	148
1.56	0.567	295	9.23	5.24	6.72	32.3	197
1.25	0.995	109	5.11	5.09	0.975	2.27	5.33
1.35	1.01	192	5.11	5.14	2.36	9.00	28.0
1.26	0.985	264	5.11	5.04	3.32	26.2	110

The rate constant for each experiment was calculated using a second order rate expression,

$$\frac{dx}{dt} = k_2 (a - x)\left(b - \frac{x}{2}\right).$$

where a = partial pressure of atomic nitrogen,
b = partial pressure of ethane,
x = partial pressure of hydrogen cyanide.

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For no interdiffusion of reaction zones in the reaction vessel, such that the concentrations of reactants change uniformly from the initial values on mixing to the final values determined by the amount of reaction during the flow time, the integrated form is

$$k_2 = \frac{1}{t}\frac{1}{(a-2b)}\ln\frac{b(a-x)}{a\left(b-\frac{x}{2}\right)}. \qquad (1)$$

If, however, turbulence is assumed such that the concentrations are uniform throughout the chamber and remain constant at values equal to those found in the gas leaving the reaction vessel, the integrated form is

$$k_2 = \frac{1}{t}\frac{x}{(a-x)\left(b-\frac{x}{2}\right)}. \qquad (2)$$

Calculations were made using both equations, to obtain the values of k_2 given in Table III. A reasonably satisfactory plot of log k_2 against $\frac{1}{T}$ is obtained using either set of k_2 values (e.g. Fig. 2) but the data are not sufficiently accurate to distinguish the superiority of one treatment over the other. There is little doubt, however, that the reaction is second order.

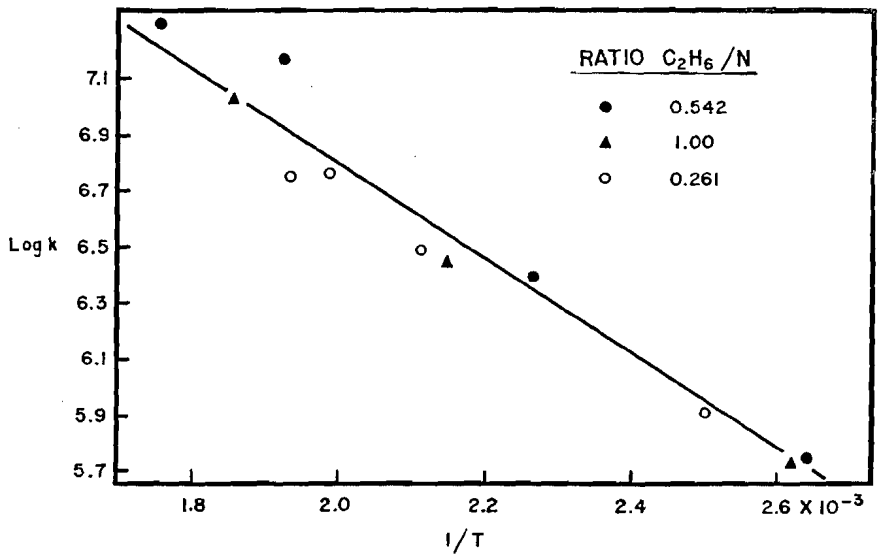

FIG. 2. *Plot of log k versus 1/T for the nitrogen atom – ethane reaction.*

Activation energy values of 6.2 and 7.9 kcal. were obtained from the Arrhenius lines plotted from the k_2 values given by Equations 1 and 2 respectively. These values may be taken to represent the limits within which the true activation energy probably lies.

The steric factor in the expression $k = PZe^{-E/RT}$ was calculated for values of k at 450°K., taken from the log $k - \frac{1}{T}$ plots corresponding to Equations (1)

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and (2). The value of Z was calculated assuming collision diameters of 3.75Å. and 3.0Å. for ethane and atomic nitrogen respectively. For the plot of log k vs. $\frac{1}{T}$, based on Equation (1), where $E = 6.2$ kcal., $k = 8.1 \times 10^{-5}$ liter mole^{-1} sec.$^{-1}$, and $P = 3 \times 10^{-3}$, while from the corresponding plot based on Equation (2), where $E = 7.9$ kcal., the values were $k = 26.9 \times 10^{-5}$ liter mole^{-1} sec.$^{-1}$ and $P = 7 \times 10^{-2}$.

Discussion

Since hydrogen cyanide was the only product obtained from either of the reactions studied, it may be inferred that no nitrogen-containing intermediate of appreciable stability (e.g. ethylenimine) was formed. It also seems unlikely that radicals such as =NH were present in significant concentration since these might be expected to give rise to ammonia or other nitrogenous products in measurable amounts.

In the present state of inadequate knowledge concerning nitrogen atom reactions generally, there would seem to be no obvious alternative to assuming a mechanism for the present reactions somewhat similar to that suggested previously for the reaction of nitrogen atoms with ethylene (1). With methane, this would be merely

$$CH_4 + N \rightarrow \text{collision complex} \rightarrow HCN + H_2 + H \quad (1)$$

$$H + H \rightarrow H_2 \quad (2)$$

With ethane, the reaction may be represented

$$C_2H_6 + N \rightarrow \text{collision complex} \rightarrow HCN + CH_3 + H_2 \quad (3)$$

$$CH_3 + N \rightarrow HCN + H_2 \quad (4)$$

It may be assumed that the measured activation energy of 7 ± 1 kcal. for the reaction with ethane is associated with one of the steps prior to Reaction (4), and that Reaction (4) is relatively much faster, to avoid the possibility of methane formation by

$$CH_3 + C_2H_6 \rightarrow C_2H_5 + CH_4.$$

While the schemes suggested above have obvious objections, no satisfactory alternatives have yet been devised. Studies, now in progress, of the reactions of atomic nitrogen with propane, propylene, and butane give promise of better understanding of this type of reaction.

Acknowledgment

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SYNTHESIS OF 5-SUBSTITUTED 1-ANILINO-4-IMINOBARBITURIC ACIDS[1]

By Paul E. Gagnon, Jean L. Boivin,[2] and Jacques Giguere[3]

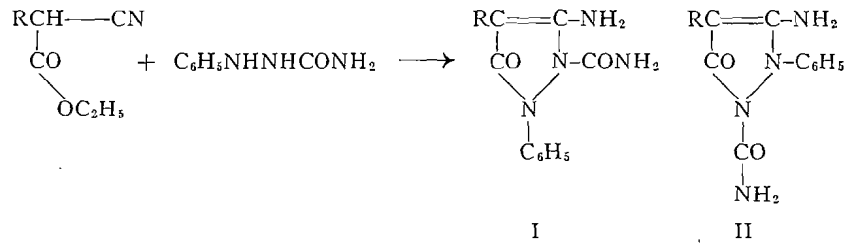
Abstract

Substituted cyanoacetic esters have been reacted with 1-phenylsemicarbazide to give rise to 5-substituted-1-anilino-4-iminobarbituric acids. The presence of an imino substituent in position 4 has been established by the hydrolysis of 5-benzyl-1-anilino-4-iminobarbituric acid into 5-benzyl-1-anilinobarbituric acid. The position of the anilino group has been ascertained by the transformation of 5-octyl-1-anilino-4-iminobarbituric acid into octylcyanoacetic phenylhydrazide, carbon dioxide, and ammonia.

Introduction

The present investigations were undertaken to study the behavior of 1-phenylsemicarbazide ($C_6H_5NHNHCONH_2$) toward substituted cyanoacetic esters in view of preparing pyrazolones or barbituric acids.

It is known that hydrazine and N-alkyl or N-arylhydrazines react with substituted cyanoacetic esters in the presence of sodium ethylate to give rise to pyrazolones (4, 5, 6, 9). However, 1-phenylsemicarbazide, a derivative of hydrazine, did not yield the expected pyrazolones (I or II) when it was reacted with these esters under the same conditions.



(1)

The compounds obtained, like pyrazolones, were soluble in alkaline solution but were insoluble in active acids. The ultraviolet absorption spectra obtained were very different from the spectra of pyrazolones. They were similar in acid and neutral solutions (Table I), whereas the pyrazolones gave different spectra.

It should be noted that 1-phenylsemicarbazide is a derivative of urea and hydrazine which is made by treating urea with phenylhydrazine:

$$C_6H_5NHNH_2 + NH_2CONH_2 \longrightarrow C_6H_5NHNHCONH_2 + NH_3. \quad (2)$$

Therefore the reaction products obtained from Equation 1 may be barbituric acids. It is known that urea and substituted ureas like phenylurea react with

[1] *Manuscript received June 11, 1951.*
Contribution from the Department of Chemistry, Laval University, Quebec, Que.
[2] *Defence Research Board, Valcartier, Que.*
[3] *Graduate Student, holder of a Studentship under the National Research Council of Canada in 1949-1950.*

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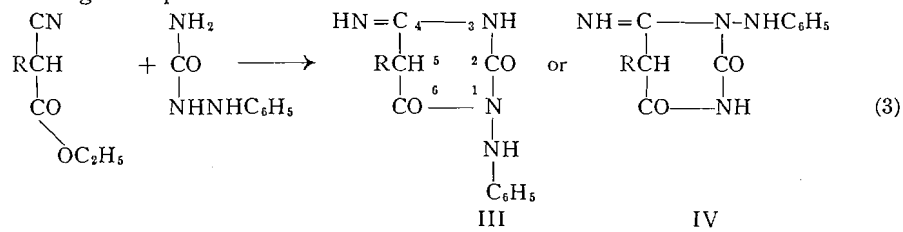
TABLE I

5-MONOSUBSTITUTED-1-ANILINO-4-IMINOBARBITURIC ACIDS

Substituent	Formula	M.p., °C.	Analysis		Ultraviolet absorption maxima			
			Nitrogen, %		Neutral		Acid	
			Calc.	Found	Log E_m	Å.	Log E_m	Å.
Methyl	$C_{11}H_{12}O_2N_4$	254–256	24.1	23.9	4.15	2250	4.12	2260
					4.37	2750	4.34	2750
Ethyl	$C_{12}H_{14}O_2N_4$	239–241	22.7	22.4	4.12	2270	4.12	2260
					4.34	2750	4.33	2750
n-Propyl[1]	$C_{13}H_{16}O_2N_4$	222–223	21.5	21.7	4.12	2270		
					4.29	2750		
n-Butyl*	$C_{14}H_{18}O_2N_4$	229–230	20.4	20.6	4.15	2270	4.22	2270
					4.36	2740	4.37	2750
n-Pentyl	$C_{15}H_{20}O_2N_4$	189–191	19.5	19.3	4.08	2270	4.12	2270
					4.26	2740	4.28	2740
n-Hexyl	$C_{16}H_{22}O_2N_4$	122–123	18.5	18.5	4.07	2270	4.19	2270
					4.28	2740	4.23	2750
n-Heptyl[2]	$C_{17}H_{24}O_2N_4$	129–130	17.7	17.7	4.14	2270	4.04	2270
					4.27	2740	4.30	2750
n-Octyl	$C_{18}H_{26}O_2N_4$	140–142	16.9	16.7	4.05	2270	4.08	2270
					4.31	2750	4.26	2750
n-Nonyl	$C_{19}H_{28}O_2N_4$	139–141	16.3	16.2	4.14	2270	4.12	2250
					4.32	2750	4.32	2750
n-Decyl	$C_{20}H_{30}O_2N_4$	136–137	15.6	15.9	4.08	2270	4.04	2270
					4.27	2750	4.29	2760
Benzyl	$C_{17}H_{16}O_2N_4$	144–145	18.3	18.5	4.18	2270	4.05	2270
					4.33	2720	4.29	2750
o-Chlorobenzyl	$C_{17}H_{15}O_2ClN_4$	202–203	16.4	16.3	4.35	2700	4.37	2700
β-*p*-Methylphenoxyethyl[3]	$C_{20}H_{19}O_3N_4$	196–197	15.9	15.6	4.35	2250	4.34	2270
					4.34	2720	4.29	2740
γ-*p*-Methylphenoxypropyl[4]	$C_{20}H_{22}O_2N_4$	130–131	15.3	15.2	4.33	2250	4.32	2250
					4.33	2730	4.31	2750
β-*p*-Ethylphenoxyethyl	$C_{20}H_{22}O_3N_4$	197–199	15.3	15.1	4.39	2270	4.45	2270
					4.37	2740	4.36	2740
γ-*p*-Ethylphenoxypropyl	$C_{21}H_{24}O_3N_4$	128–129	14.7	14.6	4.35	2250	4.32	2270
					4.32	2740	4.31	2740
γ-*p*-Chlorophenoxypropyl	$C_{19}H_{19}O_3ClN_4$	142–143	14.5	14.5	4.48	2270	4.38	2270
					4.36	2740	4.32	2740
γ-*p*-Bromophenoxypropyl	$C_{19}H_{19}O_3BrN_4$	126–128	12.9	12.7	4.47	2280	4.47	2270
					4.38	2740	4.38	2740

[1] *In alkaline solution: log E_m, 4.18 and 4.15 at 2250 and 2750 Å.*
[2] " " " " " *4.15 at 2750.*
[3] " " " " " *4.36 and 4.17 at 2250 and 2740.*
[4] " " " " " *4.36 and 4.20 at 2230 and 2740.*
**Calc. for $C_{14}H_{18}O_2N_4$: C, 61.3%; H, 6.6%. Found, 61.0%; H, 6.9%.*

cyanoacetic esters to yield iminobarbituric acids (2, 3, 7, 8). Hence, the following structures (III or IV) may be written for the compounds prepared according to Equation 3:



(3)

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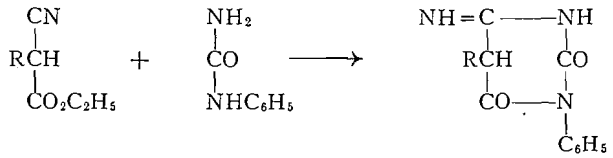
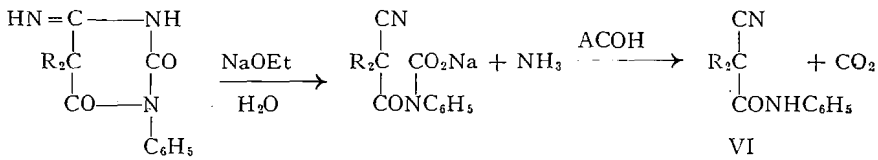
A survey of the literature revealed that substituted malonic esters condensed with 1-phenylsemicarbazide in the presence of an alkaline catalyst to yield 5-substituted-1-anilinobarbituric acids (1), although no proof of structure was given for these compounds. However, Conrad and Zart (2, 3) prepared many barbituric acids from cyanoacetic esters and phenylurea and gave evidence that formula V represents the correct structure for 5-substituted-1-phenyl-4-iminobarbituric acids (V).



V

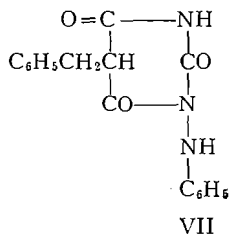
When compound V was reacted with sodium ethylate in sealed tube at high temperature, cyanoacetic anilide (VI), carbon dioxide, and ammonia were formed according to the following scheme:



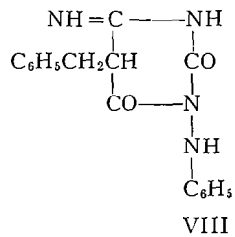
VI

From the work of Conrad and Zart it is believed that phenylurea and 1-phenylsemicarbazide should react in the same way with substituted cyanoacetic esters, and the formation of pyrazolones should be eliminated.

5-Benzyl-1-anilinobarbituric acid (VII) was prepared from benzylmalonic ester and 1-phenylsemicarbazide. By reacting under similar conditions benzylcyanoacetic ester with phenylsemicarbazide, 5-benzyl-4-imino-1- (or -3-) anilinobarbituric acid (VIII) was obtained.



VII



VIII

When 5, 5 substituted-1-phenylbarbituric acids were hydrolyzed in alkaline solution, a substance was formed which was identical with 5-benzyl-1-anilinobarbituric acid (VII). This proves that all the compounds prepared have either an actual or potential imino substituent in position 4 which is hydrolyzed into an oxo group.

The anilino substituent may be in position 1 or 3 depending on the reactivity of the cyano group of substituted cyanoacetic esters towards an amido group.

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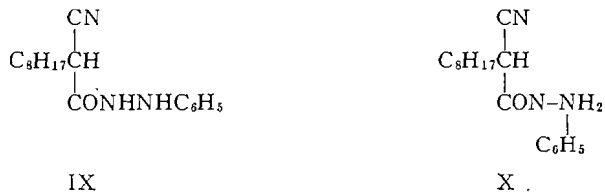
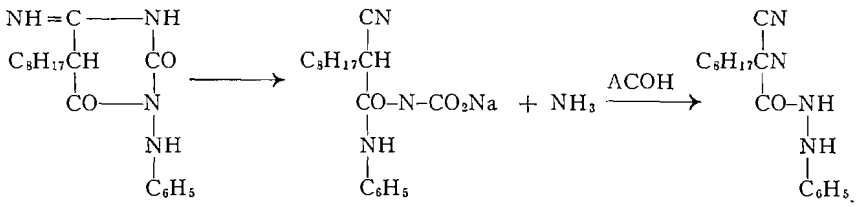
Using the method of Conrad and Zart to open the ring of barbituric acids, 5-octyl-4-imino-1 (or-3-)-anilinobarbituric acid was treated with sodium ethylate at 160°C. A compound was obtained which was insoluble in aqueous alkaline solution. Its elemental analysis corresponded to the structures IX and X.



IX X

Structure X was eliminated because the compound failed to react with aldehydes. Therefore, structure IX should be correct. This indicates that 5-substituted-1-anilino-4-iminobarbituric acids behave the same way as 5, 5-substituted-1-phenylbarbituric acids.



IX

From this study, it is concluded that 1-phenylsemicarbazide is a substance similar to phenylurea and its reaction with substituted cyanoacetic esters gives 5-substituted-1-anilino-4-iminobarbituric acids in good yields.

Experimental

5-Substituted-1-anilino-4-iminobarbituric Acids

To a cold solution of sodium (0.12 mole) in dry ethanol, substituted cyanoacetic ethyl ester (0.06 mole) and 1-phenylsemicarbazide (0.06 mole) were added. The mixture was refluxed in an oil bath at 150°C. for eight hours. The alcohol was evaporated under reduced pressure, and boiling water (250 ml.) was added to the residue. The solution was cooled and extracted with ether to remove unchanged reactants. The aqueous layer was treated with acetic acid until precipitation was complete. The solid was filtered, washed with water, and crystallized from dilute acetic acid.

The white crystalline barbituric acids were obtained in 75 to 85% yields. They are listed in Table I together with their analyses, melting points, and spectrophotometric data. Fig. 1 shows the curves obtained with 5-heptyl-4-imino-1-anilinobarbituric acid. The experimental details for the spectra measurements of similar compounds have been given previously (5).

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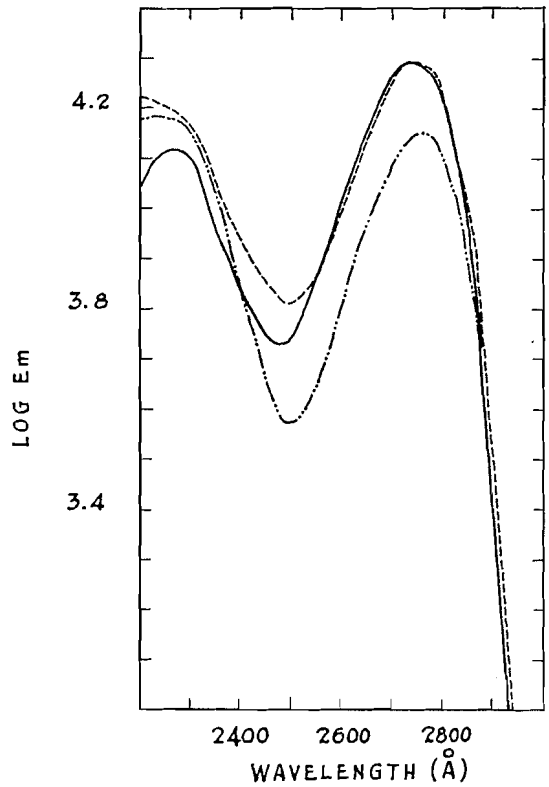

FIG. 1. *Ultraviolet absorption spectra.*
——— *5-Heptyl-4-imino-1-anilinobarbituric acid (95% ethanol).*
– – – *5-Heptyl-4-imino-1-anilinobarbituric acid (0.01 N hydrochloric acid in ethanol).*
– · · – *5-Heptyl-4-imino-1-anilinobarbituric acid (0.01 N sodium hydroxide in ethanol).*

5-Benzyl-1-anilinobarbituric Acid

To a solution of sodium (2.8 gm., 0.06 mole) in absolute ethanol (80 ml.) were added diethyl benzylmalonate (15 gm., 0.06 mole) and 1-phenylsemicarbazide (9.0 gm., 0.06 mole). The reaction mixture was refluxed for six hours at 150°C. The alcohol was evaporated and the residue dissolved in water. The solution was extracted with ether and the aqueous layer treated with hydrochloric acid until a pH of 2 was reached. A precipitate was formed which was crystallized from dilute ethanol: m.p. 107°C. Calc. for $C_{17}H_{15}O_3N_3$: N, 13.6%. Found: N, 13.9%.

5-Benzyl-1-anilino-4-iminobarbituric acid (2 gm.) was dissolved in an aqueous solution of sodium hydroxide (5%, 100 ml.). The solution was refluxed overnight while ammonia was evolved. The solution was treated with acetic acid until precipitation was complete. This precipitate was filtered off and discarded; it was the starting material. By adding hydrochloric acid until a pH of 2 was reached a new compound precipitated out which was crystallized

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from dilute ethanol: m.p. 107°C. A mixed melting point determination showed that the substance was identical with 5-benzyl-1-anilinobarbituric acid.

Hydrolysis of 5-octyl-1-anilino-4-iminobarbituric Acid

5-Octyl-1-anilino-4-iminobarbituric acid (0.33 gm., 0.001 mole) was dissolved in a solution of sodium (0.023 gm., 0.001 mole) in absolute ethanol (5 ml.). The solution was heated in a sealed tube at 165-170°C. for two hours. When the tube was opened, ammonia was evolved and a white solid was present in the mixture. Water (25 ml.) was added to dissolve the white solid. The solution was neutralized with acetic acid. Carbon dioxide was evolved and a substance precipitated. The mixture was extracted with ether. The aqueous layer did not contain any phenylhydrazine; a derivative could not be obtained with benzaldehyde. The ethereal solution was washed with sodium carbonate and water, dried over sodium sulphate, and evaporated *in vacuo*. A crystalline compound was obtained: m.p. 121-123°C. A recrystallization from ethanol raised the melting point to 125-126°C.

This compound was insoluble in water and aqueous alkaline solutions. It did not react with benzaldehyde. The substance was octylcyanoacetic phenylhydrazide (IX). Calc. for $C_{17}H_{25}ON$: N, 14.6%. Found: N, 14.8%.

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NOTE

Synthesis of *cis*- and *trans*-1, 2-Dichlorethylene-*d*[1]

The infrared absorption spectra of *cis*- and *trans*-dichlorethylene and their completely deuterated analogues were recently reinvestigated by Bernstein and Ramsay (1). In order to complete this work it was felt that *cis*- and *trans*-1, 2-dichlorethylene containing one atom of deuterium should be synthesized.

We had expected to obtain one of the desired compounds, probably *cis*-dichlorethylene-*d*, in two steps by the following reactions: (*a*) mercuration of *trans*-dichlorethylene with mercuric oxide and a trace of mercuric cyanide in the presence of sodium ethylate to mercury *bis*-dichlorethylenide, $(CHCl{:}CCl)_2Hg$, as described by Fitzgibbon (2); (*b*) hydrolysis of the mercurial in deuterium oxide containing deuterium chloride. Despite several attempts to mercurate *trans*-dichlorethylene according to the directions given by Fitzgibbon, we were never able to isolate more than traces of the mercurial which he claimed. In our experience mercury *bis*-chloracetylide, $(CCl{:}C)_2Hg$, was always obtained in addition to a large amount of polymercurated material.

The literature contains several references to the preparation of haloalkenes from salts of polyhalogenated fatty acids (7). In the present instance, sodium β-deutero-α,β,β-trichloropropionate might be expected to yield *cis*-dichlorethylene-*d*. The ordinary acid, which had not been previously reported, was prepared by chlorinating *trans*-β-chloracrylic acid at 0°C. in carbon disulphide. The *trans*-β-chloracrylic acid was in turn synthesized from propiolic acid as reported by Gryszkiewicz-Trochimowski and Schmidt (3). α,β,β-Trichloropropionic acid crystallizes from petroleum ether in white needles, m.p. 54-55°C. Neutralization equivalent: Calc. for $C_3H_3Cl_3O_2$: 177.5. Found: 176. The anilide melted at 121-122°C. When sodium α,β,β-trichloropropionate was heated under reflux in aqueous sodium carbonate, only one mole of carbon dioxide was evolved and no dichlorethylene was obtained. Apparently, hydrogen chloride was first eliminated to give α β-dichloracrylic acid which is reported to be stable in aqueous solution. It was isolated from the reaction mixture and identified by its m.p., 85-86°C., as well as that of its amide, 133-134°C. Neutralization equivalent: Calc. for $C_3H_2Cl_2O_2$: 141. Found: 143. In view of the unexpected course of the reaction, the preparation of the deuterated trichloropropionic acid was not undertaken.

Another possible route to the desired compounds appeared to be the replacement of the carboxyl group in the silver salt of α-deutero-β-bromo-α, β-dichloropropionic acid, $CHBrClCDClCO_2Ag$, by heating it under reflux with bromine in carbon tetrachloride to give 1, 2-dibromo-1, 2-dichloroethane-*d*,

[1]*Issued as N.R.C. No. 2542.*

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$CHBrClCDBrCl$. As far as is known, halogenated propionic acids have not been subjected to this reaction (5). In preliminary experiments with the silver salt of the ordinary halogenated propionic acid, the yield of polyhalide was low. For this reason the synthesis of the deuterated acid was abandoned.

It occurred to us at this stage that if deuterium bromide could be made to add abnormally to trichlorethylene, 2-bromo-1,1,2-trichlorethane-1-*d*, $CDCl_2CHClBr$, would result. This intermediate, like 1, 2-dichloro-1, 2-dibromoethane-*d* mentioned above, could then be dehalogenated to *cis*- and *trans*-dichlorethylene-*d* with zinc dust in ethanol. The abnormal addition of hydrogen bromide to trichlorethylene has been carried out by Kharasch, Norton, and Mayo (4) in the presence of ultraviolet light and peroxides. In the present work, a sealed tube containing trichlorethylene, deuterium bromide, and dibenzoylperoxide was irradiated for 42 hr. A nearly quantitative yield of 2-bromo-1,1,2-trichlorethane-1-*d*, b.p. 70-72°C. under 22 mm., n_D^{20}: 1.5295, was obtained. By treating the tetrahalide with zinc dust in ethanol, a mixture of *cis*- and *trans*-1, 2-dichlorethylene-*d* was formed. The isomers were separated by careful fractionation in a column packed with glass helices and finally distilled on a vacuum line.

In view of the fact that trichlorethylene undergoes exchange only in the presence of hydroxyl or deuteroxyl ions (6), it appeared unlikely that the compounds contained any ordinary dichlorethylene or dichlorethylene-d_2. Analysis by mass spectrometry did not definitely rule out this possibility but preliminary measurements of the infrared spectrum of each compound did not reveal significant amounts of 1, 2-dichlorethylene or its dideuterated analogue.

The results of a detailed examination of the spectra of these compounds will appear at a later date in a paper by H. J. Bernstein and A. D. Pullin.

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THE BIOGENESIS OF ALKALOIDS

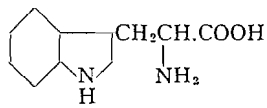
IV. THE FORMATION OF GRAMINE FROM TRYPTOPHAN IN BARLEY[1]

BY K. BOWDEN[2] AND LÉO MARION

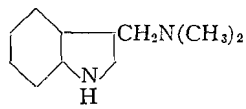
Abstract

dl-Tryptophan-β-C^{14} was fed to sprouting barley and radioactive gramine isolated from the shoots. Activity in the alkaloid resided entirely in one position, corresponding to that in the tracer administered to the plants, indicating that tryptophan is a precursor of gramine.

The alkaloid gramine, occurring in barley (4–8) and the Asiatic sedge *Arundo donax* L. (12), is a member of the indole group of alkaloids which includes abrine and hypaphorine, both of which are N-methyl derivatives of tryptophan. In view of the wide occurrence of tryptophan in the plant world and its close relationship to abrine and hypaphorine it seems very probable that it is a precursor of both these alkaloids. The same connection between tryptophan and gramine, first suggested by von Euler (8), is not as certain, as it would involve a complicated change of the side chain.



Tryptophan



Gramine

In order to examine this possibility we have administered tryptophan, labelled with C^{14} in the β-position, to barley and degraded the alkaloid formed. Barley is suitable for tracer experiments as it can be grown in glass dishes and requires only the addition of water. In addition, certain types such as Charlottetown No. 80 quickly accumulate the alkaloid in the leaves in concentrations which permit its isolation without much difficulty.

To avoid undue dispersion of radioactivity caused by metabolism the tracer was fed to the plants on the 6th day of sprouting and the leaves were harvested on the 11th day.

The alkaloid isolated from the leaves remained radioactive after repeated purification indicating that part of the tryptophan molecule has been utilized

[1] *Manuscript received August 29, 1951.*
Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2567.
[2] *National Research Council of Canada Postdoctorate Fellow (1950-51).*

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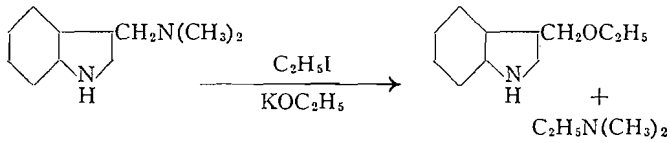
in the formation of the gramine. It was diluted with inactive gramine and subjected to two series of degradations in order to determine the location of the radioactive atom or atoms in the molecule.

(*a*) Madinaveitia (11) has shown that gramine will undergo the following reaction:



Degradation of the labelled alkaloid by this means yielded inactive ethyldimethylamine (picrate) and 3-ethoxymethylindole which had a molecular activity equal to that of the starting material, showing that the dimethylamino group in the original alkaloid contained no labelled atoms (Table I).

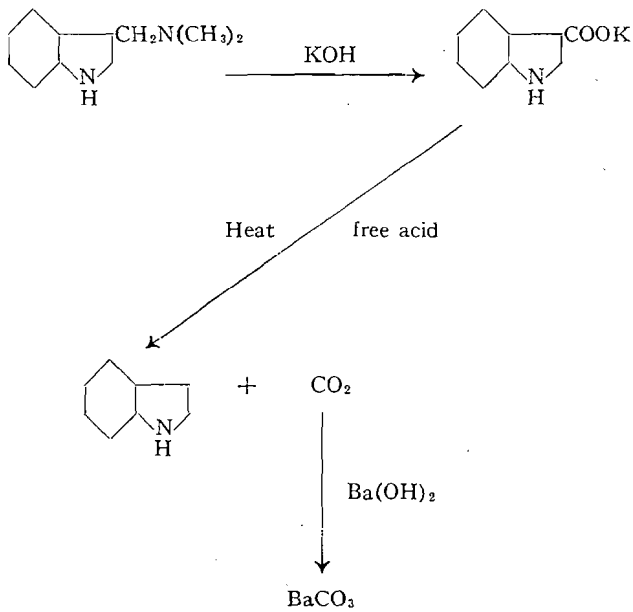
TABLE I

ACTIVITIES OF GRAMINE AND DEGRADATION PRODUCTS

Compound	Disintegrations per minute per millimole
Gramine	3.06×10^4
Ethyldimethylamine picrate	0
3-Ethoxymethylindole	3.08×10^4

(*b*) It was found that fusion of gramine with potassium hydroxide gave the potassium salt of indole-3-carboxylic acid. The free acid yielded indole and carbon dioxide on heating and the latter was converted into barium carbonate by absorption in barium hydroxide solution.

i.e.



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In order to test for possible rearrangements which might occur under the rather drastic conditions of fusion with potassium hydroxide, a synthetic sample of gramine with C^{14} in the side chain was submitted to the same treatment. The activities of the products from this material and from the natural alkaloid are given in Table II.

TABLE II

ACTIVITIES OF DEGRADATION PRODUCTS FROM NATURALLY AND SYNTHETICALLY LABELLED GRAMINE

Compound	Disintegrations per minute per millimole	
	Natural	Synthetic
Gramine	3.06×10^4	2.47×10^4
Indole-3-carboxylic acid	3.03×10^4	2.48×10^4
S-Benzyl-iso-thiouronium salt of indole-3-carboxylic acid	3.05×10^4	2.39×10^4
Indole picrate	0	0
Barium carbonate	3.04×10^4	2.46×10^4

The activities of the products obtained from the fusion of synthetic gramine with potassium hydroxide show that no rearrangements occur. The results obtained from the degradation of the natural gramine indicate that only one atom in the alkaloid molecule was labelled. The position of this labelled atom in the alkaloid corresponds with that of the C^{14} in the tryptophan fed to the plants, strongly suggesting that tryptophan is a precursor of gramine in barley.

Experimental

(All radioactive compounds were measured as thin samples in a Radiation Counters Laboratory "Nucleometer" and appropriate corrections made.)

Preparation of Labelled Tryptophan

dl-Tryptophan-β-C^{14} was prepared by suitable modifications of known procedures (1, 9, 13) using one-ninth of a millicurie of C^{14}-formaldehyde.

Administration of Tracer to Barley

A 720 gm. sample of Charlottetown No. 80 barley was grown as previously described (10), in 12 Pyrex dishes and was watered each day with distilled water, using an atomizer. The trays were stored in a closed germination cabinet.

On the 6th day of sprouting, *dl*-tryptophan acetate (0.501 gm.) containing one molecule of crystallization of acetic acid, and with an activity of 4.1×10^7 disintegrations per minute per millimole (total activity = 6.36×10^7 disintegrations per minute) was fed to the barley in 600 ml. of distilled water.

Isolation of Labelled Gramine from Barley

On the 11th day of sprouting the shoots were harvested by clipping off as close as possible to the root mat and were dried in an oven at 60°. The dry

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shoots weighed 80 gm. They were extracted without further treatment with methyl alcohol in a Soxhlet extractor for 48 hr. and the extract then evaporated down to dryness under reduced pressure.

The residue was taken up in 2*N* sulphuric acid (200 ml.) and then extracted twice with 100 ml., then four times with 50 ml. of diethyl ether. The aqueous layer was cooled in ice, and sodium hydroxide (25 gm.) in a minimum of water was added with stirring. The mixture was extracted three times with 100 ml., then four times with 50 ml. of diethyl ether and the ethereal solution washed with water (100 ml.).

The ethereal solution was dried over anhydrous sodium sulphate and the solvent removed under reduced pressure to give a crystalline residue (0.45 gm.) which distilled under reduced pressure as a liquid (b.p. 90–100° at 10^{-4} mm.) and which crystallized in the receiver (0.28 gm.). The product was recrystallized from benzene to give long needles (0.2456 gm.), m.p. 133° undepressed on admixture with an authentic specimen of gramine.

Anal. Calcd. for $C_{11}H_{14}N_2$: C, 75.84; H, 8.10; N, 16.09
Found: C, 76.01; H, 8.19; N, 16.06%.

The sample had specific activity of 583.9 disintegrations per minute per milligram. It was recrystallized from benzene and 0.2155 gm. of the product mixed with 0.4995 gm. of inactive gramine and the whole recrystallized from benzene to give 0.6574 gm. of gramine with specific activity of 3.06×10^4 disintegrations per minute per millimole. Degradation studies were carried out on this material.

Degradations of Gramine Obtained from Plant

(*a*) The diluted gramine (0.2 gm.) was dissolved in absolute alcohol (1 ml.) and freshly distilled ethyl iodide (0.2 ml.) added. Crystals of the ethiodide began to form almost immediately. After two hours at room temperature ethanolic potassium hydroxide (0.5 ml. of 25% solution) was added and the air was slowly passed through the mixture for seven hours. The issuing gases were bubbled through a saturated solution of picric acid in methyl alcohol.

The resulting ethyldimethylamine picrate was filtered off and dried (0.0777 gm.) and after recrystallization from methyl alcohol melted at 204–205°. Water was added to the reaction mixture, giving an oil which crystallized. This was filtered off, taken up in ether, dried, and after removal of the solvent, recrystallized from petroleum (b.p. 50–80°) as needles (0.112 gm.), m.p. 67.5°.

Anal. Calcd. for $C_{11}H_{13}ON$: C, 75.37; H, 7.47; N, 8.0
Found: C, 75.29; H, 7.24; N, 7.89%.

Madinaveitia (11) gives the melting point of 3-exthoxymethylindole as 93–94°. We were unable to confirm this, our product always melting at 67.5°. This was also the melting point of the product when methyl iodide,

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in ethyl alcohol, was used in place of ethyl iodide, indicating the source of the ethyl group to be the ethyl alcohol.

The activities of the compounds in the above degradation are given in Table I.

(*b*) Gramine obtained from the plant and synthetic labelled gramine were both degraded by the following method, the activities of the resulting compounds being given in Table II.

Gramine (0.4 gm.) was added in small portions to potassium hydroxide pellets (5 gm.), heated just to fusion in a platinum crucible. When the reaction was complete and the mixture had cooled, it was taken up in a little distilled water and then extracted twice with an equal volume of diethyl ether. The aqueous portion was cooled in ice and acidified with concentrated sulphuric acid, extracted well with diethyl ether, and the ethereal solution dried over anhydrous sodium sulphate. On removal of the solvent under reduced pressure, crude indole-3-carboxylic acid was obtained as a pale yellow solid, m.p. 195° (decomp.) (0.2916 gm.). After being washed with a little diethyl ether it melted at 209° (decomp.) (0.2112 gm.). The free acid readily decomposes on heating in the solid state or in solution.

The S-*benzyl-iso-thiouronium* salt crystallized from water, m.p. 157.5° (decomp.).

Anal. $C_{17}H_{17}O_2N_3S$ requires C, 62.38; H, 5.21; N, 12.83
Found: C, 62.49; H, 5.08; N, 12.80%.

It showed no depression of melting point when mixed with the corresponding salt of an authentic specimen of indole-3-carboxylic acid prepared from indole through the aldehyde (2, 3).

Indole-3-carboxylic acid, from the potassium hydroxide fusion (0.104 gm.) was decarboxylated in a small vertical tube fitted with a nitrogen inlet leading almost down to the bottom of the tube. The issuing gases were bubbled through barium hydroxide solution (5 ml. of 4%). The apparatus was first flushed out with carbon dioxide-free nitrogen and the lower part of the tube containing the indole carboxylic acid was slowly heated in a metal bath to 190°, at which temperature evolution of carbon dioxide started. Decarboxylation was complete at 220° and the temperature was finally raised to 240°, when indole distilled up the tube and crystallized out on the upper parts. Residual carbon dioxide was swept out of the tube with a stream of nitrogen. The precipitated barium carbonate was filtered off, washed well, and dried (0.0918 gm.).

The indole (0.0503 gm.) was converted into its picrate which crystallized from methyl alcohol as crimson plates and melted at 187.5°, undepressed on admixture with an authentic specimen of indole picrate.

Anal. Calcd. for $C_{14}H_{10}N_4O_7$: C, 48.54; H, 2.91; N, 16.17
Found: C, 48.78; H, 2.77; N, 15.86%.

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Acknowledgment

The authors are indebted to Mr. R. B. MacLaren of the Experimental Station, Charlottetown, P.E.I., for supplying the barley used in these experiments.

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THE BIOGENESIS OF ALKALOIDS

V. RADIOAUTOGRAPHS OF BARLEY LEAVES FED WITH TRYPTOPHAN-β-C^{14} [1]

By K. Bowden[2] and Léo Marion

Abstract

Radioautographs of leaves of barley fed with C^{14}-tryptophan have been taken at intervals. In the early stages of development a radioactive area appeared at the bottom of the leaves, which was due mainly to free tryptophan. Later an area, consisting mainly of gramine, developed at the top of the leaves.

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In a previous publication (2) we have shown that Charlottetown No. 80 barley fed with tryptophan-β-C^{14} produces in the leaves gramine, labelled in the same position in the side chain, indicating that the amino-acid is a precursor of the alkaloid.

In order to study the assimilation of tryptophan by the plant and the accumulation in it of the alkaloid, we have administered the labelled amino-acid to the plant and have taken radioautographs of the leaves harvested at intervals.

Approximately sixty seeds of Charlottetown No. 80 barley were grown in a Petri dish in a closed germination cabinet and were moistened each day with distilled water. On the fifth day of sprouting the acetate of *dl*-tryptophan-β-C^{14}(0.1 gm.), with an activity of 4.1×10^7 disintegrations per minute per millimole was fed to the plants in distilled water (30 ml.).

Twenty-four hours afterwards and each day following, for five days, seven leaves were harvested by clipping them off as close as possible to the seeds and were dried flat between glass slides (2 in. × 7 in. × $\frac{1}{4}$ in.) in an oven at 65°. In order to obtain some measure of the rate of absorption of the amino-acid by the plant and the exposure to the X-ray film that each leaf would require to give a satisfactory radioautograph, two dried leaves were assayed from each day's harvest. The leaves, cut into suitable portions, were pressed flat on to the sticky surface of cellophane tape covering a small cardboard disk. The leaf-covered disk was then assayed in a Radiation Counters Laboratory "Nucleometer". The "count", without any corrections for sample thickness, geometry, etc., for leaves harvested 24 hr. after the administration of the tracer was 409 per leaf per minute, indicating that entry of the amino acid into the plant was fairly rapid. The count rose to 2000 per leaf per minute for leaves harvested subsequently.

Axelrod (1) has found that about ten million β-particles per square centimeter produce a satisfactory radioautograph. As the total activity of a leaf

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Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2544.
[2] *National Research Council of Canada Postdoctorate Fellow (1950-1951).*

gives only a rough indication of the exposure to X-ray film required, five leaves from each day's harvest were set up in separate radioautograph units and were developed after varying lengths of exposure.

Each unit consisted of a strip of Kodax "No Screen" X-ray film (7 in. × 2 in.) against which the flat leaf was placed. The two were sandwiched between glass slides (7 in. × 2 in. × $\frac{1}{4}$ in.) held together by metal clips along the long edges. Each unit was wrapped in light-proof paper and stored in a refrigerator until developed.

Development was carried out in Ansco "Liquadol" X-ray developer for three minutes at 20° and the films were fixed for five minutes at 20° in Ansco "Liquafix" acid fixer. All manipulations of the X-ray film were carried out by the light of a Kodax 6B safelight.

A series of radioautographs, each of one week's exposure to X-ray film, are given in Plate I. The first is of a leaf harvested one day after the tracer was fed to the plants and those which follow are of leaves harvested at daily intervals from then onwards.

Discussion

As may be seen from the radioautographs, an active area appears at the bottom of the leaf on the first day and slowly extends upwards on the second and third days. On the fourth day an active area makes its appearance at the top of the leaf and this area of concentration increases on the fifth and sixth days.

It has been shown by ultraviolet absorption studies that the concentration of gramine in a barley leaf increases towards the tip of the leaf (3). It seemed to us likely, therefore, that the area of activity in the lower part of the leaf might be due to tryptophan or a gramine precursor, whilst the area at the tips of the leaves might be due to an accumulation of gramine.

Although tryptophan occurs widely in plants and has been isolated from barley protein (4) it could not merely be assumed to exist in a simple form in the lower area of the leaves of Charlottetown No. 80 barley.

In order to test whether this was so, a dried radioactive leaf, harvested six days after the administration of the tracer, was cut transversely, separating from each other the two areas of radioactivity shown by radioautography. The two areas were then assayed separately in the "Nucleometer".

The top section of the leaf was cut into portions and soaked overnight in methyl alcohol (5 ml.) containing inactive gramine (25 mgm.). The solution was then filtered and the alcohol removed under reduced pressure and the gramine recrystallized from benzene to constant activity.

The lower portion of the leaf was treated similarly with a solution of inactive tryptophan acetate (25 mgm.) in glacial acetic acid (2.5 ml.). After filtration

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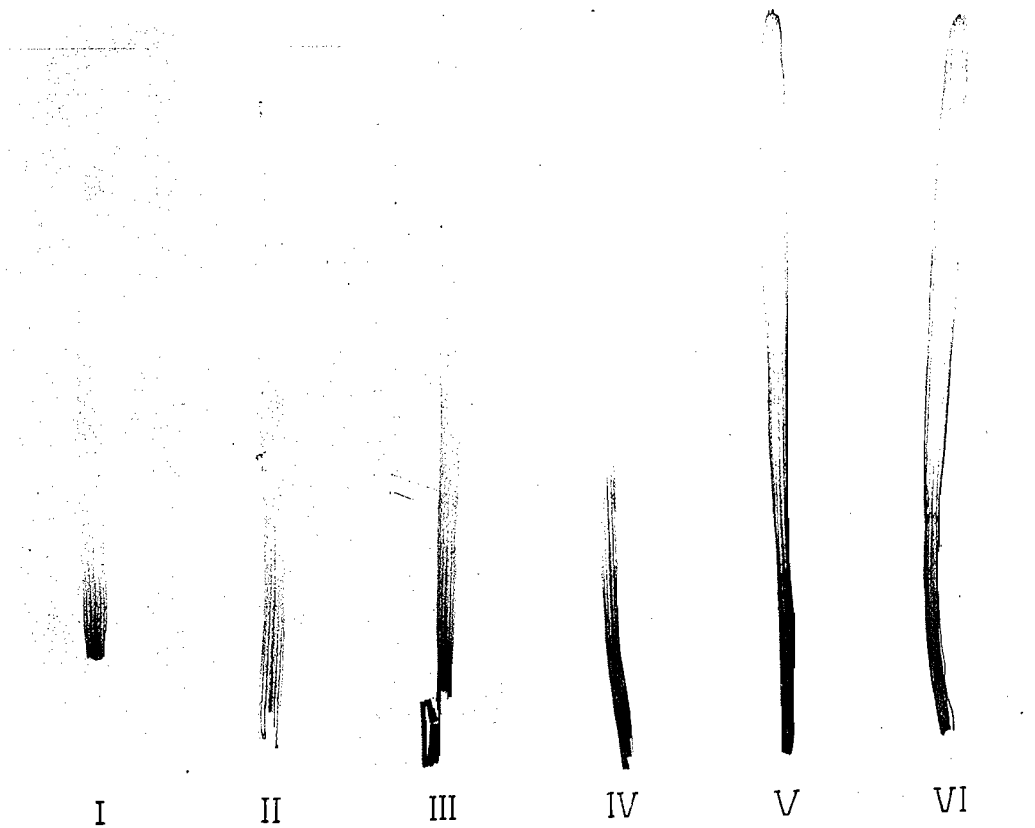
PLATE I



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of the solution, the tryptophan was recrystallized to constant activity from glacial acetic acid.

By this means it was possible to show that approximately 58% of the activity in the area at the top of the leaf was due to free gramine, whilst approximately 77% of the activity in the lower part of the leaf was due to free tryptophan, thus confirming that the radioactive areas were mainly concentrations of gramine and its probable precursor, tryptophan, respectively.

Although these figures are only approximate, the lower proportion of gramine extracted in comparison to the tryptophan is probably significant, suggesting the presence of metabolites closely related to gramine in the area of activity at the top of the leaf.

By feeding labelled gramine (as acetate) to the barley, radioautographs were obtained showing the active areas only at the bottom of the leaves, indicating that gramine does not tend to travel to the top of the leaf and accumulate there. It would appear then that the active area which appears at the top of the leaf when the plant is fed with labelled tryptophan is the site of formation of the gramine and not just an area of accumulation of the alkaloid.

Our experiments show that tryptophan is readily absorbed by the plant and can exist as such in the leaves and also that gramine is formed in the leaves at least up to the 11th day of growth. It has been shown by spectroscopic means that during this period the total amount of gramine in the leaves remains constant (3). Therefore it appears probable that during this period the rates of formation and utilization of the gramine in the plant are approximately equal. After one month the gramine disappears from the leaf (3) indicating that in later stages of development of the plant this relationship no longer holds.

Acknowledgments

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CINÉTIQUE DE L'OXYDATION DE LA FORMALDÉHYDE PAR L'EAU OXYGÉNÉE EN SOLUTION ALCALINE[1]

PAR JEAN-B. JAILLET[2] ET CYRIAS OUELLET

Résumé

L'oxydation de la formaldéhyde a été étudiée, par mesure de l'hydrogène dégagé, dans des solutions aqueuses de pH 12-13, entre 0° et 35°C. et à des concentrations de 0.05 à 0.4 mole/litre. La réaction est du second ordre par rapport au temps, mais le taux varie par un facteur de 30 suivant les concentrations et proportions initiales des réactifs. L'énergie d'activation est de 14.5 kcal./mole. L'addition d'hydroquinone ou de sulfate de sodium ou un accroissement modéré de la surface de Pyrex sont sans influence. La vitesse de décomposition du peroxyde de diméthylol est identique à celle du mélange formaldéhyde—eau oxygénée équivalent. Le delta cryoscopique des solutions passe par un minimum. On examine l'hypothèse de la décomposition bimoléculaire d'un peroxyde intermédiaire et de l'intervention de polymères de la formaldéhyde.

Introduction

En solution aqueuse fortement alcaline, le réaction de l'eau oxygénée avec la formaldéhyde donne lieu à un dégagement quantitatif d'hydrogène suivant l'équation:

$$2HCHO + H_2O_2 + 2NaOH = 2HCOONa + 2H_2O + H_2.$$

Cette réaction, découverte par Blank et Finkenbeiner (3), a été utilisée pour le dosage gazométrique de la formaldéhyde. L'oxygène et l'acide carbonique peuvent aussi se former dans certaines conditions (1, 7, 8, 11, 14, 19), mais nous avons opéré en solutions diluées et fortement alcalines (pH 13) où l'on obtient seulement l'acide formique et l'hydrogène. On obtient aussi ces deux produits en remplaçant l'eau oxygénée par l'oxyde cuivreux (10) ou par une oxydation anodique (15). Glasstone et Hickling (9) attribuent ce dernier effet à l'eau oxygénée formée par la recombinaison des radicaux hydroxyles provenant de la décharge des ions hydroxyles à l'anode. L'oxydation de la vanilline (16) semble être le seul autre cas connu de production d'hydrogène par oxydation d'une aldéhyde au moyen de l'eau oxygénée.

Dans le but d'élucider le mécanisme de la réaction entre l'eau oxygénée et la formaldéhyde, Fry et Payne (7) ont étudié les produits obtenus dans diverses conditions. Wirtz et Bonhoeffer (22) ont montré, à l'aide du peroxyde de deutérium, que l'oxygène dégagé provient uniquement de la formaldéhyde, tel que prévu par la théorie de la déshydrogénation de Wieland (20, 21). Du point de vue cinétique, Kastle et Loevenhart (12) ont calculé des constantes du second order à 50, 60 et 70°C., Hatcher et Holden (11) ont suivi la neutralisation de la soude par l'acide formique produit. Pour compléter ces données, nous avons étudié la cinétique de la réaction dans les conditions où elle obéit à l'équation chimique donnée ci-dessus.

[1] *Manuscrit original reçu le 20 décembre 1950, et sous forme revisée le 5 septembre, 1951. Contribution du Département de Chimie, Université Laval, Québec. P.Q.*

[2] *Boursier Cominco. Adresse actuelle: Ecole Polytechnique, Montréal, P.Q.*

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Méthode experimentale

Pour suivre la marche de la réaction, on mesurait la pression de l'hydrogène dégagé au moyen d'un manomètre différentiel à mercure. Dans le but de prélever, pour fins d'analyse, plusieurs échantillons de gaz au cours d'une même réaction, on s'est servi d'un appareil de grand volume (1600 cc.), qui se composait d'un ballon en Pyrex contenant un agitateur magnétique et relié aux autres organes au moyen d'un réfrigérant à reflux qui empêchait la distillation de la vapeur d'eau. Après avoir introduit la solution alcaline de formaldéhyde, on évacuait le système au moyen d'une trompe à eau puis on injectait rapidement une quantité mesurée de solution d'eau oxygénée au moyen d'une burette soudée au col du ballon et dont l'orifice était un long tube capillaire. Pour empêcher la solution de s'échauffer au début des réactions les plus rapides, on ajoutait graduellement par le capillaire une quantité connue (10-20 cc.) d'eau glacée; dans le cas des réactions à 0°C., on incorporait à la solution de formaldéhyde 10 grammes de glace pulvérisée. La réaction terminée, on aspirait un échantillon du gaz dans une ampoule évacuée préalablement au moyen d'une pompe Hyvac et on refoulait cet échantillon dans un analyseur à gaz de Haldane, modèle C, comportant une burette de 21 cc. dont 6 cc. sont gradués au centième de cc.

Une solution fraîche de soude et de formaldéhyde était préparée avant chaque expérience en dissolvant dans une solution de soude fraîchement titrée une quantité pesée à 0.001 gramme près de paraformaldéhyde de marque Eastman, qui se dépolymérise rapidement en milieu alcalin pour donner de la formaldéhyde monomérique. Des analyses de la paraformaldéhyde, effectuées au moyen de la réaction même que nous voulions étudier, ont indiqué une teneur de 99.2 à 99.7% en formaldéhyde. Les solutions d'eau oxygénée étaient titrées au permanganate après avoir été préparées par dilution soit de solutions à 90% de Buffalo Electrochemical Co., soit d'une solution à 30% de McArthur Chemical Co. On a obtenu des vitesses de réaction identiques avec des solutions d'eau oxygénée contenant des stabilisateurs ou n'en contenant pas.

Résultats

Observations préliminaires

Pour des motifs de commodité, la plupart des réactions ont été effectuées dans des conditions telles que le volume d'hydrogène dégagé fût de l'ordre de 500 cc. ramené aux conditions normales (T.P.N.). Sauf indication contraire, le volume de la solution était de 450 cc. Les quantités de réactifs employées dans les divers mélanges étaient généralement des multiples simples d'une quantité unitaire de 0.0225 mole, correspondant à une concentration de 0.05 mole par litre. Pour faciliter les références aux diverses réactions, les trois réactifs sont partout désignés dans l'ordre: formaldéhyde-eau oxygénée-soude (F-P-S) et leurs concentrations indiquées par trois chiffres placés dans le même ordre. Par exemple, la cote 4-1-2 représente un mélange de 0.2 mole/litre de HCHO, 0.05 mole/litre de H_2O_2, 0.1 mole/litre de NaOH. Le chiffre 1 représente 0.05 mole/litre.

TABLEAU I

RENDEMENTS DE DIVERSES RÉACTIONS EN CC. DE H_2 RAMENÉS À 0°C. ET 760 MM. (T.P.N.)

Solution F-P-S	H_2 cc. T.P.N.	H_2 obs. / H_2 calc.	Solution F-P-S	H_2 cc. T.P.N.	H_2 obs. / H_2 calc.	O_2 %
2-1-2	492	0.98	1-1-2	263	1.05	–
2-1-8	508	1.01	2-2-2	355	0.71	–
6-1-2	498	1.00	8-1-2	485	0.97	–
4-1-2	485	0.97	16-1-2	466	0.93	3.5
			20-1-2	407	0.81	9
10-1-2	490	0.98	24-1-2	365	0.73	6
6-1-2	492	0.98	24-1-0	–	–	1
8–¾–2	393	1.05	0-2-2	–	–	1

Des mesures préliminaires ont vérifié que la quantité d'hydrogène dégagée était, dans presque tous les cas, celle que prévoit l'équation:

$$2HCHO + H_2O_2 + 2NaOH = 2HCOONa + 2H_2O + H_2$$

On voit, par les exemples donnés au tableau I, comment cette quantité est limitée par celle de l'un des réactifs. On y trouve aussi les rare exceptions où le rendement est inférieur au rendement théorique.

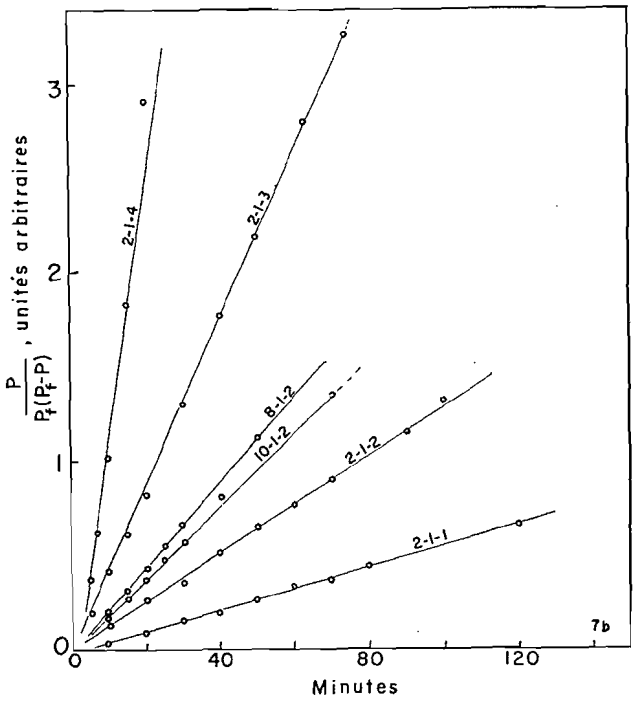

FIG. 1. *Série de réactions à 0°C. dans 450 cc. de solution, montrant la variation linéaire en fonction du temps de l'expression*

$$\frac{P}{P_f(P_f - P)}.$$

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Trois solutions, contenant chacune de la formaldéhyde en grand excès, ont fourni des quantités d'oxygène appréciables, pas suffisantes cependant pour combler le déficit en hydrogène. Afin de voir si cet oxygène devait être attribué à la simple décomposition de l'eau oxygénée durant ces réactions très lentes, des mesures ont été effectuées sur des solutions d'eau oxygénée avec de la formaldéhyde seulement (24-1-0) ou de la soude seulement (0-2-2). Les quantités d'oxygène recueillies au bout de trois et une heures respectivement sont très faibles. Il semble donc que l'oxygène dégagé en présence d'un grand excès de formaldéhyde soit véritablement un produit latéral de la réaction d'oxydation.

La recherche de l'oxyde de carbone au moyen de papiers imbibés de chlorure de palladium a donné des résultats négatifs dans tous les cas. Il en fut de même

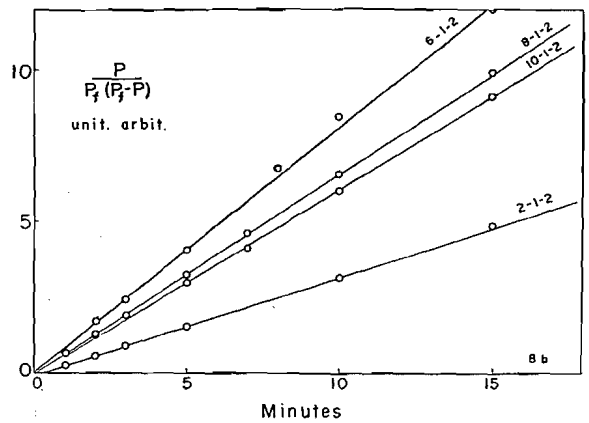

FIG. 2. *Série de réactions à 25°C. dans 450 cc. de solution, montrant la variation linéaire en fonction du temps de l'expression*

$$\frac{P}{P_f(P_f - P)}.$$

de celle de l'anhydride carbonique, soit par l'hydroxyde de baryum dans la solution après la réaction, soit par la potasse dans l'appareil de Haldane.

A la suite de ces constatations, nous nous sommes contentés d'analyser le gaz chaque fois que le rendement s'écartait de plus de 2% du rendement théorique. Le prélèvement d'échantillons de gaz au cours de la réaction est devenu, à plus forte raison, superflu. Les trois réactions indiquées au tableau I restent les seules qui aient produit de l'oxygène.

Les courbes de la figure 8 indiquent l'allure générale de la réaction. Les vitesses sont reproductibles avec une précision de l'ordre de 2%, à condition que le taux d'agitation soit supérieur à un taux minimum qui fut déterminé dans des essais préliminaires.

L'addition de sulfate de sodium à la concentration de 0.5 mole/litre et celle d'hydroquinone à la concentration de 0.001 mole/litre ont donné des courbes superposables à celles obtenues avec les mêmes solutions sans ces additions.

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L'étape qui limite la vitesse n'est donc pas de nature ionique et ne comporte probablement pas de chaînes. De même, l'addition de Pyrex pulvérisé présentant une surface de l'ordre de deux fois celle du ballon n'a produit aucun effet. Cependant, l'addition de 64 grammes de Pyrex pulvérisé, dont nous avons estimé la surface à 8000 cm.^{2}, a modifié radicalement l'allure de la réaction. Cette réaction est plus lente au début que la réaction normale, mais sa vitesse reste constante (ordre zéro) et elle parvient à terme avant l'autre. Le produit de cette réaction était normal, soit 99% du rendement théorique en hydrogène. Cet effet remarquable mériterait d'être étudié en détail. On peut cependant conclure que la réaction ordinaire, dans les conditions où nous l'avons étudiée, est homogène.

Ordre de la réaction

L'analyse des courbes a révélé qu'elles n'obéissent à aucun ordre simple si l'on introduit dans les équations les valeurs des concentrations initiales des réactifs et celles des concentrations de l'hydrogène produit. Par contre, toutes les réactions, à de très rares exceptions près, suivent avec une assez bonne approximation la relation (1*a*)

$$A = \frac{1}{t} \cdot \frac{P}{P_f(P_f - P)} \quad (1a); \quad k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)} \qquad (1b)$$

où P est la pression de l'hydrogène au temps t, P_f la pression finale et A une constante. Les droites des figures 1 et 2 illustrent cette relation par deux séries d'exemples.

La forme de (1*a*) est identique à celle de (1*b*), équation du second ordre pour le cas spécial où les deux réactifs sont à des concentrations initiales égales, soit $a = b$. Ici, la pression P de l'hydrogène représente la concentration x d'un produit de la réaction, tandis que la concentration initiale a des réactifs correspond à la concentration finale de l'hydrogène, proportionnelle à P_f. La constante A est l'analogue d'une constante du second ordre k_2. Tout indique que la première étape de la réaction est la formation rapide et probablement irréversible d'un complexe, dont la quantité est forcément limitée par celle de l'un des réactifs, et qui se décompose ensuite suivant une loi du second ordre.

Quelques mesures de la variation du pH en fonction du temps, effectuées au moyen d'une électrode de verre sur des mélanges 2-1-2 et 2-1-1 à 25°C., indiquent que la concentration des ions H^+ croît suivant une loi du second ordre. Mais ces résultats, obtenus sans précaution spéciale et en présence du système oxydo-réducteur formaldéhyde-eau oxygénée, ne constituent qu'une confirmation semi-quantitative de l'ordre de la réaction.

Influence des concentrations

Le comportement de la réaction se complique de façon inattendue lorsque l'on fait varier les concentrations et les proportions initiales des réactifs. A diverses concentrations d'une solution dans laquelle la formaldéhyde, l'eau oxygénée et la soude se trouvent dans les proportions 4-1-4, la vitesse initiale v_i,

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exprimée en cm. Hg par minute, varie sensiblement comme le carré de la concentration (Tableau II), comme on devait s'y attendre. Cependant le coefficient A de l'équation (1a), loin de rester constant, varie à peu près comme v_i.

TABLEAU II

VARIATION DE LA VITESSE INITIALE v_i ET DU COEFFICIENT A À 25°C., EN FONCTION DE LA CONCENTRATION C_F EN MOLES PAR LITRE DE LA FORMALDÉHYDE POUR DES MÉLANGES DE COMPOSITION 4-1-4

C_F moles/litre	0.125	0.16	0.23	0.30	0.45	0.83
v_i	1.5	2.6	5.5	8.8	17.9	–
v_i / C_F^2	95	105	95	105	85	–
A	0.224	–	0.79	–	3.53	14.1
A / C_F^2	14.5	–	15	–	17	20

En appelant $\left(\frac{dP}{dt}\right)_i$ le taux initial de dégagement de l'hydrogène, on peut donc écrire:

$$v_i = \left(\frac{dP}{dt}\right)_i = A(P_f - P)^2 \qquad (1c)$$

Mais nous allons voir que A, qui joue le rôle d'une constante du deuxième ordre pour chaque réaction individuelle, dépend du rapport initial des concen-

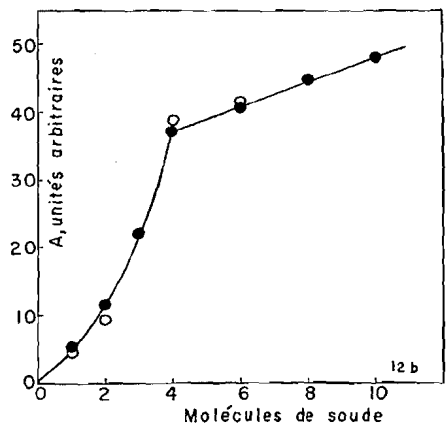

FIG. 3. *Influence de la proportion de la soude sur la vitesse représentée par le facteur A (équation 1a). Réactions à 0°C. dans 450 cc. (cercles noirs) et 210 cc. (cercles blancs), valeurs de A réduites proportionnellement pour montrer la coincidence des courbes. En abcisses, le nombre de molécules de NaOH pour 2HCHO et 1 H_2O_2 (série 2-1-S).*

trations des réactifs. En effet, si l'on modifie les rapports des concentrations des réactifs, chaque réaction obéit encore à l'équation (1a), mais la valeur de A (comme celle de v_i qui lui est sensiblement parallèle) varie d'une façon complexe comme le montrent les figures 3, 4 et 5. Chacun de ces graphiques illustre l'effet de la variation de la concentration de l'un des réactifs, celles des deux autres étant constantes. La vitesse croît rapidement avec la con-

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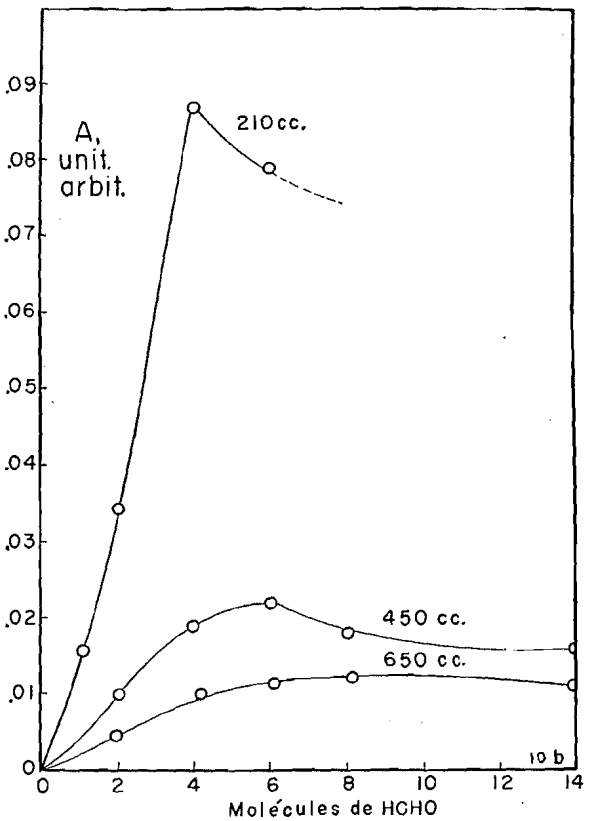

FIG. 4. *Valeurs de A en fonction de la proportion de formaldéhyde à 0°C. En abcisses, nombre de molécules de HCHO pour 1 H_2O_2 et 2 NaOH (série F-1-2). Les ordonnées sont à des échelles différentes.*

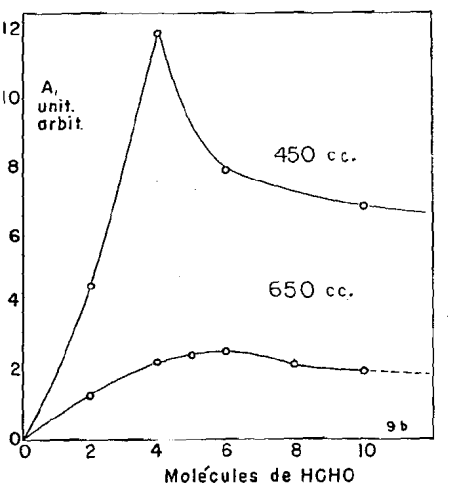

FIG. 4*a*. *Valeurs de A en fonction de la proportion de formaldéhyde à 25°C. En abcisses, nombre de molécules de HCHO pour 1 H_2O_2 et 2 NaOH (série F-1-2).*

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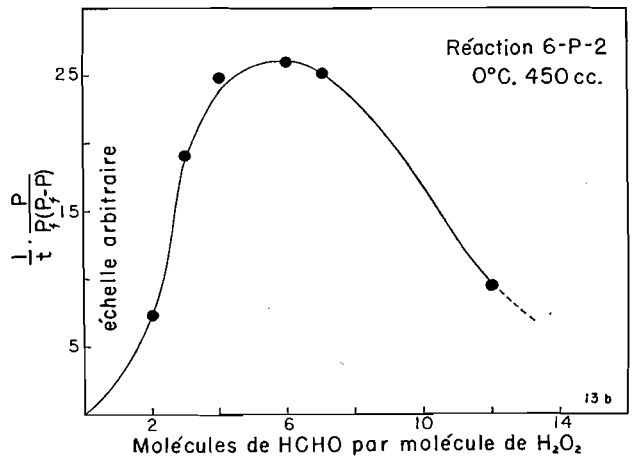

FIG. 5. *Influence de la proportion de l'eau oxygénée à 0°C., pour la série de compositions 6-P-2*

centration de la soude, mais une discontinuité apparaît à la composition $S/P = 4$ et $S/F = 2$. Lorsqu'on augmente la proportion de la formaldéhyde, on obtient une vitesse maximum à une composition qui dépend de la concentration de la solution. On observe aussi un maximum en fonction de la proportion de l'eau oxygénée. Les variations brusques d'allure semblent confirmer l'hypothèse de la formation d'un composé intermédiaire.

Le maximum de vitesse obtenu en faisant varier la proportion de la formaldéhyde se déplace en fonction de la concentration absolue de la façon indiquée sur les figures 4, 4*a* et 6. Il semble tendre vers la composition stoechiométrique 2-1-2 à concentration infinie.

Coefficient de température

Malgré ces complications, le coefficient de température est remarquablement simple. Si l'on porte log A contre l'inverse $1/T$ de la température absolue, on

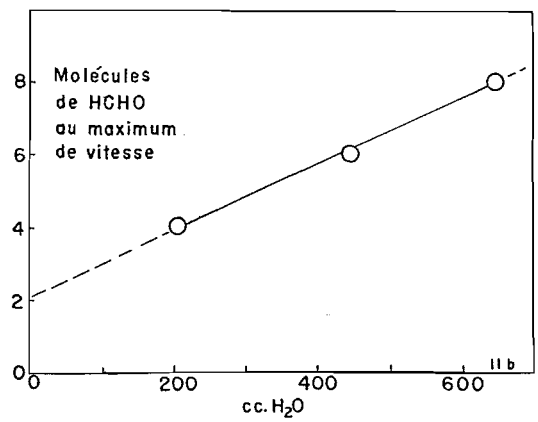

FIG. 6. *Déplacement de la position du maximum de vitesse en fonction de la dilution, pour la série de compositions F-1-2 à 0°C.*

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obtient, pour des solutions de compositions très différentes, l'ensemble de droites parallèles de la figure 7. Le coefficient de température reste constant entre 0° et 25°C., est indépendant de la composition et correspond à une énergie d'activation $\Delta H_a = 14.5 \pm 0.3$ kcal./mole. A partir de cette valeur de ΔH_a et du temps de demi-réaction d'un mélange 2-1-2 à 0°C., nous avons calculé en supposant le second ordre, ce que seraient la valeur de k en litres $\times$ moles^{-1} $\times$ secondes^{-1} et celle du facteur S dans l'équation

$$k = Se^{-14500/RT}.$$

On obtient ainsi $S = 5 \times 10^{10}$, tandis que la valeur la plus fréquente est de l'ordre de 3×10^{11}. Cette réaction n'est donc pas affectée d'un facteur stérique

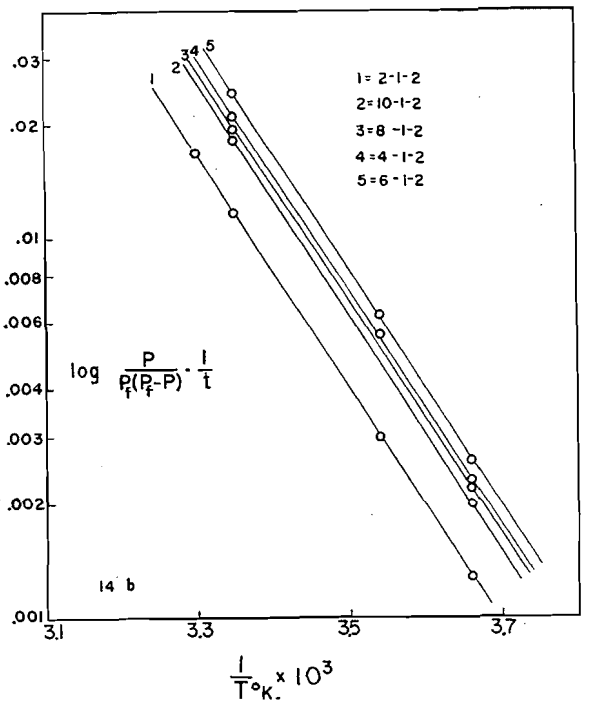

FIG. 7. *Variation de log A en fonction de 1/T °K. pour des réactions aux compositions 2-1-2, 10-1-2, 8-1-2, 4-1-2 et 6-1-2.*

appréciable et ne semble pas non plus comporter de longues chaînes. Naturellement, ceci n'indique que l'ordre de grandeur, puisque notre facteur A varie suivant la composition du mélange.

Décomposition du peroxyde de diméthylol

D'après Rieche et Meister (17, 18), le peroxyde de diméthylol (19) se décompose en solution alcaline suivant:

$$HOCH_2-O-O-CH_2OH + 2NaOH = 2HCOONa + 2H_2O + H_2.$$

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Nous avons préparé ce peroxyde par la méthode de Fenton (6) et obtenu comme lui des cristaux fondant à 63-65°C. Des mesures cryoscopiques faites sur ce composé ont montré qu'il se trouve à l'état monomérique en solution aqueuse, les poids moléculaires trouvés étant de 87 et 98, tandis que celui de ce peroxyde est de 94.

Dissous dans l'eau et additionné de soude pour donner un mélange de composition équivalente à 2-1-2, ou de soude et de formaldéhyde pour donner 4-1-2, ce composé PF_2 nous a donné des réactions dont les courbes se superposent exactement à celles des mélanges 2-1-2 et 4-1-2 correspondants (Fig. 8).

Du point de vue de l'interprétation de notre réaction, ces résultats peuvent s'expliquer de deux façons: (*a*) en solution aqueuse, P et $2F$ forment PF_2 qui réagit ensuite avec la soude pour donner de l'hydrogène et les autres produits

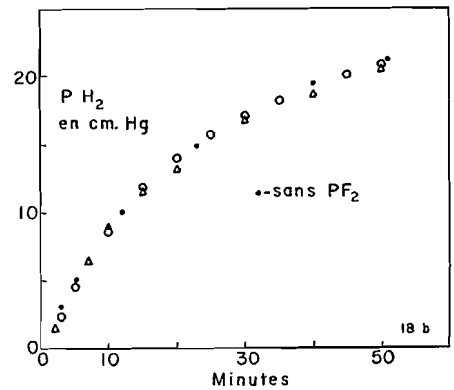

FIG. 8. *Identité des taux de deux réactions du peroxyde de diméthylol PF_2 additionné de soude, et d'un mélange de composition correspondante (2-1-2) à 0°C.*

ou bien, (*b*) PF_2 en solution alcaline se dissocie en $P + 2F$, qui réagissent avec la soude suivant un mécanisme inconnu. La seconde hypothèse nous ramène au cas trivial où PF_2 servirait seulement à fournir les ingrédients de la réaction.

Cryoscopie de mélanges d'eau oxygénée et de formaldéhyde

Dans l'espoir de résoudre le problème du complexe intermédiaire, posé par ces derniers résultats et par les discontinuités des courbes des figures 3, 4 et 4*a*, nous avons amorcé une étude cryoscopique des mélanges d'eau oxygénée et de formaldéhyde en solution aqueuse. Il a été malheureusement impossible de faire porter cette étude sur des solutions fortement alcalines parce que la réaction serait très rapide aux concentrations où il faut opérer pour observer des abaissements suffisants du point de congélation. Nous avons ajouté seulement la trace de soude nécessaire pour obtenir la dépolymérisation de la paraformaldéhyde.

Une solution de 0.33 mole/litre de formaldéhyde a donné un abaissement cryoscopique de 0.64°C. correspondant au poids moléculaire normal. La figure 9 montre ce qui arrive lorsqu'on ajoute à cette solution de l'eau oxygénée. A

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mesure que la concentration de l'eau oxygénée augmente, l'abaissement cryoscopique décroît au lieu de croître, indiquant une diminution du nombre des molécules présentes dans la solution. A la proportion de 1 molécule d'eau oxygénée pour 3 de formaldéhyde, on atteint un abaissement cryoscopique minimum égal aux 3/4 de celui de la formaldéhyde seule. A première vue, on pense à la formation d'un complexe PF_3, mais ceci impliquerait que l'abaissement cryoscopique soit réduit à 1/3 de sa valeur initiale. Il s'agit plus vraisemblablement d'un équilibre entre les espèces PF, PF_2, PF_4, qui sont des composés connus.

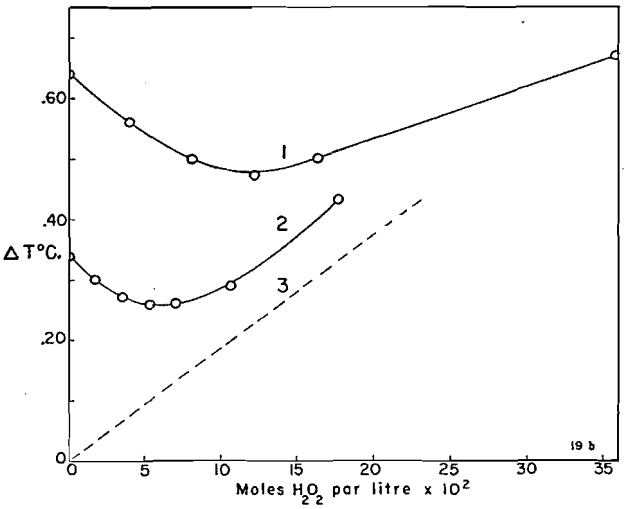

FIG. 9. *Variations de l'abaissement du point de congélation de deux solutions de formaldéhyde 0.33 molaire (1) et 0.165 molaire (2) en fonction de la concentration d'eau oxygénée ajoutée. La droite (3) indique l'abaissement que produirait l'eau oxygénée seule.*

Une étude détaillée de cet effet révélerait peut-être une correspondance significative entre ces minima cryoscopiques et les maxima des taux de réaction. Toutefois, l'apparition d'une légère opalescence dans la solution aux concentrations les plus élevées d'eau oxygénée laisse croire qu'il y avait formation d'un précipité colloïdal. En présence d'un tel effet, on ne peut attribuer une signification univoque à la position du minimum cryoscopique.

Discussion

Les résultats exposés ci-dessus révèlent que la réaction est très complexe. Si le coefficient de température est constant pour des réactions effectuées aux mêmes concentrations, par contre l'ordre par rapport aux concentrations initiales n'est pas celui que l'on obtient par rapport au temps. Il semble bien qu'on soit en présence de la décomposition bimoléculaire d'un intermédiaire dont la concentration ou la réactivité est une fonction complexe des concentrations relatives initiales.

A première vue, l'intermédiaire le plus vraisemblable est le peroxyde de dimé-

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thylol, dont la formation (6, 17) et la décomposition (17) suivant l'équation:

$$2HCHO + H_2O_2 \rightarrow HOCH_2OOCH_2OH \xrightarrow{2NaOH} 2HCOONa + 2H_2O + H_2$$

sont connues. Nous avons montré que le taux de décomposition de ce peroxyde est égal au taux de réaction du mélange équivalent de formaldéhyde et d'eau oxygénée, mais les positions des minima cryoscopiques et la présence dans les solutions les plus concentrées d'un trouble suggérant la formation d'un polymère laissent entrevoir une situation beaucoup plus compliquée.

L'influence de la concentration de la soude est relativement simple. Le genou de la figure 3 correspond au point d'équivalence de la neutralisation de la formaldéhyde hydratée considérée comme acide faible:

$$HCHO \xrightarrow{H_2O} H_2C(OH)_2 \xrightarrow{2NaOH} H_2C(ONa)_2$$

Le sel de sodium, d'ailleurs fortement hydrolysé, est probablement la forme réactive de la formaldéhyde.

Puisque nous avons postulé l'intervention d'un intermédiaire du type du peroxyde de diméthylol, rappelons que ces peroxydes du type ROOR ont tendance à se trouver en solution sous la forme de radicaux libres RO· possédant un oxygène monovalent (4). En supposant que cette dissociation soit pratiquement complète dans les conditions de nos expériences, la recombinaison de deux de ces radicaux nous donnerait une réaction du second ordre. Suivant un mécanisme analogue à celui que Pearl (16) a proposé pour l'oxydation de la vanilline, ces étapes essentielles seraient les suivantes:

$$HCHO + H_2O \rightarrow H_2C\begin{matrix}OH\\OH\end{matrix} \xrightarrow{NaOH} H_2C\begin{matrix}O^-\\OH\end{matrix} + H_2O + Na^+$$

$$H_2C\begin{matrix}O^-\\OH\end{matrix} + Na^+ + HOOH \rightarrow H\dot{C}\begin{matrix}O^-\\OH\end{matrix} + OH^\cdot + H_2O + Na^+$$

$$2H\dot{C}\begin{matrix}ONa\\OH\end{matrix} \rightarrow 2\ HC\begin{matrix}ONa\\O\end{matrix} + H_2.$$

On suppose que les deux premières étapes sont rapides et complètes, laissant libre un excès éventuel soit de formaldéhyde, soit d'eau oxygénée contenant beaucoup d'ions OOH^-.

Ces substances en excès sont susceptibles d'inhiber la réaction principale en réagissant avec les radicaux $OH^\cdot$ et $H\dot{C}(OH)O^-$. On peut supposer, par exemple, que ce dernier radical sert à amorcer et à propager la formation d'un polymère d'addition

$$H\dot{C}(OH)O^- + n\ HOCH_2OH \rightarrow n\ H_2O + HOCH_2(OCH_2)_{n-1}\dot{C}H(OH)O^-$$

dans lequel la formaldéhyde se trouverait protégée contre la réaction principale. Rieche et Meister (18) ont démontré l'existence de tels polymères et leur présence rendrait compte du léger trouble observé dans nos solutions. Rappelons

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que l'hydrolyse par la soude des polymères de la formaldéhyde est affectée d'une énergie d'activation de l'ordre de 15 kcal./mole (13) voisine de celle que nous avons mesurée.

Il se peut que les maxima de vitesse résultent de l'action de deux processus antagonistes: l'un de polymérisation et l'autre de dépolymérisation par la soude. Ce dernier libérerait les espèces réactives et imposerait peut-être son énergie d'activation. Cependant, il semble difficile d'expliquer les discontinuités des courbes et l'ordre de la réaction si l'on n'assigne pas le rôle central à un complexe intermédiaire relativement simple.

Rappelons en terminant que les réactions du permanganate de potassium avec l'eau oxygénée (2) et l'acide oxalique (5) présentent aussi des vitesses maxima difficiles à expliquer.

Remerciements

L'un de nous (J. B. J.) exprime ses plus vifs remerciements à la Consolidated Mining and Smelting Company, pour la bourse de recherches dont il a bénéficié.

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THE OXIDATION OF CARBON MONOXIDE BY SOLID SILVER PERMANGANATE REAGENTS

IV. CHEMICAL COMPOSITION IN RELATION TO ACTIVITY[1]

By Morris Katz, L. G. Wilson, and R. Riberdy

Abstract

The activity after progressive aging and thermal treatment of silver permanganate supported on zinc oxide and beryllium oxide was found to be closely related to the extent of decomposition of the crystalline silver permanganate. The silver salt decomposed, with loss of active oxygen, to a relatively insoluble, amorphous product resembling a manganito-manganate of the composition, $Ag_2O \cdot Mn_2O_5$ or $[AgMnO_3]_2$. From a mass balance of solid–gas reactants in a reacting column, it was demonstrated that in the most active stage, during which the efficiency of oxidation did not fall below 90%, the course of the reaction was about evenly divided between stoichiometric and catalytic processes.

Introduction

Investigations on the heterogeneous oxidation of carbon monoxide over silver permanganate supported on various metallic oxides, in particular zinc oxide, have been reported by Katz *et al.* (6, 7). The methods of preparation in relation to activity of the granules have been described elsewhere (4). For each metallic oxide support there is apparently an optimum mole composition range of the silver salt and oxide for maximum life and activity.

It was found by Katz and Halpern (7) that some silver permanganate reagents (notably those containing nickel oxide and cobalt oxide, Co_2O_3) were highly reactive towards carbon monoxide when freshly prepared, but this activity declined rapidly after several days' thermal treatment at 60°C. In other instances there was a more or less steady decline with prolonged heating. However, some preparations, which were only moderately active initially, showed an improvement after several days' thermal treatment, for example—a lead peroxide, Pb_3O_4, preparation. Improved thermal characteristics were found to depend not only upon the type of metallic oxide support, but also on the mole composition of oxide and silver salt.

Dry, crystalline silver permanganate slowly undergoes a change at ordinary temperatures, with spontaneous evolution of oxygen, gradually losing its water solubility. The reaction is autocatalytic in nature and is characterized by an induction period. The decomposition velocity increases with rising temperature and the rate becomes appreciable above 90° to 100°C. The reaction is catalyzed by small amounts of water and by the addition of end products, as well as by some metallic oxides (5, 10, 11).

Various end products have been reported in the literature. Gorgeu found that moist silver permanganate decomposed thermally to a product,

[1] *Manuscript received August 23, 1951.*
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$AgMnO_3.\frac{1}{2}H_2O$ (2). Sieverts and Theberath (11) confirmed substantially the findings of Gorgeu, although they found that the inactive oxygen in the decomposition product was always somewhat lower than that required by the above formula. In confirmation of this, the moist silver permanganate yielded slightly more oxygen than that required according to the simple equation, $AgMnO_4 \rightarrow AgMnO_3 + \frac{1}{2}O_2$.

Hein (5) found that dry thermal decomposition of the silver permanganate at 100°C. yielded an amorphous water-insoluble black product, $[8Ag_2O \cdot 15MnO_2 \cdot MnO_3 \cdot O]$. When the moist salt was decomposed at 100°, the end product was also a graphite-like, water-insoluble material corresponding to the composition $[8Ag_2O \cdot 15MnO_2 \cdot MnO_3 \cdot 6O \cdot 8H_2O]$, or $AgMnO_{2.94} \cdot \frac{1}{2}H_2O$. The water is apparently firmly bound to the molecule as it is not removed by drying over concentrated sulphuric acid.

In the present paper the results of a study of the intermediate and end products after prolonged aging, thermal and carbon monoxide treatment are presented in an attempt to elucidate the course of the reaction between the silver salt and carbon monoxide. The solid products were investigated by chemical analysis and X-ray diffraction.

Materials and Analytical Methods

The reagents employed in these experiments contained silver permanganate and zinc oxide or beryllium oxide in definite molecular proportions. The method of preparation has been outlined in previous publications (4, 7). Briefly, crystals of silver permanganate are deposited on the oxide carrier, *in situ*, by the action of a solution of potassium permanganate on concentrated silver nitrate solution intimately mixed with the oxide to form a paste. In contrast to these reagents, samples were also prepared by mechanical mixing of pure silver permanganate and zinc oxide, in the presence of a small amount of water, the mixture pressed at 10 tons per sq. in., and the pressed cake cured and broken up into granules, as in the regular method of preparation. These samples have been denoted as "mechanical mixture" in the tables. All samples were dried at room temperature and screened from -8 to $+24$ mesh Tyler.

The apparatus and experimental methods employed in the carbon monoxide activity tests, including the preparation and purification of the carbon monoxide, measurement of the initial and escaping concentrations of gas in the reaction cell and other details, have already been described in previous publications (8, 3, 7). The glass reaction cell was 2.84 cm. in diameter and was usually filled with granules to a column length of 4 cm. The gas and air mixtures were passed through this bed at a space velocity of 625 cm. $min.^{-1}$, at concentrations of 1.0% or 0.5%, as indicated. The breakdown time of the bed was chosen arbitrarily as the time at which the escaping concentration exceeded a value which was 10% of the influent concentration.

Standard methods of analysis were employed in determining the chemical

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composition of the various preparations before and after treatment (1). Total silver was determined gravimetrically as silver chloride (1, pp. 821-23). Total manganese was estimated by the Volhard method or gravimetrically as the pyrophosphate (1, pp. 560-61). Zinc oxide was separated as zinc sulphide and titrated in acid solution against potassium ferrocyanide (1, pp. 1060-61). Beryllium was separated from the silver, precipitated as the hydroxide, redissolved in 10% sodium bicarbonate to remove manganese hydroxide, and reprecipitated as the hydroxide. It was then determined gravimetrically as the oxide after ignition (1, pp. 140-41).

Crystalline silver permanganate was determined by treatment of the sample with distilled water, filtering through a Gooch crucible packed with purified asbestos wool, and analysis of the filtrate by the volumetric method, using an excess of standard sodium oxalate solution in the presence of sulphuric acid, the excess being titrated with standard potassium permanganate solution.

Higher manganese oxides, containing "active" oxygen, were determined by treating a sample directly with an excess of standard sodium oxalate solution and 5% sulphuric acid, agitating the mixture heated to 60 to 65°C. until the sample dissolved and then back titrating the excess oxalate with 0.1 *N* potassium permanganate solution.

The portion of the total silver and manganese not accounted for in the water-soluble fraction was expressed, empirically, as $AgMnO_3$ or $Ag_2O \cdot Mn_2O_5$.

X-Ray Diffraction Method

A standard X-ray diffraction technique was employed to study crystallinity. Spectra were photographed for stationary and for rotating specimens in flat and cylindrical cameras respectively. From these spectra, the substances present, their crystalline sizes, and the relative proportions of the various compounds, could be noted. A copper target diffraction tube was used in all cases.

Results

Effect of Aging on Activity

The silver permanganate reagents undergo a change during progressive aging. The magnitude of this trend is indicated by the activity data given in Table I. The standard preparation of $AgMnO_4$-ZnO, 31-69 mole %, showed little, if any, loss in activity towards carbon monoxide after six months, and only a small decrease after 14 months' aging at room temperature. The activity of all preparations in Table I decreased markedly on prolonged heating at 60°C. The standard zinc oxide supported reagents were markedly superior to those prepared by mechanical mixing of the ingredients. The beryllium oxide preparations, although possessing good activity initially, were found to be inferior to those containing zinc oxide when subjected to aging or heat treatment.

Influence of Aging on Chemical Composition

The influence of aging and thermal treatment on chemical composition of a series of standard preparations containing zinc oxide or beryllium oxide is

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TABLE I

EFFECT OF THERMAL TREATMENT ON ACTIVITY

Reagent	Composition, mole % $AgMnO_4$	Age at room temp., months	Thermal treatment at 60°C., hr.	Activity towards carbon monoxide, space velocity, 625 cm. min.$^{-1}$, column length, 4.0 cm.	
				Concentration, %	Breakdown time to 90% efficiency, min.
$AgMnO_4$–ZnO standard preparation	31	0.75		1.0	96
		6		1.0	93
		8		1.0	86
		8	160	1.0	24
		14		0.50	143
		0.75	506	0.50	81
$AgMnO_4$–ZnO standard preparation	33	0.5		1.0	94
	36	0.75		1.0	103
		2	160	1.0	51
		0.75	506	0.50	65
$AgMnO_4$–ZnO "mechanical mixture"	31	0.5		1.0	63
		0.5	160	1.0	Nil
		0.75		1.0	73
		2	148	1.0	29
$AgMnO_4$–BeO standard preparation	15	0.5		0.50	108*
		5	160	0.50	Nil
$AgMnO_4$–BeO standard preparation	25	0.5		0.50	106*
		6		0.50	86

* *Breakdown time for a 3.0 cm. column length.*

illustrated in Table II. The content of the water-soluble, crystalline, silver permanganate fraction decreases with time or thermal treatment as conversion takes place to a relatively insoluble amorphous reaction product. This product

TABLE II

CHEMICAL COMPOSITION DURING THERMAL AGING OF STANDARD PREPARATIONS

Description of sample	Age at room temp., months	Hours of heating at 60 °C.	Composition in % by weight			
			$AgMnO_4$	$AgMnO_3$	ZnO	Total
$AgMnO_4$–ZnO, 36-64 mole %	2	Nil	56.07	3.16	40.80	100.03
"	2	160	25.98	32.60	41.40	99.98
"	4*	160	14.72	42.23	41.92	98.87
$AgMnO_4$–ZnO, 31-69 mole %	9	Nil	46.40	6.20	46.68	99.28
"	14	Nil	44.04	8.31	47.15	99.50
					BeO	
$AgMnO_4$–BeO, 25-75 mole %	6	Nil	58.12	15.06	28.18	101.36
$AgMnO_4$–BeO, 15-85 mole %	5	160	0.00	53.52	46.87	100.39

* *Sample aged two months longer at room temperature after thermal treatment at 60°C.*

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PLATE I

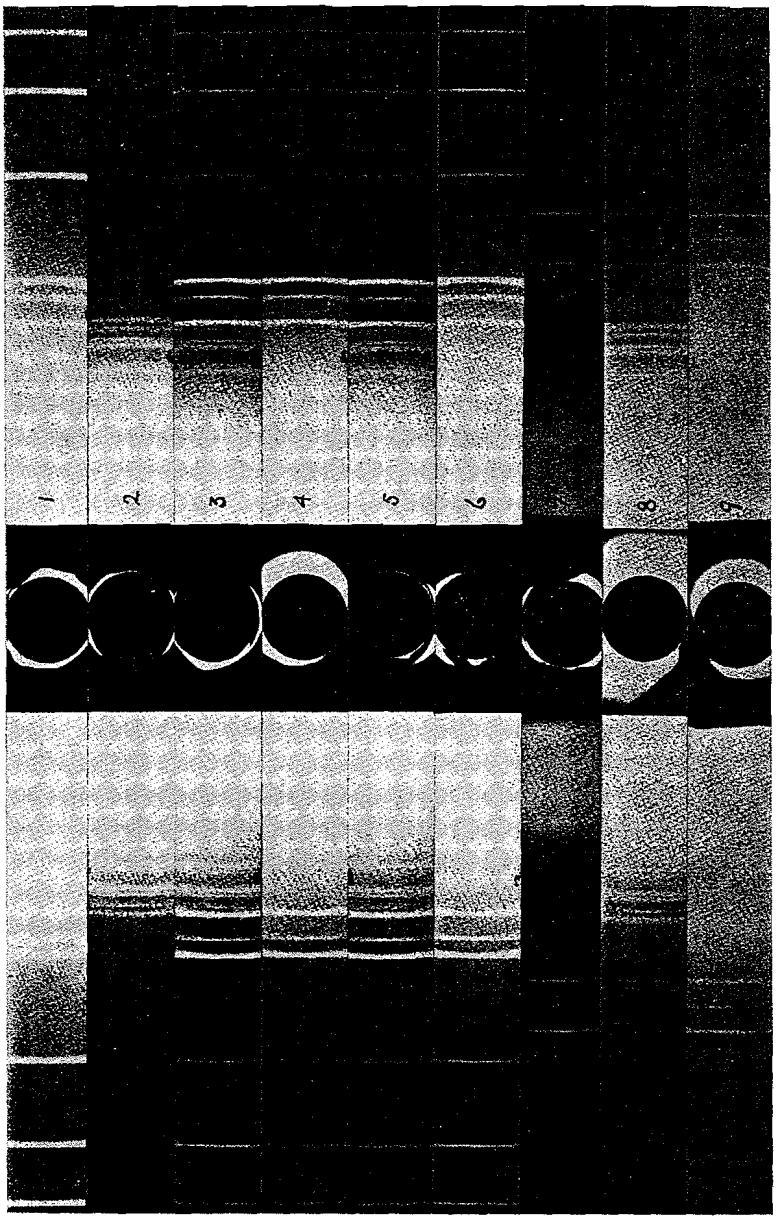

FIG. 1. *Pure zinc oxide spectrum.*
FIG. 2. *Pure silver permanganate spectrum.*
FIG. 3. *Reagent containing originally 31 mole % $AgMnO_4$–69 mole % ZnO, nine months old.*
FIG. 4. *A mechanical mixture containing originally 31 mole % $AgMnO_4$–69 mole % ZnO, heated for 148 hr. at 60°C.*
FIG. 5. *A mechanical mixture containing originally 31 mole % $AgMnO_4$–69 mole % ZnO, three weeks old.*
FIG. 6. *Same reagent as in Fig. 3, but X-ray pattern taken after sample had been reacted completely with carbon monoxide as in Experiment No. 3.*
FIG. 7. *Pure beryllium oxide spectrum.*
FIG. 8. *Beryllium oxide reagent, containing originally 15 mole % $AgMnO_4$, not heat treated.*
FIG. 9. *Beryllium oxide reagent, same original composition as in Fig. 8, aged 160 hr. at 60°C.*

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PLATE II

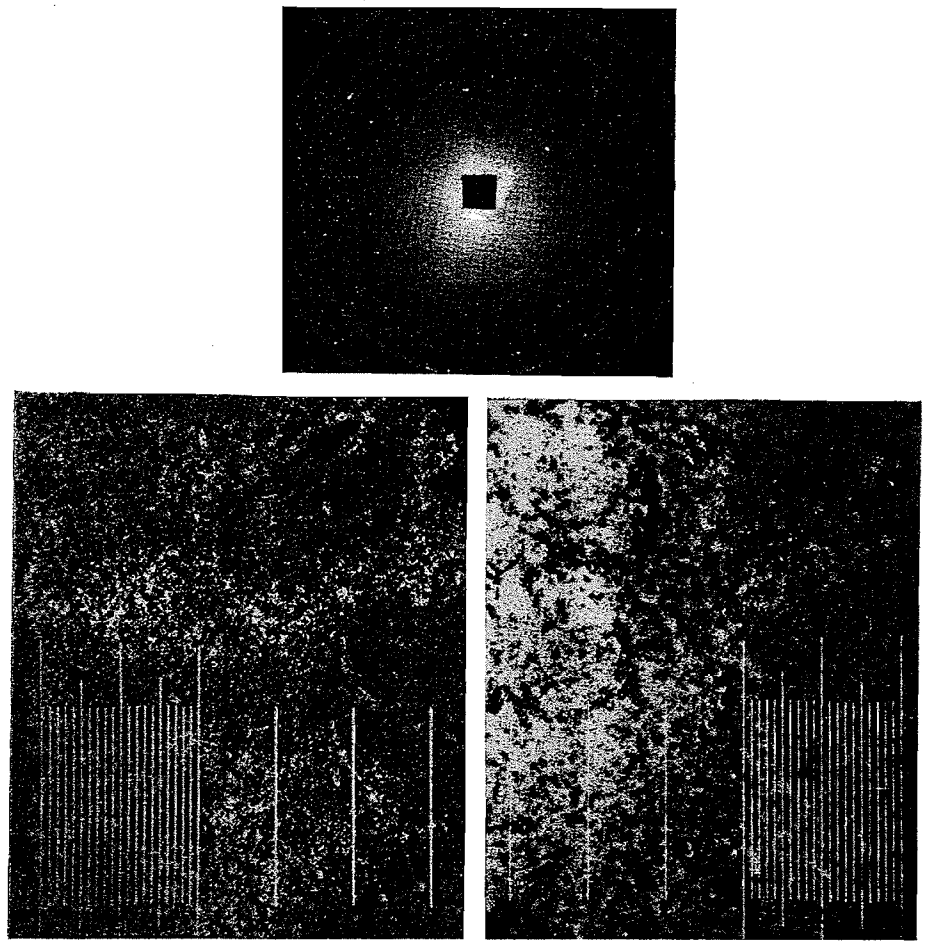

FIG. 10. *Zinc oxide reagent, containing originally 31 mole % $AgMnO_4$, aged eight months at room temperature, and then aged 160 hr. at 60°C. "Spotty" rings are from $AgMnO_4$.* FIG. 11. *Photomicrograph of standard zinc oxide – silver permanganate reagent, showing particle size. (Small scale division = 10 μ.)* FIG. 12. *Photomicrograph of a mechanical mixture of zinc oxide and 30% silver permanganate. (Small scale division = 10 μ.)*

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contains available oxygen and from the analytical results is best represented as a manganito-manganate of the composition $Ag_2O \cdot Mn_2O_5$ or $AgMnO_3$, closely resembling the product obtained by Hein in the thermal decomposition of the moist salt at 100°C., i.e., $AgMnO_{2.94} \cdot \frac{1}{2}H_2O$. Compounds of this type containing available oxygen to manganese in the atomic proportions of 1.5 to 1.6 have been discussed by Mellor (9).

It is also evident from Table II that the reagent containing zinc oxide as the carrier is much more stable than the one containing beryllium oxide. Prolonged thermal treatment at 60°C. of the beryllium oxide reagent produced complete conversion of the silver permanganate fraction to lower oxidation products, whereas corresponding treatment of the zinc oxide reagent resulted in about 54% decomposition of the permanganate.

TABLE III

CHEMICAL COMPOSITION DURING AGING OF A MECHANICAL MIXTURE

Description of sample	Age at room temp., months	Hours of heating at 60°C.	Composition in % by weight			
			$AgMnO_4$	$AgMnO_3$	ZnO	Total
$AgMnO_4$–ZnO, 31-69 mole %	0.75	Nil	50.00	5.53	44.40	99.93
"	4	Nil	20.30	32.07	45.39	97.76
"	6	Nil	10.21	43.45	45.73	99.39
"	6	148	0.40	53.0	46.40	99.80
Standard preparation, $AgMnO_4$–ZnO, 31-69 mole %	9	Nil	46.40	6.20	46.68	99.28

This retarding influence of zinc oxide on the thermal decomposition of the silver salt is not achieved by mere mechanical mixing and pressing of the ingredients of the reagent, as shown in Table III. The aging of a mechanical mixture is poor by comparison with that of a standard preparation, as judged by the relatively rapid disappearance of the crystalline silver salt fraction.

The data in Tables I to III, inclusive, indicate that there is a direct relation between the extent of decrease of the silver permanganate concentration and the reduction in breakdown time or oxidation activity towards carbon monoxide on prolonged aging. Samples in which the soluble silver salt had been decomposed completely showed virtually no activity.

The X-ray diffraction patterns of a number of samples are given in the photographs, Figs. 1-10 inclusive. Pure zinc oxide and pure silver permanganate are shown in Figs. 1 and 2 respectively. Fig. 7 indicates the spectrum of pure beryllium oxide. The remaining photographs show the spectra of various samples after treatment. Reagents which exhibited a high reactivity with carbon monoxide showed also that a large proportion of the original silver permanganate was still present in the crystalline state. Those samples which had lost their oxidizing power for carbon monoxide showed only the spectrum of the metallic oxide carrier. The products formed from the breakdown of the permanganate are apparently a chemically bound mixture of amorphous oxides

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TABLE IV

MASS BALANCE IN HETEROGENEOUS REACTION SYSTEM

	Run No. 1	Run No. 2	Run No. 3
Weight of sample, gm.	62.0	65.0	101.0
Weight of $AgMnO_4$ in sample before reaction, gm.	27.30	35.20	46.86
Weight of $AgMnO_4$ in sample after reaction, gm.	12.94	9.89	0.06
Weight of CO oxidized, gm.	4.131	4.754	9.05
Weight of O_2 required to oxidize CO, gm.	2.361	2.717	5.17
Weight of O_2 lost by sample, gm.	1.100	1.495	3.587
Weight of $AgMnO_4$ which reacted with CO, gm.	14.36	25.31	46.80
Weight of O_2 supplied by $AgMnO_4$, gm., according to the reaction:			
(*A*) 2 $AgMnO_4 \longrightarrow$ 1.5 $O_2(+Ag_2O + 2\ MnO_2)$	1.520	2.678	4.952
(*B*) 2 $AgMnO_4 \longrightarrow$ $O_2(+2AgMnO_3)$	1.013	1.785	3.302

which from chemical analytical evidence may be represented as a silver manganito-manganate. The products obtained by Hein from the thermal decomposition of both the dry and the moist salt at elevated temperatures were also amorphous (5).

The difference in particle size between a standard reagent containing silver permanganate deposited on the zinc oxide by chemical reaction, *in situ*, and that of a mechanical mixture is illustrated by the photomicrographs in Figs. 11 and 12. The standard reagent shows a much smaller particle size and more uniform distribution.

Nature of Heterogeneous Oxidation of Carbon Monoxide

A mass balance was made of the reactants during the oxidation of carbon monoxide in a reacting column containing various standard samples of granules. The mass balance in three experiments is shown in Table IV. The amount of oxygen removed from the silver permanganate during the oxidation represents the stoichiometric reaction between carbon monoxide and the solid reagent. Any additional oxidation would be catalytic, at the expense of oxygen

TABLE V

STOICHIOMETRIC AND CATALYTIC OXIDATION OF CARBON MONOXIDE

	Run No. 1		Run No. 2		Run No. 3	
	% Oxidation					
	Stoichiometric	Catalytic	Stoichiometric	Catalytic	Stoichiometric	Catalytic
1. Calculated on the actual weight loss of oxygen	46.63	53.37	55.02	44.98	69.4	30.6
2. Calculated on the amount of oxygen supplied by $AgMnO_4$, according to the reaction:						
(*a*) 2 $AgMnO_4 \longrightarrow$ 1.5 O_2 $(+Ag_2O + 2MnO_2)$	64.36	35.64	98.57	1.43	95.77	4.23
(*b*) 2$AgMnO_4 \longrightarrow$ O_2 $(+2AgMnO_3)$	42.90	57.10	65.70	34.30	63.85	36.15

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in the gas phase. Two alternative reaction paths for liberation of oxygen from the silver salt are shown in Table IV. Reaction (*B*) is more nearly in accord with the actual weight of oxygen released from each sample during reaction with carbon monoxide and is also more nearly representative of the solid products formed during aging and thermal decomposition, as shown by chemical analysis.

The calculated percentage conversion of CO to CO_2 according to stoichiometric and catalytic reactions is given in Table V. The chemical composition of each sample immediately before and after treatment with carbon monoxide is shown in Table VI. The stoichiometric reaction may be represented best by the following equation

TABLE VI

COMPOSITION AFTER REACTION WITH CARBON MONOXIDE

Original composition of sample in % by weight	Age of sample	Quantity of carbon monoxide oxidized, gm.	Composition in % by weight			
			$AgMnO_4$	$AgMnO_3$	ZnO	Total
Run No. 1						
$AgMnO_4$–ZnO, 55.6-44.4	14 mos.	Nil	44.04	8.31	47.15	99.50
"	14 mos.	4.13	20.88	31.11	47.86	99.85
Run No.2						
$AgMnO_4$–ZnO, 57.8-42.2	12 days	Nil	54.15	1.00	44.87	100.02
"	12 days	4.75	15.21	35.85	45.84	99.60
Run No. 3						
$AgMnO_4$–ZnO, 55.6-44.4	9 mos.	Nil	46.40	6.20	46.68	99.28
"	9 mos.	9.05	0.06	51.23	47.86	99.15

$$2\ AgMnO_4 + 2\ CO \longrightarrow 2\ CO_2 + Ag_2O{\cdot}Mn_2O_5. \quad (1)$$

An alternative possibility is

$$16\ AgMnO_4 + 17\ CO + 8\ H_2O_{vapor} \longrightarrow 17\ CO_2 + [8\ Ag_2O{\cdot}15\ MnO_2{\cdot}MnO_3{\cdot}3O_2{\cdot}8\ H_2O]. \quad (2)$$

The solid reaction product in the second equation represents the thermal decomposition product reported by Hein (5). It has been mentioned that a little water vapor is necessary to initiate the oxidation of carbon monoxide, although the standard reagent is substantially nonhygroscopic. Samples in equilibrium with an atmosphere at 89% relative humidity for 48 hr. at room temperature showed a moisture absorption of only 0.09% by weight, whereas the thermally decomposed product absorbed 0.35 to 0.46% water.

From the data in Tables IV and V, it is evident that when the efficiency of oxidation in a reacting column does not go below 90%, the percentage conversion of carbon monoxide to carbon dioxide is, roughly, evenly divided between the stoichiometric and catalytic processes. Below 90% efficiency, a greater proportion of the carbon monoxide is oxidized stoichiometrically as the active sites in the granular mass become depleted or "poisoned" with time.

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Because of this direct reaction with the silver salt, the granular reagent oxidizes carbon monoxide effectively in gas mixtures which do not contain gaseous oxygen. When a stream of 1.0% carbon monoxide in nitrogen containing about 0.1% oxygen was passed through a column of granules of standard reagent consisting of 31 mole % silver permanganate on zinc oxide, under the test conditions indicated in Table I, the breakdown time was 77 min. When the oxygen in the nitrogen was removed completely, by passage through a purification train, the breakdown time was 68.5 min.

Discussion

There is a close correlation between the disappearance of the crystalline state of the silver salt and loss of activity as shown by chemical analysis and X-ray diffraction. Decay in activity produced either by reaction with carbon monoxide or by thermal treatment is paralleled by the conversion of the crystalline silver salt to an amorphous reaction product of the approximate composition, $Ag_2O \cdot Mn_2O_5$.

Prout and Tompkins (10) have recently proposed that pure dry silver permanganate may decompose thermally, as follows, from kinetic data,

$$2\,AgMnO_4 \longrightarrow 1.5\,O_2 + Ag_2O \cdot 2\,MnO_2. \qquad (3)$$

Such a reaction, if applied to the stoichiometric oxidation of carbon monoxide, would imply the reduction of two molecules of the silver salt by three molecules of carbon monoxide. However, the above authors did not analyze the solid products of the thermal decomposition. Apart from this, the present work deals with a reaction which takes place in the presence of water vapor, consequently, only data dealing with the thermal decomposition or reduction of the moist salt are relevant.

The mechanism of the heterogeneous oxidation of carbon monoxide by these solid reagents is complex and there is, as yet, insufficient experimental evidence for a complete explanation. The stoichiometric reaction between carbon monoxide and the silver salt involves the reduction of one molecule of silver permanganate per molecule of carbon monoxide, based on the chemical analysis of the solid products. Some confirmation of this has been obtained from kinetic data (8). It is also supported by the data on thermal decomposition reported here.

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DIPHENYLCYANAMIDE DERIVATIVES[1]

By J. R. Robinson[2] and W. H. Brown

Abstract

Diphenylcyanamide is conveniently prepared by the action of cyanogen chloride on diphenylamine. When it is hydrolyzed in the presence of hydroxylated solvents, of the type ROH, stable isoureas are formed. These are readily hydrolyzed in aqueous alkaline medium to the corresponding urea derivative. Chlorination of diphenylcyanamide occurs in the *para* positions yielding a nitrogen analogue of DDT. This chlorinated derivative is only 1/80th as toxic as DDT to *Sitophilus granarius* (L).

Diphenylcyanamide (I) has been reported by von Braun (2), Werner (26), and Kurzer (10). Since only a few direct derivatives have been recorded (3, 4, 5, 9, 26), an investigation of this compound is of interest. For example, *p*, *p'*-dichlorodiphenylcyanamide (II) is a nitrogen analogue of 1,1-*bis*-(*p*-chlorophenyl)-2,2,2-trichlorethane (DDT) and might show insecticidal activity.

It has been found that diphenylcyanamide (I) is formed in excellent yield by treating diphenylamine (IX) with cyanogen chloride at 60°C. and 5 atm. pressure. When it is hydrolyzed in aqueous alkaline medium, N, N-diphenylurea (III) results. Michler (16) and Kurzer (11) have reported other methods for preparing this latter compound. When a solution of diphenylcyanamide (I) in methanolic potassium hydroxide is refluxed for 72 hr., diphenylamine (IX) is produced. If, however, the reaction is interrupted after two hours, N, N-diphenylmethylisourea (IV) is the major product. The isourea is readily converted to N, N-diphenylurea (III) by boiling with aqueous potassium hydroxide for 2.5 hr.

When ethanol is used as solvent instead of methanol, the corresponding ethylisourea (V) is readily obtained.

Pyrolysis of N, N-diphenylmethylisourea (IV) leads to the formation of N, N-diphenylurea (III) in poor yield.

Treatment of a chloroform solution of diphenylcyanamide (I) with chlorine gives *p*, *p'*-dichlorodiphenylcyanamide (II). This latter compound when refluxed in a solution of potassium hydroxide in methanol for two hours forms N, N-di-*p*-chlorophenylmethylisourea (VIII). If the reaction is allowed to proceed for 24 hr., *p*, *p'*-dichlorodiphenylamine (VII) results. An authentic sample of *p*, *p'*-dichlorodiphenylamine was prepared by the methods of Claus and Shaare (8) and Chapman (7).

Aqueous alkaline hydrolysis of *p*, *p'*-dichlorodiphenylcyanamide (II) gives N, N-di-*p*-chlorophenylurea (VI), which hydrolyzes with difficulty in dilute hydrochloric acid solution to *p*, *p'*-dichlorodiphenylamine (VII).

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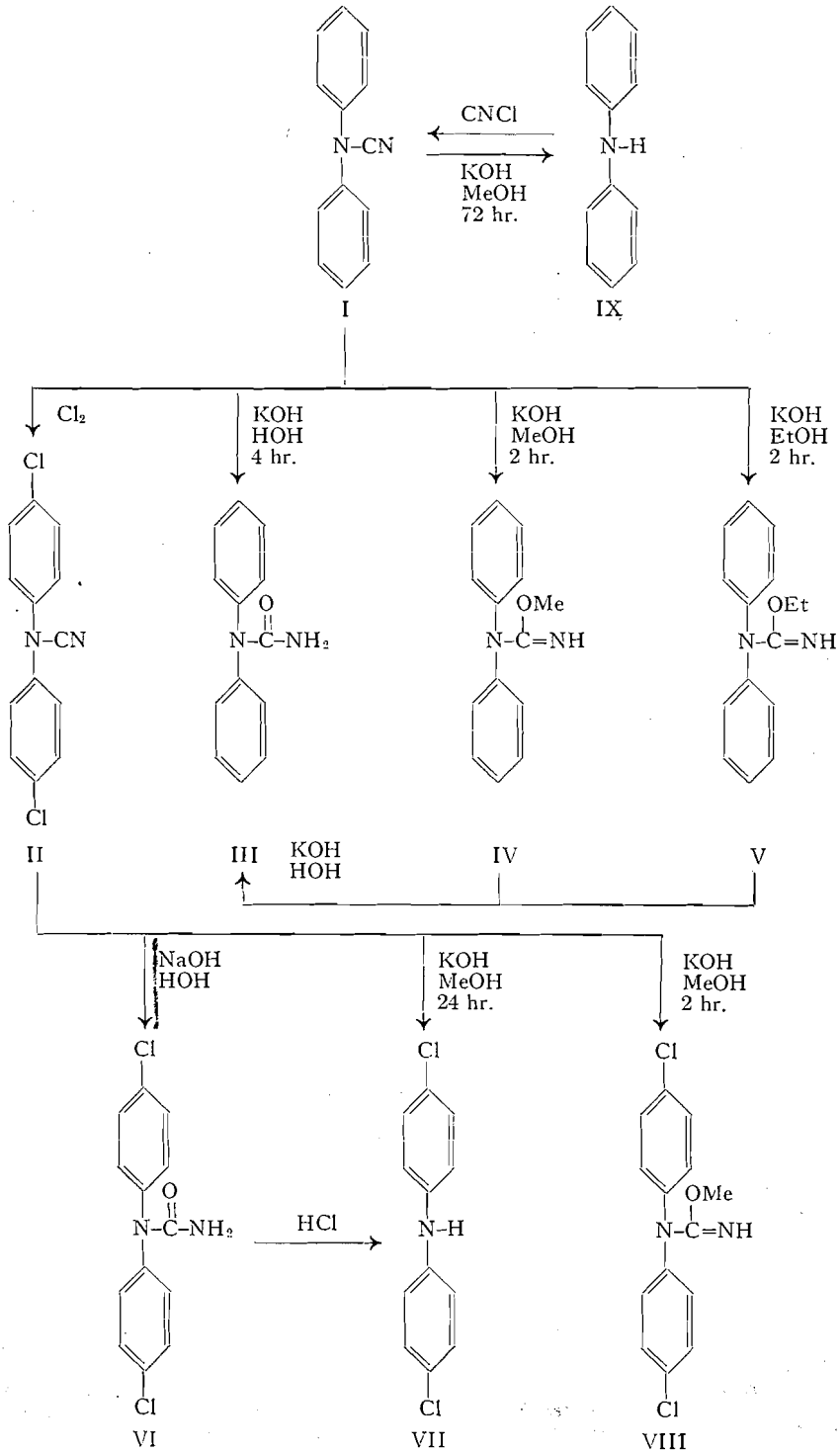

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Discussion

Pinner (18) was among the first to report the synthesis of iminoethers.* Many investigators (1, 12, 13, 14, 15, 17, 19, 20, 21, 22, 23, 24, 25) have extended the field, but none of the N, N-diphenyl type is reported. McKee (13) predicted that disubstituted cyanamides would most readily add alcohols when catalyzed by the corresponding alkoxide ion, rather than by protons. The authors' findings with respect to diphenylcyanamide bear this out. Methanol adds to diphenylcyanamide in two hours in the presence of methoxide ion in 88% yield, whereas the reaction requires 80 days in the presence of hydrogen chloride to give a yield of 3.5%.

Toxicology

Tests† show that *p, p'*-dichlorodiphenylcyanamide (II) possesses an estimated median lethal concentration of about eighty times that of DDT to *Sitophilus granarius* (L). The other derivatives of diphenylcyanamide were also screened for activity, but did not indicate toxicity great enough to warrant quantitative investigation.

Browning *et al.* (6) have tested a number of N-substituted *p,p'*-dichlorodiphenylamines for biological activity. Their results show that groups such as methyl, trichloromethyl, and trichloroacetyl do not increase the toxicity of the parent compound. The cyanide group does have an enhancing effect according to the present authors' findings.

Experimental‡

Diphenylcyanamide

After treating 34 gm. (0.2 mole) of diphenylamine with 12.3 gm. (0.2 mole) of cyanogen chloride at 60°C. for one and one-half hours in a capped ginger ale bottle, the reaction mixture was allowed to stand at room temperature for 24 hr. As a safety precaution, the bottle was kept immersed in a steel-jacketed water bath throughout the course of the reaction.

The ether-soluble portion of the resulting solid was crystallized three times from absolute ethanol, giving 17.5 gm. (90%) of a white granular solid, which melted at 73°C.

p, p'-Dichlorodiphenylcyanamide

Chlorine was bubbled into a solution of 7.76 gm. (0.04 mole) of diphenylcyanamide in 30 ml. of chloroform at 5-6°C. for one hour. The solution was

* *These compounds are recorded in the literature under various names; imino- or imidoethers imino- or imidoesters and esters of imidic acids. Those of the type* $R_2N\text{-}C(OR')=NH$ *are called isocarbamides, carbimidoethers (esters), pseudoureas, or isoureas.*

† *Material tested by the Entomology Section, Defence Research Board Experimental Station, Suffield, Alta.*

‡ *All melting points have been corrected against reliable standards. Combustion analyses are by A. E. Ledingham, Dominion Rubber Research Laboratories, Guelph, Ont.; R. G. Pyke, Department of Chemistry, University of Toronto, and J. F. Eagen, National Research Council, Ottawa.*

treated with 10% aqueous sodium carbonate, washed with water, and finally dried over anhydrous sodium sulphate. When the chloroform was distilled off, there remained 12.1 gm. of golden yellow oil which crystallized spontaneously. Crystallization from ethanol yielded 6.1 gm. (58%) of long colorless needles melting at 114-115°C. Calc. for $C_{13}H_8Cl_2N_2$: C, 59.31; H, 3.06; Cl, 26.94; N, 10.65%. Found: C, 59.06; H, 3.06; Cl, 26.90; N, 10.64%.

N, N-Diphenylurea

To a solution of 1.12 gm. (0.02 mole) of potassium hydroxide in 100 ml. of water was added 3.88 gm. (0.02 mole) of diphenylcyanamide, and the mixture refluxed for four hours. The resulting solid weighed 4.2 gm. (100%) and melted at 192-193°C. A mixed melting point with an authentic sample of N, N-diphenylurea (EK 4979) was not depressed.

N, N-Diphenylmethylisourea (alkoxide catalysis)

To a solution of 0.28 gm. (0.005 mole) of potassium hydroxide in 20 ml. of methanol was added 0.97 gm. (0.005 mole) of diphenylcyanamide. The resulting solution was refluxed for two hours. After cooling, the solution was diluted with 100 ml. of water. An oil separated and crystallized after vigorous stirring. The product was found to be extremely soluble in all the common organic solvents as well as in 10% hydrochloric acid solution. Purification was achieved by dissolving it in excess acetone, then adding water dropwise while stirring at high speed. By this means 1.0 gm. (88%) of long fine needles was obtained melting at 77-78°C. Calc. for $C_{14}H_{14}ON_2$: C, 74.30; H, 6.24; $-OCH_3$, 13.71; N, 12.40%. Found: C, 74.55; H, 6.20; $-OCH_3$, 13.97; N, 12.57%.

The same product was obtained (82%) when 0.23 gm. (0.01 gm-atom) of sodium metal was used in place of potassium hydroxide.

N, N-Diphenylmethylisourea (proton catalysis)

A solution of 1.94 gm. (0.01 mole) of diphenylcyanamide in 60 ml. of methanol was saturated with dry hydrogen chloride at 6°C. After standing 80 days at 10°C., 0.08 gm. (3.5%) of N, N-diphenylmethylisourea was isolated from the solution.

N, N-Diphenylethylisourea (alkoxide catalysis)

To a solution of 2.8 gm. (0.05 mole) of potassium hydroxide in 50 ml. of absolute ethanol was added 9.7 gm. (0.05 mole) of diphenylcyanamide and the resulting solution refluxed for two hours. The reaction mixture was cooled, diluted with 150 ml. of water, and extracted with four 25 ml. portions of ether. The ether extract was treated with an excess of concentrated hydrochloric acid and the resulting precipitate taken up in 75 ml. of water. This aqueous solution was made alkaline with 20% potassium hydroxide solution. The resulting precipitate was purified by crystallization from acetone–water as described above, yielding 9.0 gm. (75%) of white crystals melting at 55-56°C. Calc. for $C_{15}H_{16}ON_2$: C, 74.96; H, 6.72; $-OC_2H_5$, 18.76%. Found: C, 74.92; H, 6.70; $-OC_2H_5$, 18.69%.

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N, N-Di-p-chlorophenylurea

A suspension of 1.05 gm. (0.004 mole) of dichlorodiphenylcyanamide in 15 ml. of 6 *N* aqueous sodium hydroxide solution was refluxed for 17 hr. Bumping became so severe that the refluxing had to be stopped. The suspension was left standing at room temperature for an additional 10 days. A white crystalline solid, which melted at 220-222°C., weight 1.1 gm. (98%), was filtered off. Crystallization from ethanol and acetone–water did not raise the melting point. Calc. for $C_{13}H_{10}ON_2Cl_2$: C, 55.52; H, 3.58; N, 9.97%. Found: C, 57.20; H, 3.42; N, 10.28%.

p, p'-Dichlorodiphenylamine

A solution of 1.32 gm. (0.005 mole) of *p, p'*-dichlorodiphenylcyanamide in 50 ml. of 20% methanolic potassium hydroxide was refluxed for 24 hr. After cooling and diluting with 100 ml. of water a white precipitate was obtained which was crystallized from petroleum ether (65-110°C.). In this manner 1.03 gm. (87%) of purified material was obtained, melting at 77-78°C. A mixed melting point with an authentic sample of *p, p'*-dichlorodiphenylamine was not depressed.

N, N-Di-p-chlorophenylmethylisourea

A solution of 2.1 gm. (0.008 mole) of *p, p'*-dichlorodiphenylcyanamide in 15 ml. of methanol containing 0.56 gm. (0.01 mole) of potassium hydroxide was refluxed for two hours. The solution was cooled and diluted with 50 ml. of water. The crystalline precipitate was filtered off and crystallized four times from ethanol, yielding 1.7 gm. (72%) of purified product melting at 109-110°C. Calc. for $C_{14}H_{12}ON_2Cl_2$; C, 56.95; H, 4.08; N, 9.50; Cl, 24.04; $-OCH_3$, 10.52%. Found: C, 57.05; H, 4.28; N, 9.41; Cl, 24.14; $-OCH_3$, 10.49%.

Pyrolysis of N, N-Diphenylmethylisourea

After heating 0.9 gm. (0.004 mole) of N, N-diphenylmethylisourea in a pyrex test tube at 140-160°C. for four hours, the reaction mass was treated with 5 ml. of ether. Immediate crystallization resulted. The crystals weighed 0.1 gm. (12%) and melted at 192-193°C. after crystallization from methanol. A mixed melting point with N, N-diphenylurea showed no depression.

N, N-Diphenyl-N'-methylurea

This compound was prepared for comparison with N, N-diphenylmethylisourea in the early stages of the investigation.

A solution of 0.46 gm. (0.002 mole) of diphenylcarbamyl chloride (E.K. 801) in 25 ml. anhydrous ether was treated with excess methylamine which was distilled from a 33% aqueous solution. After one hour the reaction was stopped, the solid material filtered off, and the ether evaporated to give 0.6 gm. of crude product, which melted at 167-168°C. The crude material was purified by crystallization from methanol–water and ethanol–water giving 0.35 gm. (78%) of product melting at 173°C. Calc. for $C_{14}H_{14}ON_2$: C, 74.30; H, 6.24; N, 12.40%. Found: C, 74.40; H, 6.20; N, 12.61%.

Acknowledgments

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THE ADDITION COMPOUNDS OF SILICON TETRACHLORIDE WITH ALIPHATIC AMINES[1]

By W. R. Trost

Abstract

Some diaminate and tetraminate addition compounds of silicon tetrachloride with butylamine, diethylamine, piperidine, triethylamine, and tributylamine have been prepared and analyzed. The tetraminates begin to decompose at temperatures above and below 200° C. The thermal stabilities and the products of the decompositions of these compounds indicate that coordinate bonds, and hydrogen bonds when possible, are involved in the formation of the tetraminates of silicon tetrachloride.

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Addition compounds between silicon tetrachloride and aromatic amines have been reported (2) in which the silicon tetrachloride molecule adds one, two, or four amine groups to form stable substances. Coordinate bonds were considered to be principally responsible for the stability of these addition compounds. From this point of view, it was necessary to assume the presence of orbitals in silicon tetrachloride that could accept electron-pairs. These orbitals, to be associated with the silicon tetrachloride molecule as a whole, were assumed to be derived from $4s$, $3d$, $4p$ atomic orbitals. Accordingly the amines would be expected to add as an envelope around the silicon tetrachloride molecule. Aliphatic amines also form addition compounds with silicon tetrachloride. These should be the stabler substances, as the aliphatic amines are much stronger bases than the aromatic amines and would therefore be supposed to be able to form stronger coordinate bonds.

Experimental

The tetraminates of silicon tetrachloride with butylamine, piperidine, diethylamine, triethylamine, and tributylamine were prepared by adding 10 ml. of 1.74 *M* silicon tetrachloride in ether solution to 100 ml. of the distilled, chilled, pure amine. The mixture was diluted with ether and the solid filtered and washed with ether until free of unbound amine, when it was dried *in vacuo*. The yields were quantitative.

The dry powders were analyzed for amine, chlorine, and silicon. The analytical results are reported in Table I. The amines were determined by back titrating the acid-fixed condensate from the boiling alkaline solution of the solid. The chlorine was separately measured in neutral solution with standard silver nitrate, after the volatile amine had been removed by distillation from basic solution, and the silica had been precipitated by acid. Silicon was calculated from silica, recovered as the ash in the ignition of the tetraminate.

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Contribution from the Department of Chemistry, Dalhousie University, Halifax, Canada, with financial assistance from the National Research Council of Canada.

TABLE I

RESULTS OF THE ANALYSES OF THE ADDITION COMPOUNDS

Compound	Experimental			Calculated		
	% Si	% Cl	% Amine	% Si	% Cl	% Amine
$SiCl_4(Et_3N)_4$	4.75	23.6	69.6	4.88	24.7	70.5
$SiCl_4(Bu_3N)_4$	3.16		81.0	3.09		81.3
$SiCl_4(Bu_3N)_2$	5.15		68.1	5.19		68.5
$SiCl_4(Et_2NH)_4$	6.07	30.3	63.2	6.08	30.7	63.3
$SiCl_4((CH_2)_5NH)_4$	5.50	27.2	65.5	5.51	27.8	66.6
$SiCl_4(BuNH_2)_4$	6.01	31.0	63.8	6.08	30.7	63.3

Tributylamine is not volatile. Therefore, in analyses for this amine, as it was possible, the method applied before to the aromatic amines was used (2).

The aliphatic tetraminates, particularly those derived from tertiary amines, are relatively inert to water. They are not hygroscopic and must be refluxed in such solvents as boiling dilute alkali to obtain complete decompositions. They are insoluble in common organic liquids, including amines.

Thermal Stability

The aliphatic tetraminates decomposed without melting when kept at high temperatures. The recognizable products of the early stages of the decomposition were volatile colorless liquids and white crystalline solids, at room temperature. The crystals were tentatively identified as the corresponding amine hydrochloride by their melting points, and because of positive qualitative tests for ionically bound chlorine. The volatile liquids neutralized acids and had the proper amine odors and were therefore taken to be the corresponding amines. The lowest temperatures at which the decompositions of these substances were observed to begin are compared with the basic dissociation constants (1) of the relevant amines in Table II.

TABLE II

THE THERMAL STABILITY OF THE ADDITION COMPOUNDS COMPARED WITH THE BASIC STRENGTH OF THE CORRESPONDING AMINES

Compound	Decomposition temperature, °C.	Amine	K_B (1)
$SiCl_4(Et_3N)_4$	210	Triethylamine	6.4×10^{-4}
$SiCl_4(Bu_3N)_4$	185	Tributylamine	8.5×10^{-5}
$SiCl_4(Me_2Aniline)_4$ (2)	100	Dimethylaniline	1×10^{-9}
$SiCl_4((CH_2)_5NH)_4$	220	Piperidine	1.6×10^{-3}
$SiCl_4(Et_2NH)_4$	215	Diethylamine	1.26×10^{-3}
$SiCl_4(BuNH_2)_4$	215	Butylamine	4.09×10^{-4}
$SiCl_4(Aniline)_4$ (2)	185	Aniline	4.6×10^{-10}

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1. $SiCl_4(Et_3N)_4$

The tertiary amine tetraminates were refluxed in excess amine and inert solvent at 80° C., then washed, and dried *in vacuo* again, prior to their thermal decompositions.

The triethylamine compound began to decompose at about 210° C. The solid remained dry, but soon started to char. Triethylamine was the principal product at first, but white crystals also began to collect, condensing from the gas phase away from the reaction zone. On further heating at higher temperatures the amine disappeared, the charring solid turned black, the white crystals continued to gather, and other volatile products appeared. The black ash, burnt in air, transformed to silica.

2. $SiCl_4(Bu_3N)_4$

The tributylamine tetraminate is a pale yellow powder that began to decompose at about 185°, becoming brown and sticky with liquid amine that was only partly volatile. The first stages of the decomposition were followed at higher temperatures by charring in the dry solid and the formation of amine chlorides.

3. $SiCl_4(Et_2NH)_4$

The white powder started to decompose without charring at about 215°, releasing some amine, while amine hydrochloride also formed as white crystals that had condensed from the vapors. Charring in the solid began only at higher temperatures.

4. $SiCl_4((CH_2)_5NH)_4$

Decomposition, without charring of the white powder, began at about 220°. The principal volatile product was the amine hydrochloride, although some free amine might have been present. When charring began at higher temperatures, the solid had already lost most of its chlorine.

5. $SiCl_4(BuNH_2)_4$

Decomposition of the primary amine addition compound began at about 215° with the appearance of a colorless liquid that clotted the white powder and froze to form a white solid that corresponded to butylammonium chloride. No free amine was observed.

Aliphatic Diaminates

What were presumed to be the diaminates of the five aliphatic amines were observed, but only the tributylamine diaminate was analyzed (Table I). It is a brown solid that reacts quickly with moist air, water, or excess amine. It was recovered from silicon tetrachloride mixed with tributylamine in the ratio of 15/1. The other addition compounds, assumed to be diaminates, were all yellow in color, and generally reactive.

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Discussion

The decomposition of the tetraminates of the tertiary amines apparently begins with the liberation of the amine from the addition compound. The temperature at which decomposition begins is lowest for the weakest base, dimethylaniline (100° C.), and highest for the strongest base, triethylaniline (210°). These comparisons are shown in Table II. The strength of coordinate bonds would also be expected to increase with the basicity of the donor group. Therefore the relative stabilities of the tertiary amine addition compounds will be associated with the strengths of the coordinate bonds between the amine and the silicon tetrachloride.

The compounds formed from primary amines decompose initially without charring, with the formation of the appropriate amine hydrochloride. The temperature required for decomposition is higher for the stronger base, butylamine (215° C.) than for the weaker base, aniline (185° C.). But the first steps in the decomposition must now include the elimination of hydrogen chloride from the addition compound. If this precedes, or is simultaneous with, the dissociation of free amine from the addition compound, rather good mechanistic evidence for the presence of hydrogen bonds in the addition compounds would be provided. No free amine was detected in the decomposition of the primary amine compounds. Again, the aniline tetraminate is thermally much stabler (185° C.) than the tetraminate of the stronger base, dimethylaniline (100° C.). It therefore appears plausible, and perhaps necessary, to assume that, in addition to coordinate bonds, these addition compounds are stabilized by hydrogen bonds to the chlorine atoms in silicon tetrachloride, when the amine nitrogen is hydrogenated.

As the thermal decompositions of the tertiary amine compounds and of the primary amine compounds are different chemical reactions, the decomposition temperatures of these compounds do not properly compare their relative stabilities, for a limit to the thermal stability of the compounds is the temperature at which the disruptive chemical reaction, the formation of amine hydrochlorides, occurs, and not simply the dissociation of the addition compounds. It might be expected that heats of formation would better show the stability of the primary amine compounds, relative to the tertiary amine compounds, than do the decomposition temperatures.

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THE MERCAPTOLYSIS OF GLUCOSE AND GALACTOSE PENTAACETATES[1]

By R. U. Lemieux

Abstract

The mercaptolysis of the α-and β-pentaacetyl derivatives of glucopyranose and galactopyranose at 0°C. with zinc chloride catalyst was studied. The β-pentaacetates were rapidly transformed to the corresponding ethyl tetraacetyl-1-thio-β-D-glycosides in excellent yields; however, the α-anomers were highly resistant to the mercaptolytic conditions. The results are interpreted on the basis of a participation by the C_2-acetoxy group in the replacements at the lactol carbon atom of the β-pentaacetates with the intermediate formation of a resonance stabilized cyclic carbonium ion.

Brigl and Schinle (8) first studied the interaction of acylated cyclic sugars with ethyl mercaptan in the presence of an acid catalyst. Hydrochloric acid was used as catalyst and the too rapid deacetylation of the pentaacetyl glucoses led to the use of the pentabenzoyl derivatives. Under the conditions used, the pentabenzoyl glucopyranoses remained unchanged. In 1934, Wolfrom and Thompson (36) modified the procedure by substituting anhydrous zinc chloride as catalyst and by operating in the presence of either anhydrous sodium sulphate or Drierite (anhydrous calcium sulphate) as drying agents. In this manner, the acid hydrolysis of the acetyl derivatives was minimized. They showed that the treatment of the fully acetylated cyclic form of a ketose with ethyl mercaptan and zinc chloride led to the replacement of the acetoxy group at the lactol carbon atom by the ethylthio group. Furthermore, they showed that the acetyl derivatives of *aldehydo-* and *keto*-sugars yielded the diethyl thioacetals without loss of acetoxy group. These conditions for mercaptolysis therefore comprised a valuable method for the differentiation of cyclic and open-chain acetyl derivatives of ketoses (36). However, statements (27, p. 154) to the contrary not withstanding, there appears to be no report of applications of this mercaptolysis procedure to fully acetylated cyclic aldoses.

This communication deals with the results obtained when the α- and β-pentaacetyl derivatives of D-glucopyranose and D-galactopyranose were interacted with ethyl mercaptan and zinc chloride. Ethyl tetraacetyl-1-thio-β-D-glucopyranoside was obtained in 71.2% yield by the mercaptolysis of pentaacetyl-β-D-glucopyranose. Mercaptolysis of pentaacetyl-β-D-galactopyranose yielded ethyl tetraacetyl-1-thio-β-D-galactopyranoside in 75.6% yield. However,

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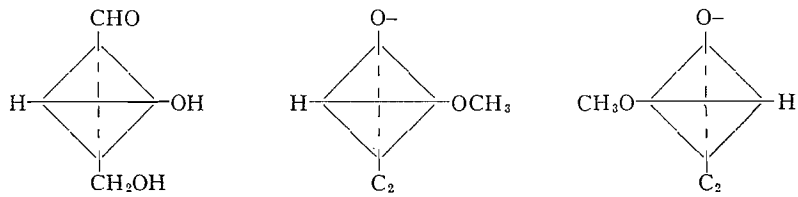
the mercaptolysis of the α-pentaacetyl compounds was not a practical means for the preparation of 1-thioglycosides. Schneider, Sepp, and Stiehler (32) prepared ethyl tetraacetyl-1-thio-β-D-glucopyranoside in 19% yield through the interaction of acetobromoglucose with potassium mercaptide. Ethyl 1-thio-α-D-glucopyranoside was obtained in 20% yield by treating glucose diethyl mercaptal with 22% hydrochloric acid (6, 26). Fried and Walz (9) have prepared the anomeric ethyl tetraacetyl-1-thio-D-manno- and galactopyranosides in low yield by the prolonged treatment of the sugar with ethyl mercaptan and concentrated hydrochloric acid followed by acetylation.

The melting point, 82.5-83°C. and $[\alpha]_D -28°$ found for ethyl tetraacetyl-1-thio-β-D-glucopyranoside were higher than the values, m.p. 78-79°C. (32), $[\alpha]_D -25.6°$ (25), previously reported. However, Schneider, Sepp, and Stiehler (32) have reported that some of their preparations melted at 82°C. The identity of the compound was established by deacetylation to the thioglucoside and reductive desulphurization to tetraacetyl-1,5-anhydro-D-sorbitol. The physical constants found for the ethyl tetraacetyl-1-thio-β-D-galactopyranoside and its deacetylated derivative were in agreement with those recently reported by Fried and Walz (9).

Hudson's Rules of Isorotation (15) state that for an α, β-pair of anomers the more dextrorotatory member is designated either α-D or β-L and the more levorotatory member is termed either β-D or α-L. As pointed out by Hudson (16, p. 17) these rules are no longer of a wholly empirical nature and at least for the methyl glycosides of many sugars (20) the rules have consistently allocated, to each of the α-and β-series, compounds of like configuration for the lactol carbon atoms. Ballou, Roseman, and Link (1) recently have reviewed the basis for the allocation of anomeric configurations. However, these authors overlooked the important and decisive argument for the configuration of methyl β-D-glucopyranoside advanced by Hudson (16, p. 17) based on the methanolysis of D-glucosan $<1, 5>_\alpha$ $<1, 2>$ (13). Thus, for the many methyl glycosides studied (20), it seems clear that the configurations of the lactol carbon atoms relative to the configuration of D-glyceraldehyde (I) are as shown



α – D or β – L

β – D or α – L

I II III

in II and III. These configurations are homologous to the accepted configurations of the α- and β-glucopyranoses (4). Ballou, Roseman, and Link (1) have

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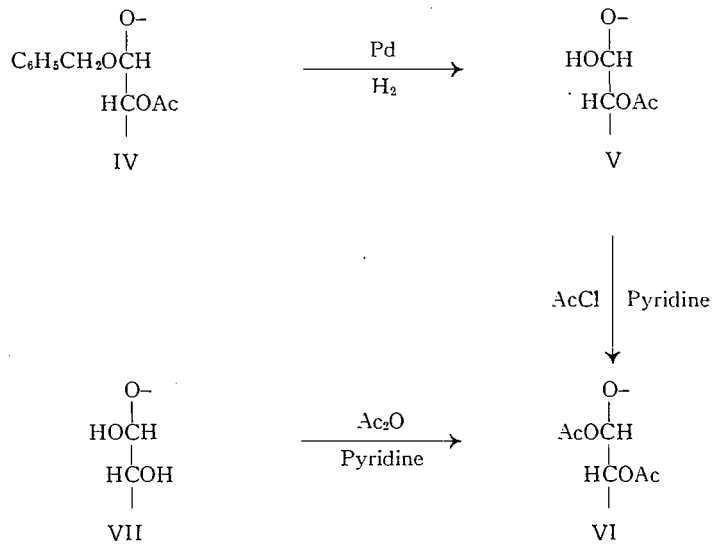
converted some acetylated benzyl glycosides to the corresponding 1-hydroxy polyacetyl aldoses by catalytic hydrogenolysis and have thus related the anomeric configurations of these compounds. Thus, benzyl tetraacetyl-β-D-glucopyranoside (IV) was converted to 2,3,4,6-tetraacetyl-β-D-glucopyranose (V). We have acetylated the latter compound (12) with acetyl chloride in benzene-pyridine to pentaacetyl-β-D-glucopyranose (VI) in 70% yield. Since this



acetylation would be expected not to affect the configuration of the lactol carbon atoms, the relative configurations of V and VI would be as shown. It has long been observed (2) that the low temperature acetylation of a free sugar by acetic anhydride in pyridine solution yields a polyacetyl derivative of the same anomeric configuration. Thus, the acetylation of β-D-glucopyranose (VII) under these conditions yields the β-D-pentaacetyl derivative (17). Considering the fact that these chemical transformations infer the same relative configurations for the substances IV to VII and that these conclusions are in accord with the predictions based on Hudson's Rules of Isorotation, there can be little doubt that the structure of pentaacetyl-β-D-glucopyranose (VI) is as shown. Furthermore, considering the success of the Rules of Isorotation in the correlation of the anomeric configurations of several methyl glycosides (20), there can be little doubt about the configurations of any pair of truly anomeric aldoses or their simple derivatives as allocated on the basis of these rules.

The treatment of pentaacetyl-β-D-glucopyranose with 10% zinc chloride in dry ethyl mercaptan at 0°C. for 12 hr. gave ethyl tetraacetyl-1-thio-β-D-glucopyranoside in a minimum yield of 71.2%. The residual sirups could not be

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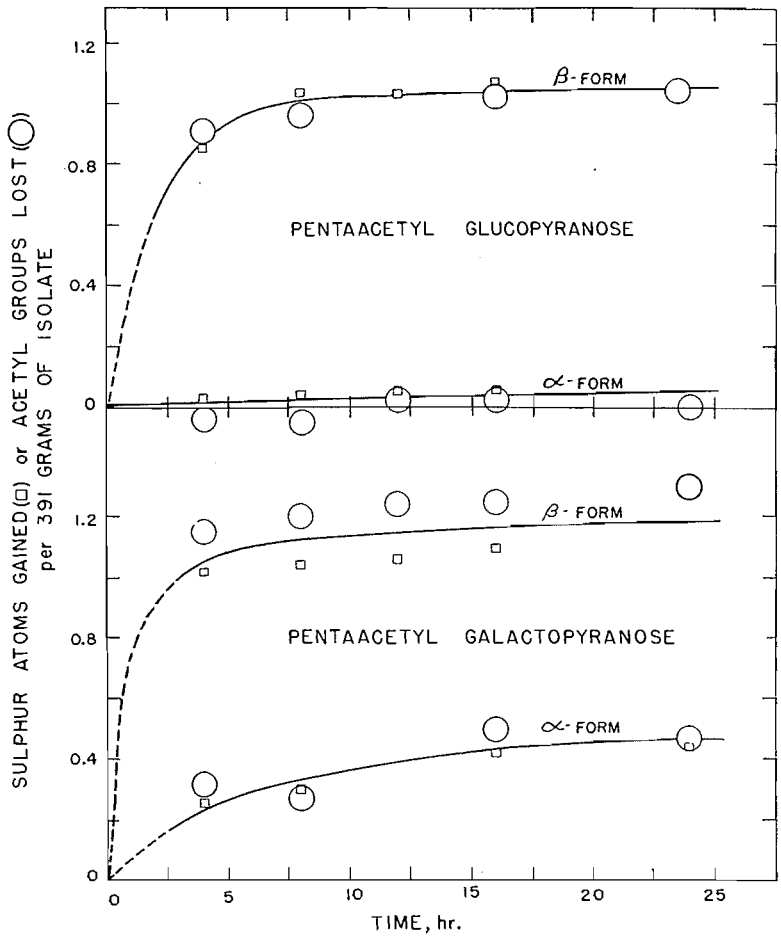

FIG. 1. *The rates of mercaptolysis of the anomeric pentaacetates of* D-*glucose and* D-*galactose in zinc chloride–ethyl mercaptan solution at 0°C.*

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made to yield starting material. A similar treatment of pentaacetyl-α-D-glucopyranose brought about little reaction and the starting material was recovered nearly quantitatively. However, by operating at room temperature and extending the reaction time to 42 hr., the α-anomer was transformed to an isolable amount of ethyl tetraacetyl-1-thio-β-D-glucopyranoside but a large quantity of the starting material remained unaffected. In order to more definitely establish this marked difference in reactivity between the two anomers toward the mercaptolytic conditions, the rates of mercaptolysis were determined at 0°C. At various time intervals, the glucose derivatives in an aliquot of the reaction mixture were isolated and the product was analyzed for acetyl group and sulphur content. Although it was clear that the replacement of the C1-acetoxy group by the ethylthio group was accompanied by other reactions, the curves in Fig. 1 were obtained by plotting against time both the number of acetyl groups lost and the number of sulphur atoms gained calculated on the assumption that both the starting material and the reaction products possessed a molecular weight of 391. The figure 391 is purely arbitrary and was chosen because of its close agreement with the molecular weights of both the starting materials, 390, and ethyl tetraacetyl-1-thio-β-D-aldohexopyranoside, 392. Thus, Fig. 1 shows clearly the great difference in reactivity between the anomeric glucose pentaacetates under the reaction conditions used and it is clear that the main reaction involved the substitution of acetoxy groups by ethylthio groups.

Therefore, the mercaptolytic replacement of the C1-acetoxy group of pentaacetyl-β-D-glucopyranose, which contains the C1- and C2-acetoxy groups in *trans* relationship, proceeded with retention of configuration while the C1-acetoxy bond of pentaacetyl-α-D-glucopyranose, which contains the C1- and C2-acetoxy groups in *cis* relationship, underwent mercaptolysis with inversion of the configuration of the lactol carbon. The stereochemical routes of the reactions are therefore reminiscent of the findings by Winstein and Buckles (35) on the role of neighboring groups in replacement reactions. Furthermore, these authors pointed out that the participation of a neighboring group greatly facilitates a replacement reaction. Thus, they showed that under conditions more drastic than those needed to bring about reaction of the *trans*-1-acetoxy-2-chlorocyclohexane with silver acetate, the *cis*-isomer remained completely unchanged. The results led the authors to state, "The *trans*-acetoxy group seems to be able to supply some driving force for the reaction and the *cis*-acetoxy group is essentially unable to do this." Similar effects have been noted for the replacement of mesyloxy (23) and tosyloxy (3) groups situated in ring structures and the activating effect of a participating neighboring group appears widespread.

It was thus apparent that the mechanisms of the main reactions for the mercaptolyses of the anomeric glucose pentaacetates could be formulated as follows.

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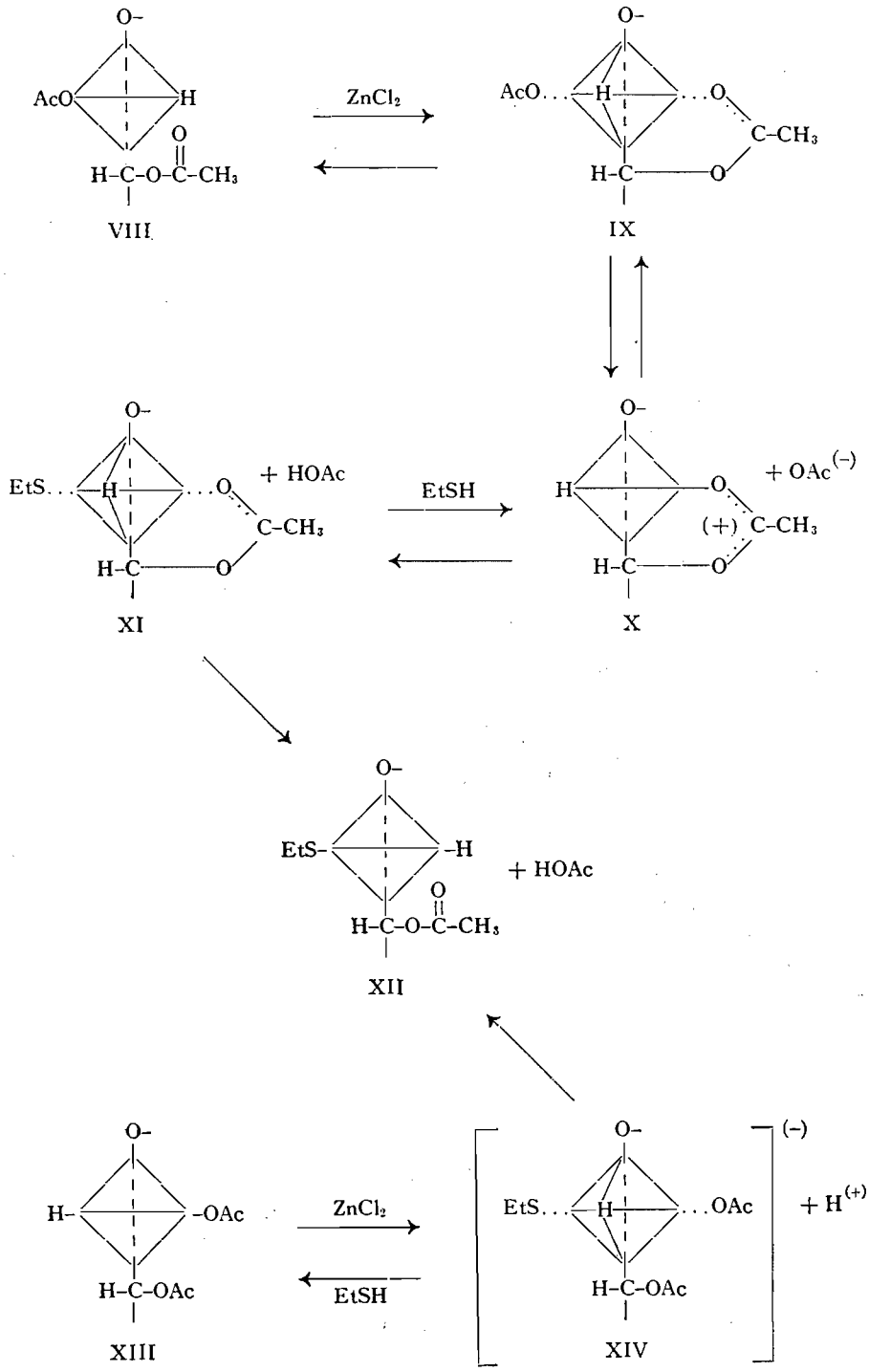

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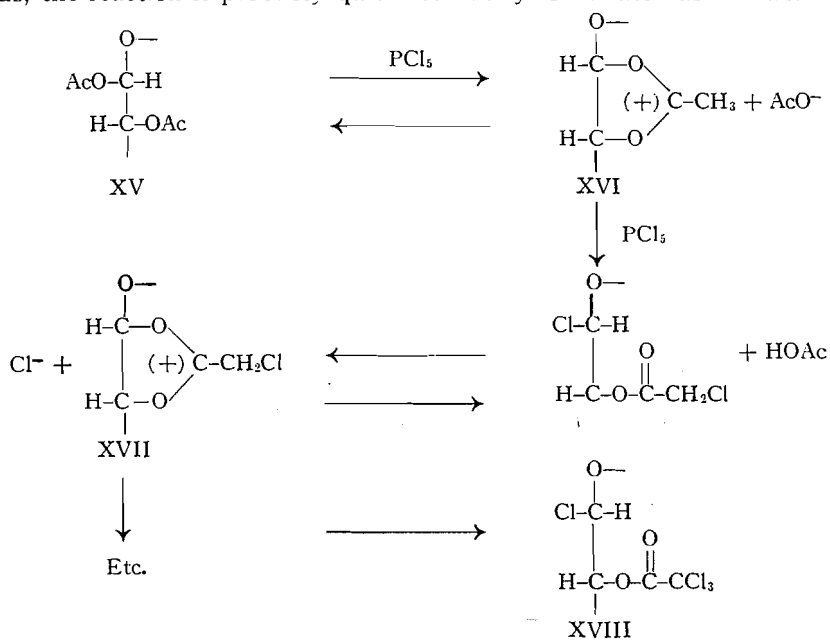
For the pentaacetyl-β-D-glucopyranose (VIII), the acid catalyzed removal of the C1-acetoxy group was likely facilitated (11, p. 131; 34, p. 216) by the backside approach of the nucleophilic C2-acetoxy group with the transition state (IX) decomposing to the resonance stabilized α-D-carbonium ion (X). The neutralization of this ion, under the prevailing acidic conditions, would proceed through the transition state (XI) with inversion of the lactol carbon atom to yield the ethyl tetraacetyl-1-thio-β-D-glucopyranoside (XII) a substance which is known (32) to be highly stable under acidic conditions. The acid catalyzed removal of the C1-acetoxy group of the pentaacetyl-α-D-glucopyranose (XIII) was probably facilitated through a backside approach by a nucleophilic group provided by the solvent, ethyl mercaptan, to yield the transition state (XIV) which decomposed to the ethyl tetraacetyl-1-thio-β-D-glucopyranoside (XII).

Isbell (19) has noted that reactions of acetohalogeno-sugars tend to yield derivatives with the C1 and C2 atoms in *trans*-relationship. The possible formation of cyclic carbonium ions of the type of structure shown for X was definitely established by Lucas, Mitchell, and Garner (22). Hurd and Holysz (18) have established the formation of 1, 2-ketal derivatives of 3, 4, 6-triacetyl-α-D-glucopyranose on the interaction of tetraacetyl-α-D-glucopyranosyl bromide with dialkylcadmium. Thus, it is sterically possible for the carbonyl oxygen of an acetoxy group situated at the C2-position of glucopyranose to interact with the lactol carbon atom. The preparation by Brigl (5) of 2-trichloroacetyl-3,4,6-triacetyl-β-D-glucopyranosyl chloride (XVIII) by the interaction of pentaacetyl-β-D-glucopyranose (XV) with phosphorus pentachloride appears best rationalized, on the basis of modern chemical theory, by the assumption that the preferential chlorination of the C2-acetoxy group is related to an activation of the C-H bonds by the formation under the reaction conditions of the cyclic carbonium ion intermediates such as XVI and XVII. Thus, the reaction is probably quite accurately formulated as follows.



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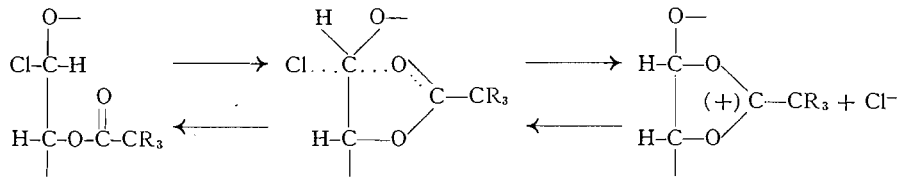
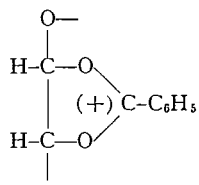
Schlubach, Stadler, and Wolf (31) have shown that tetraacetyl-β-D-glucopyranosyl chloride (30), although quite stable in benzene, ether, or carbon tetrachloride solution, rapidly mutarotated in acetonitrile or chloroform solution and the transformation was nearly complete after 96 hr. On the other hand, Hickinbottom (14) has shown that trichloroacetyl-3,4,6-triacetyl-β-D-glucopyranosyl chloride does not exhibit any appreciable anomerization in benzene or acetonitrile after 500 hr. and only a slight increase in rotation occurs in chloroform after 540 hr. This stabilizing effect may be related to the weaker nucleophilic properties of the carbonyl oxygen of the trichloroacetyl group as compared to the carbonyl oxygen of the acetyl group. That is, it is reasonable to expect that the establishment of the transition state (XIX) and the carbonium ion (XX) would be more difficult with R = Cl than R = H.



XIX XX

Thus, it is apparent that the postulation of the cyclic carbonium ion (X) as an intermediate in many replacement reactions at the lactol carbon atom of acylated glucose derivatives is not pure speculation since the idea is strongly supported by highly plausible interpretations of a variety of established experimental facts. It is noteworthy that Ballou, Roseman, and Link (1) have recently reported that, on hydrogenolysis, the acetylated benzyl glucoside, xyloside, and arabinoside in which the aglycon and C2-acetoxy groups are *trans* cleave much more easily than those with a *cis* relationship. Ness, Fletcher, and Hudson (24) have recently shown that the β-forms of both tribenzoyl-D-ribopyranosyl chloride and bromide reacted much more rapidly in 1: 9-dioxane-methanol than did the corresponding α-anomers and in each case methyl tribenzoyl-β-D-ribopyranoside was the principal product formed. It was postulated that the reactions of the β-D(*trans*)-halides involved the intermediate formation of the cyclic carbonium ion (XXI).



XXI

As was found for the pentaacetyl glucoses, under the same reaction conditions, the mercaptolysis of pentaacetyl-β-D-galactopyranose proceeded much more rapidly than did the mercaptolysis of the α-anomer (see Fig. 1). Only starting material could be isolated by crystallization of the product from the

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mercaptolysis of the α-anomer for 60 hr. at 0°C. On the other hand, the same treatment of the β-pentaacetate for only 12 hr. gave ethyl tetraacetyl-1-thio-β-D-galactopyranoside in high yield. It is therefore probable that the mercaptolysis of pentaacetyl-β-D-galactopyranose involved the participation of the C2-acetoxy group with the formation of a transient cyclic carbonium ion in the manner indicated above for pentaacetyl-β-D-glucopyranose.

Deacetylation of the residual sirupy materials from the mercaptolysis at room temperature of both the α- and β-pentaacetates of glucose yielded the 2-dehydroxy-2-ethylthio-D-glucose (D-mannose?) diethyl mercaptal of Brigl, Mühlschlegel, and Schinle (7).

The mercaptolysis of other anomeric pairs of sugar acetates is being studied.

Experimental

The rotations were measured at room temperature, 23-28°C., and the melting points were corrected.

Ethyl tetraacetyl-1-thio-β-D-glucopyranoside

Dry pentaacetyl-β-D-glucopyranose, 20 gm., was dissolved at 0°C. in anhydrous ethyl mercaptan, 100 ml., which contained 10 gm. of anhydrous zinc chloride. The mixture was shaken until solution was complete and left for a total of 12 hr. in ice water. The resulting mixture was poured into a stirred, saturated aqueous solution of sodium bicarbonate, 500 ml. The precipitate was collected by filtration and it was stirred with 150 ml. of boiling chloroform. The residue was collected by filtration and the chloroform filtrate was used to extract the aqueous filtrate from the first filtration. The procedure for the extraction of the precipitate and aqueous solution was repeated twice more. The combined chloroform extracts were washed with water and dried over sodium sulphate. The solvents were removed *in vacuo* to yield a colorless sirup which soon crystallized. The crystalline mass was extracted with 10 ml. of ether followed by 30 ml. of 50% ether–Skellysolve F. The air-dried material, m.p. 78-80.5°C., weighed 10.26 gm. The ethereal filtrate was evaporated to sirup which was dissolved in 20 ml. of ether and Skellysolve F was added to turbidity. After standing in the cold for 24 hr. a second crop was obtained, 4.01 gm., which melted at 79-81°C. The total crude yield was 71.2%. The two crops were combined and recrystallized from 10 ml. of ethanol to yield 13.23 gm. of product, m.p. 80.5-82°C. After several further recrystallizations from ethanol, the substance melted at 82.5-83°C. with $[\alpha]_D -28°$ (*c*, 0.9 in chloroform). Calc. for $C_{16}H_{24}O_9S$: S, 8.16; acetyl, 45.84%. Found: S, 8.13; acetyl, 44.1%. Schneider, Sepp, and Stiehler (32) have reported the constants, m.p. 78-79°C., $[\alpha]_D^{20} -22.27°$ (*c*, 2.6 in acetylene tetrachloride), while Pacsu and Wilson (25) have recorded $[\alpha]_D -25.6°$ (*c*, 1.464 in chloroform) for ethyl tetraacetyl-1-thio-β-D-glucopyranoside.

When 20 gm. of pentaacetyl-β-D-glucopyranose was mercaptolyzed under the above conditions, with the exception that 15 gm. of anhydrous calcium

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sulphate, "Drierite", was added to the reaction mixture and that the solution was kept at room temperature for 17 hr., the yield of crude product was only 6.90 gm. The residual sirupy material was deacetylated in methanol solution with barium methylate as catalyst in the usual manner. Extraction of the product with ether yielded a substance which after two recrystallizations from water melted at 101-102°C. with $[\alpha]_D$+ 2.3° (*c*, 1.2 in acetone). These constants are in close agreement with those recorded for the 2-dehydroxy-2-ethylthio-D-glucose (mannose?) diethyl mercaptal of Brigl, Mühlschlegel, and Schinle (7), m.p. 102°C. (little sintering at 101°C.), $[\alpha]_D$+ 2.27° (*c*, 2.2 in acetone). Calc. for $C_{12}H_{26}O_4S_3$: S, 29.1%. Found: S, 28.6%.

Dry pentaacetyl-α-D-glucopyranose, 5 gm., was dissolved in dry ethyl mercaptan (27 ml.) which contained anhydrous zinc chloride, 4 gm., and 4 gm. of anhydrous sodium sulphate. After standing at room temperature for 42 hr., the mixture was poured with stirring into 200 ml. of saturated aqueous sodium bicarbonate solution. The resulting mixture was extracted with chloroform in the manner described above. The extract was reduced to a sirup which was treated with about 25 ml. of Skellysolve F and the solvent was removed by blowing. After this procedure was repeated three times, crystallization soon began. Ether was added to dissolve the sirupy phase and Skellysolve F was added to turbidity. The crystals which formed weighed 1.40 gm. and melted at 109-111°C. and were found to be essentially pure pentaacetyl-α-D-glucopyranose. The mother liquor was reduced to yield 3.25 gm. of a pale-yellow sirup, $[\alpha]_D$+ 28° (chloroform). This substance was dissolved in ether and Skellysolve C was added to turbidity. After seeding with ethyl tetraacetyl-1-thio-β-D- glucopyranoside, the solution was allowed to stand overnight at 4°C. Crystals, 0.73 gm., $[\alpha]_D$− 0.1° (chloroform), were deposited which, after two recrystallizations from ethanol, yielded 275 mgm. of material, m.p. 81-82°C., $[\alpha]_D$− 25.8° (chloroform). This melting point was not depressed on admixture with ethyl tetraacetyl-1-thio-β-D-glucopyranoside. The main mother liquors were reduced to sirup which was dissolved in ether and Skellysolve F was added to turbidity. After standing at 4°C. for some time 0.15 gm. of pentaacetyl-α-D-glucopyranose was deposited. The mother liquors were taken to a dry sirup which was deacetylated in methanol solution with barium methylate catalyst. Extraction of the product with ether yielded a crystalline material which after recrystallization from ethanol–water melted at 100-101°C. with $[\alpha]_D$+ 1.4° (*c*, 1 in acetone) and this melting point was not depressed on admixture with the above described 2-dehydroxy-2-ethylthio-D-glucose (mannose?) diethyl mercaptal. The yield of recrystallized product was 110 mgm. The sirup which remained after the above ether extraction was dissolved in water and treated with yeast for one day. After removal of the yeast cells, the solution was concentrated *in vacuo* to a dry sirup, 230 mgm., which was acetylated with acetic anhydride and sodium acetate. The product, $[\alpha]_D$+ 40° (chloroform) has not crystallized. It was therefore apparent that little, if any, ethyl tetraacetyl-1-thio-α-D-glucopyranoside, $[\alpha]_D$+ 194° (chloroform) (25), was present in the reaction product.

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Deacetylation of the ethyl tetraacetyl-1-thio-β-D-glucopyranoside in methanol solution and barium methylate catalyst (9) yielded a product which after three recrystallizations from ethanol – ethyl acetate melted at 99.5-100.5°C. with $[\alpha]_D - 57°$ (*c*, 0.9 in water). Schneider, Sepp, and Stiehler (32) have reported ethyl-1-thio-β-D-glucopyranoside to melt at 99-100°C. with $[\alpha]_D^{25} - 55.14°$ (*c*, 4 in water).

1, 5-Anhydro-D-sorbitol (polygalitol)

Ethyl tetraacetyl-1-thio-β-D-glucopyranoside, 1. 0 gm., was dissolved in 70% aqueous ethanol and 20 ml. of settled Raney nickel catalyst was added. After refluxing for five hours, the catalyst was removed by filtration and washed three times with hot ethanol. The combined filtrates were reduced *in vacuo* to a sirup which crystallized after 10 days. After recrystallization from ether-Skellysolve F the yield was 500 mgm. of a substance, m.p. 55-65°C., which was recrystallized from water followed by recrystallization from ether-Skellysolve C. The nicely crystalline product melted at 65-66°C. with $[\alpha]_D + 40°$ (*c*, 0.6 in chloroform). Calc. for $C_{14}H_{20}O_9$: acetyl, 51.81%. Found: acetyl, 51.5%. Richtmyer and Hudson (29) have definitely established the dimorphous character of tetraacetyl polygalitol, $[\alpha]_D^{20} + 38.9°$ (*c*, 2 in chloroform), with melting points at 65-67°C. and 73-74°C.

A solution of tetraacetyl polygalitol, 150 mgm., in 15 ml. of dry methanol was saturated with ammonia. After four hours at room temperature, the solution was reduced to a sirup which soon crystallized. Recrystallization from dry methanol gave 60 mgm., 81% yield, of a substance, m.p. 141-141.5°C., $[\alpha]_D + 43°$ (*c*, 0.5 in water). Polygalitol is reported (28) to melt at 141-142°C. with $[\alpha]_D + 42.4°$ (*c*, 2 in water).

Ethyl Tetraacetyl-1-thio-β-D-galactopyranoside

Dry pentaacetyl-β-D-galactopyranose, 5 gm., was dissolved at 0°C. in 25 ml. of dry ethyl mercaptan which contained 2.5 gm. of anhydrous zinc chloride and the reaction mixture was kept in ice water for 12 hr. The reaction product was isolated as described above and the sirupy material soon crystallized. The material was dissolved in 15 ml. of ether and 5 ml. of Skellysolve F and the solution was cooled and seeded. After crystallization appeared complete, 10 ml. of Skellysolve F was added and the mixture was kept at 4°C. for two hours. Filtration gave 3.78 gm. of material, m.p. 71.5-73°C., 76.5% yield. After two recrystallizations from ether-Skellysolve F, the material melted at 74.5-75°C. with $[\alpha]_D - 8.5°$ (*c*, 2.3 in chloroform). Calc. for $C_{16}H_{24}O_9S$: acetyl, 43.64%. Found: acetyl, 43.8%. Fried and Walz (9) have reported the constants, m.p. 74-75°C., $[\alpha]_D^{26} - 8.0°$ (*c*, 2.1 in chloroform) for ethyl tetraacetyl-1-thio-β-D-galactopyranoside.

The substance, 500 mgm., was deacetylated in methanol solution with barium methylate catalyst to yield a product which was recrystallized from ethanol – ethyl acetate. The yield was 200 mgm., m.p. 122-122.5°C., $[\alpha]_D -$

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23.5° (*c*, 1.1 in water). Fried and Walz reported (9) the constants, m.p. 121.5-122.5°C., $[\alpha]_D^{26} - 23.5°$ (*c*, 0.89 in water), for ethyl 1-thio-β-D-galactopyranoside.

Dry pentaacetyl-α-D-galactopyranose, 5 gm., was subjected to mercaptolysis under the conditions described for the β-anomer except that the reaction time was extended to 60 hr. The sirupy reaction product was isolated in the usual way and was freed of chloroform by the addition of Skellysolve C followed by removal of the solvents *in vacuo*. This procedure was repeated several times. The resulting sirup was dissolved in ether and Skellysolve C was added to turbidity. After cooling, the solution was seeded with pentaacetyl-α-D-galactopyranose and left at 4°C. for 14 days. The crystals, 0.73 gm., which deposited were washed with a little ether and recrystallized from alcohol. The melting point was 91-93.5°C. with $[\alpha]_D + 98°$ (*c*, 1.8 in chloroform) and this melting point was not depressed on admixture with the starting material, m.p. 94-95°C., $[\alpha]_D + 105°$ (*c*, 1 in chloroform). The residual sirup, $[\alpha]_D + 22°$ (*c*, 3.6 in chloroform), could not be made to crystallize.

Rates of Mercaptolysis

Ethyl mercaptan, 90 ml., dried over anhydrous sodium sulphate, was added to 10.1 gm. of anhydrous zinc chloride at 0°C. and the mixture was shaken until solution was complete. At zero time, 15 ml. aliquots of the solution were added at 0°C. to 3.0 gm. samples of the sugar acetates. The glass-stoppered flasks were shaken until solution appeared complete. The contents of each flask were then distributed by means of a syringe as 2 ml. aliquots into dry test tubes. At the various time intervals, the content of a test tube was poured into 25 ml. of saturated sodium bicarbonate solution. After stirring until reaction appeared complete, the white precipitate was collected by filtration and stirred with 15 ml. of boiling chloroform. The mixture was filtered and the filtrate was collected with the aqueous filtrate of the first filtration. After shaking, the chloroform layer was washed twice with water. This extraction procedure was repeated two more times using the same equipment and wash waters. The chloroform extracts were combined, dried by filtration through dry filter paper, and reduced *in vacuo* to a sirup. The sirup was first dried at 65°C. under partial vacuum in a stream of air, then at 10^{-2} mm. for two days at room temperature. The acetyl group contents were determined at 0°C. by the procedure developed by Kunz (21) but on a semimicro scale. The sulphur estimations were by the volumetric dry combustion technique (33).

Acetylation of 2, 3, 4, 6-Tetraacetyl-β-D-glucopyranose

Acetyl chloride, 0.28 gm., was dissolved in 20 ml. of dry benzene and 5 ml. of dry pyridine was added at 0°C. 2,3,4,6-Tetraacetyl-β-D-glucopyranose (10), 1 gm., was added and the mixture was shaken for 15 min. at 0°C., and for 1.5 hr. at room temperature. Ice water, 100 ml., was added and, after vigorous shaking, the benzene layer was separated and washed with water. The dried benzene solution was reduced in a stream of air to a crystalline material which

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was recrystallized from ethanol. The yield was 0.75 gm., 70%, m.p. 131-132°C. The melting point was not depressed on admixture with penta-acetyl-β-D-glucopyranose, m.p. 131-132°C.

Acknowledgments

The valuable technical assistance provided by Miss Carol Brice and R. Charanduk is gratefully acknowledged.

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PHOTOLYSIS OF 2, 2′, 4, 4′-TETRADEUTERODIETHYL KETONE[1]

By M. H. J. Wijnen[2] and E. W. R. Steacie

Abstract

The photolysis of $CH_3CD_2COCD_2CH_3$ has been studied over a temperature range from 25°C. to 365°C. The results confirm several features of the mechanism, previously proposed for the photolysis of diethyl ketone. It is concluded that disproportionation of ethyl radicals occurs by a "head to tail" mechanism. As activation energy for the reaction

$$CH_3CD_2 + CH_3CD_2COCD_2CH_3 = CH_3CD_3 + CH_3CDCOCD_2CH_3 \quad (4)$$

a value $E_4 = 8.7$ kcal. was found. As activation energy for Reaction (5)

$$CH_3CD_2 + CH_3CD_2COCD_2CH_3 = CH_3CD_2H + CH_2CD_2COCD_2CH_3 \quad (5)$$

a value of $E_5 = 11.7$ kcal. was found. An activation energy of $\backsim$ 17 kcal. is estimated for the thermal decomposition of the pentanonyl radical.

Introduction

As a result of previous investigations at Rochester and at Ottawa the following reactions were given (2) to explain the mechanism of the photolysis of diethyl ketone.

$C_2H_5COC_2H_5 + h\nu$	$= 2C_2H_5 + CO$	I_a	(1)
$C_2H_5 + C_2H_5$	$= C_4H_{10}$	$k_2(C_2H_5)^2$	(2)
$C_2H_5 + C_2H_5$	$= C_2H_6 + C_2H_4$	$k_3(C_2H_5)^2$	(3)
$C_2H_5 + C_2H_5COC_2H_5$	$= C_2H_6 + C_2H_4COC_2H_5$	$k_4(C_2H_5)(C_2H_5COC_2H_5)$	(4)
$C_2H_4COC_2H_5$	$= C_2H_4 + CO + C_2H_5$	$k_5(C_2H_4COC_2H_5)$.	(5)

To obtain further information about this mechanism the photolysis of $CH_3CD_2COCD_2CH_3$ has been studied. Since this compound will produce CH_3CD_2 radicals it is at the same time a promising source of ethyl radicals for the study of hydrogen-abstraction reactions of the type $C_2H_3D_2 + RH = C_2H_4D_2 + R$, and work along these lines is in progress.

Experimental

The apparatus was the same as that used in the photolysis of ordinary diethyl ketone (2). One Ward still was replaced by a pump-down liquid nitrogen trap which allowed the CO fraction to be pumped off at about −220°C. The C_2 fraction was pumped off at −175°C. and divided into two parts. From one part the ethylene was removed by absorption on a mercuric acetate bead in a Blacet–Leighton apparatus (1). The residual ethane was analyzed by means of a mass spectrometer. The other part was analyzed directly by the mass spectrometer. The spectrum of peak heights of the ethane fraction obtained from the first part was subtracted from the total C_2 spectrum and so the

[1] *Manuscript received August 17, 1951.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa. Issued as N.R.C. No. 2584.
[2] *National Research Council of Canada Postdoctorate Fellow, 1949-51.*

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ethylene spectrum obtained. The C_4 fraction was pumped off at $-115°C$. Owing to the complicated cracking-pattern of butane, no results were obtained for the isotopic composition of this fraction. As light source a Hanovia 500 w. type A medium-pressure quartz lamp was used.

The diethyl ketone was prepared by Dr. L. C. Leitch and Mr. A. T. Morse of this laboratory. Mass spectrometer analysis showed the following composition: $C_4D_3H_7CO$, 4.2%; $C_4D_4H_6CO$, 91.8%; $C_4D_5H_5CO$, 2.47%; and $C_4D_6H_4CO$, 1.51%. The same analysis showed that $92 \pm 1\%$ of the ethyl radicals (produced by cracking of $C_2D_2H_3COC_2D_2H_3$) contained two deuterium atoms. Considering the method of preparation of the compound (exchange of light ketone with heavy water) it has been assumed that these two deuterium atoms are present predominantly on the α-carbon atoms. The amounts of diethyl ketones other than $CH_3CD_2COCD_2CH_3$ are, in general, too small to affect the results significantly and may be neglected in the subsequent discussion.

Results

In Table I are given the results of experiments done at various temperatures and diethyl ketone pressures. The initial intensity of the light source in several experiments was cut down by the use of neutral density filters. This is indicated in Column 2. The pressure of diethyl ketone (Column 5) has been given in mm. at °C., converted to this temperature from the pressure measured at the reaction temperature. All products are given in mm.[3] at N.T.P. Four different ethanes were found, $C_2D_4H_2$, $C_2D_3H_3$, $C_2D_2H_4$, and C_2DH_5. The amounts of $C_2D_4H_2$ produced (given in Column 10) are too small to allow accurate determination. The amounts of C_2DH_5 produced (Column 13) are, owing to overlapping of the several ethane spectra, to be considered as very inaccurate. The error for this ethane may amount to ca. 50%. It is, however, to be expected that the error will be consistent for all the determinations. Inaccurate also are the values for C_2DH_3 (last column). A much higher precision is obtainable for $C_2D_3H_3$, $C_2D_2H_4$, and $C_2D_2H_2$ and these are the most significant from the point of view of the mechanism.

To give a more simple picture of the C_2 fraction, Table II shows the components of the ethane and ethylene fraction as percentages.

Interpretation of Results

In the introduction the reaction mechanism for the photolysis of light diethyl ketone has been given. The photolysis of $CH_3CD_2COCD_2CH_3$ produces $C_2H_3D_2$ radicals which by Reaction (2) may recombine to form butane. Reactions (3), (4), and (5) become rather complex owing to the fact that here the ethyl radical contains H and D, and several isotopic reactions are thus possible in each case. We will, therefore, discuss the disproportionation reactions, the hydrogen-abstraction reactions and the thermal decomposition of the pentanonyl radicals in separate sections.

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TABLE I

PRODUCTS OF THE PHOTOLYSIS OF $C_4H_6D_4CO$

Expt. No.	Intensity, relative	Temp., °C.	Time, sec.	Pressure of diethyl ketone, mm. at °C.	Products in mm.³ (N.T.P.)				Isotopic analysis					
									Ethane fraction				Ethylene fraction	
					CO	Ethane	Ethylene	C_4	$C_2D_4H_2$	$C_2D_3H_3$	$C_2D_2H_4$	C_2DH_5	$C_2D_2H_2$	C_2DH_3
6	100	24	6090	25.9	232	31.0	23.0	206	0.26	0.6	25.4	4.7	20.4	2.6
7	10	24	34530	26.8	176	24.0	19.0	151	0.35	1.3	19.3	3.1	17.6	1.4
19	10	50.5	41640	23.2	218	27.2	20.3	185	0.0	3.4	21.0	2.8	19.4	0.9
20	100	50.5	5040	25.5	261	30.8	25.4	221	0.0	1.9	26.8	2.1	22.2	3.2
16	100	101	3215	20.7	159	26.4	9.2	133	1.3	4.6	18.4	2.0	8.3	0.9
17	10	101	45180	17.5	196	41.6	15.2	155	0.4	13.3	21.0	6.9	13.3	1.9
15	10	105.5	38400	22.2	197	39.3	12.9	152	0.4	14.0	19.0	5.9	11.5	1.4
27	10	138	43200	19.4	222	70.0	21.0	145	0.0	37.1	22.5	10.3	15.3	5.7
28	10	138	56100	14.3	205	61.9	16.7	139	0.3	29.9	21.5	10.1	14.7	2.0
1	100	180	3445	19.0	176	56.0	9.5	123	2.1	23.2	18.0	12.6	8.0	1.5
2	100	180	4160	19.5	218	71.0	15.4	137	3.1	29.3	22.0	16.6	–	–
3	10	180	24720	18.8	140	70.5	14.0	62	1.6	44.7	18.8	5.5	11.8	2.2
4	100	180	1960	17.9	98	31.4	8.6	69	–	–	–	–	–	–
5	100	180	7440	6.7	151	35.0	13.0	108	1.0	14.6	16.8	2.9	–	–
10	100	236	3035	16.4	150	94	16.0	70	0.5	56.6	21.9	14.8	14.0	2.0
11	10	236	37680	16.4	202	20.4	20.0	44	1.3	132	40.2	30.6	17.1	3.0
12	10	236	45420	9.5	157	138	19.7	36	0.1	84.8	27.2	25.5	18.0	2.0
13	26.5	236	14000	16.6	167	140	17.0	46	0.6	97	30.8	28.6	14.4	2.6
44	100	250	3320	15.9	166	119	11.4	73	0.0	73.8	23.5	21.2	11.4	–
46	30	250	9675	15.9	–	146	19.0	37.0	0.0	89.7	27.4	28.4	16.6	2.4
45	10	250	34680	16.2	–	238	28.0	–	0.0	149	41.6	48.0	22.1	5.9
47	3	250	72000	16.6	–	179	20.6	–	0.0	111	31.2	37.0	16.7	3.9
14	100	273	3000	16.65	163	143	21.6	42.4	0.5	99	32.2	32.2	18.3	3.3
23	100	300	2850	15.5	163	158	38.0	29.1	0.5	93	33.8	30.7	30.2	8.6
24	100	300	2400	13.65	131	129	30.0	25.2	0.4	75.6	26.4	26.4	23.5	6.5
50	30	300	5400	16.8	–	131	36.0	–	0.0	74.5	28.3	28.3	28.3	7.7
54	10	300	14280	16.75	–	150	46.4	–	0.0	83.2	35.4	31.4	34.2	12.2
52	3	300	80220	16.5	–	324	138	–	0.0	155	87.4	81	96.5	41.5
56	100	331	2100	15.0	–	149	62.6	–	0.0	75.6	37.7	34.8	44.9	17.7
40	100	350	1980	15.3	263	264	140	25.0	0.0	119	75.5	70	97.5	42.5
25	100	365	3000	14.1	338	403	272	25.4	1.8	165	138	98	190	82
26	100	365	1260	14.9	180	169	115	15.9	0.8	70.5	55.4	42	84.4	30.1
51	30	365	2280	14.2	–	165	112	–	0.0	60.3	61.9	42.8	81.0	31.0
48	10	365	7080	15.0	–	292	232	–	0.0	92.4	115	84	162	70
53	1.1	365	57600	15.0	–	97	91	–	0.0	23.4	45.8	27.8	–	–

NOTE:—*Indicates that no determination was made, frequently because of accidental loss of the sample.*

TABLE II

ISOTOPIC COMPOSITION OF C_2 FRACTION

Expt. No.	Ethane, cc. N.T.P.	Ethylene, cc. N.T.P.	Ethane, %				Ethylene, %	
			$C_2D_4H_2$	$C_2D_3H_3$	$C_2D_2H_4$	C_2DH_5	$C_2D_2H_2$	C_2DH_3
6	0.031	0.023	0.8	2.0	82.1	15.1	89	11
7	0.024	0.019	1.4	5.5	80.3	12.8	92.5	7.5
19	0.0272	0.0203	–	12.4	77.3	10.30	99	1
20	0.0308	0.0254	–	6.3	86.9	6.8	98	2
16	0.0264	0.0092	4.7	17.9	69.8	7.6	90.5	9.5
17	0.0416	0.0152	0.9	32.0	50.6	16.5	87.5	12.5
15	0.0393	0.0129	1.0	35.6	48.4	15.2	89.6	10.4
27	0.070	0.021	–	53.0	32.2	14.8	–	–
28	0.0619	0.0167	0.5	48.4	34.8	16.3	–	–
1	0.056	0.0095	3.7	41.5	32.1	22.6	84.5	15.5
2	0.071	0.0154	4.4	41.2	31.0	23.4	–	–
3	0.0705	0.0140	2.2	63.4	26.6	7.8	84.2	15.8
4	0.0314	0.0086	–	–	–	–	–	–
5	0.035	0.013	3.1	41.8	46.9	8.2	–	–
10	0.094	0.016	0.5	60.3	23.3	15.8	87.6	12.4
11	0.204	0.020	0.6	64.7	19.7	15.0	85.6	14.4
12	0.1375	0.0197	0.1	61.6	19.7	18.6	90	10
13	0.140	0.017	0.4	61.8	19.6	18.2	84.6	15.4
44	0.118	0.0114	0.0	62.3	19.8	17.9	100	0
46	0.146	0.019	0.0	61.7	18.8	19.5	87.5	12.5
45	0.238	0.028	0.0	62.4	17.5	20.2	79	21
47	0.179	0.0206	0.0	62.0	17.4	20.6	81.3	18.7
14	0.143	0.0216	0.3	60.4	19.6	19.6	84.6	15.4
23	0.158	0.038	0.3	58.7	21.4	19.5	79.4	20.6
24	0.129	0.030	0.3	58.7	20.5	20.5	79.6	20.4
50	0.131	0.036	0.0	56.8	21.6	21.6	78.6	21.4
54	0.150	0.0464	0.0	55.5	23.6	20.9	73.8	26.2
52	0.324	0.138	0.0	47.9	27.0	25.1	70	30
56	0.149	0.0626	0.0	51.0	25.4	23.6	71.7	28.3
40	0.264	0.140	0.0	44.9	28.6	26.5	69.6	30.4
25	0.403	0.272	0.5	40.9	34.2	24.5	69.5	30.5
26	0.169	0.115	0.5	41.8	32.8	24.9	63.5	26.5
51	0.165	0.112	0.0	36.5	37.5	26.0	72.4	27.6
48	0.292	0.232	0.0	31.6	39.5	28.9	69.7	30.3
53	0.097	0.091	0.0	23.4	45.8	27.8	–	–

A. Disproportionation Reactions

$$CH_3CD_2 + CH_3CD_2 = C_2H_3D_3 + C_2H_3D \quad (3a)$$

$$CH_3CD_2 + CH_3CD_2 = C_2H_4D_2 + C_2H_2D_2. \quad (3b)$$

It has been shown that in the photolysis of diethyl ketone the disproportionation reaction is alone responsible for the ethylene produced at low temperatures. In the runs at 24°C. and 50.5°C. more than 90% of the ethylene produced consists of $C_2D_2H_2$ indicating that Reaction (3*b*) is much more important than (3*a*). If we assume that C_2DH_3 found at this temperature is produced by Reaction (3*a*) then we should expect to find at least an equivalent amount of $C_2H_3D_3$. This is not so in Experiments 6 and 19. Later it will be shown that all the $C_2H_3D_3$ found at these temperatures may be accounted for by other reactions. The small amount of C_2DH_3 formed at these temperatures must therefore be attributed to the presence of ketone with less than four D atoms and we may rule out Reaction (3*a*). If $C_2D_2H_2$ is formed by dispro-

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portionation and if, as shown previously, both disproportionation and combination of ethyl radicals have very low activation energies, then $R_{C_2D_2H_2}/R_{C_4}$ should be constant. Column 5 (Table III) shows this is true for runs from 24°C. to 180°C. The increase in $C_2D_2H_2$ at 180°C. and higher temperatures may be explained by other reactions as will be shown later. For the ratio of the rate constants for disproportionation and combination we obtain $k_{3b}/k_2 \backsim 0.1$.

TABLE III

RATE CONSTANT RELATIONSHIPS

Expt. No.	Temp., °C.	$R_{C_4} \cdot 10^{12}$	$\frac{R_{C_4}^{\frac{1}{2}}}{(D)} \cdot 10^{12}$	$\frac{R_{C_2D_2H_2}}{R_{C_4}}$	$k_4/k_2^{\frac{1}{2}} \cdot 10^{14}$	$k_5/k_2^{\frac{1}{2}} \cdot 10^{13}$
6	24	9.1	3.3	0.10	0.99	0.77
7	24	1.18	1.14	0.12	0.99	0.31
19	50.5	1.19	1.33	0.10	2.45	0.18
20	50.5	11.8	3.79	0.10	3.28	0.80
16	101	11.2	4.57	0.06	15.8	0.17
17	101	0.92	1.55	0.09	13.3	0.41
15	105.5	1.06	1.31	0.08	12.0	0.32
27	138	0.90	1.38	0.11	35.3	0.76
28	138	0.67	1.60	0.11	34.6	0.89
1	180	9.6	4.59	0.06	86.2	2.12
2	180	8.8	4.32	–	92.5	2.62
3	180	0.67	1.24	0.19	89.5	2.52
4	180	9.4	4.84	–	–	–
5	180	3.9	8.31	–	111	4.6
10	236	6.2	4.27	0.20	348	9.2
11	236	0.31	0.96	0.39	291	7.9
12	236	0.21	1.38	0.50	323	9.0
13	236	0.88	1.60	0.31	340	9.2
44	250	5.9	4.30	0.16	438	9.7
46	250	1.0	1.79	0.45	433	11.3
14	273	3.8	3.30	0.43	772	21.8
23	300	2.7	3.01	1.04	957	31.9
24	300	2.8	3.89	0.93	1170	36.6
40	350	3.4	3.40	3.9	1610	99.2
25	365	2.3	3.03	7.5	1970	162
26	365	3.4	3.49	5.3	1550	118

B. Hydrogen Abstraction Reactions

$$CH_3CD_2 + CH_3CD_2COCD_2CH_3 = C_2H_3D_3 + CH_3CDCOCD_2CH_3 \quad (4)$$

$$CH_3CD_2 + CH_3CD_2COCD_2CH_3 = C_2H_4D_2 + CH_2CD_2COCD_2CH_3. \quad (5)$$

The attack of an ethyl radical on diethyl ketone may result in the removal of a primary or of a secondary hydrogen atom, i.e. of a D-atom (Reaction (4)) or of an H-atom (Reaction 5)). Reaction (4) produces $C_2H_3D_3$ which has been identified as one of the reaction products. Following the derivations made in the photolysis of diethyl ketone we find that if Reaction (4) occurs,

$$k_4/k_2^{\frac{1}{2}} = \frac{R_{C_2D_3H_3}}{R_{C_4}} \times \frac{R_{C_4}^{\frac{1}{2}}}{(D)}. \qquad I$$

Independent of pressure or intensity used, we should find constant values for

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$k_4/k_2^{\frac{1}{2}}$ at constant temperature. The results obtained for $k_4/k_2^{\frac{1}{2}}$ (Column 6, Table III) confirm Equation I. By plotting log $k_4/k_2^{\frac{1}{2}}$ against $1/T$ (Fig. 1) we obtain, assuming $E_2 = 0$ kcal., as activation energy for Reaction (4), $E_4 = 8.7$ kcal.

An equation similar to Equation I may be derived for Reaction (5). We have to consider, however, that the ethane produced by this reaction ($C_2H_4D_2$)

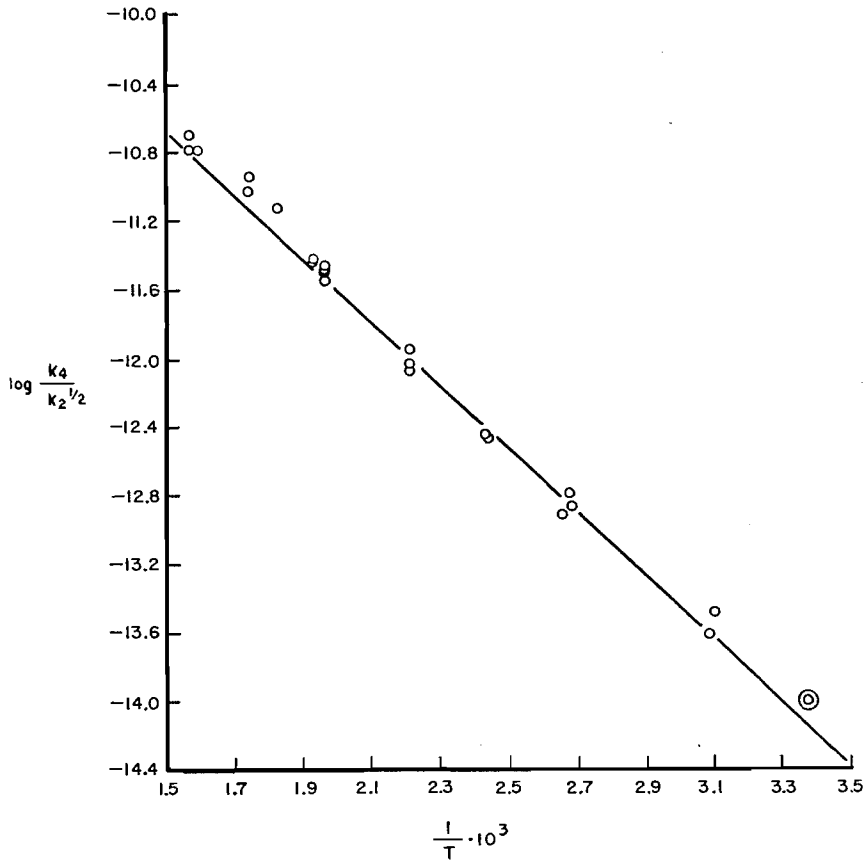

FIG. 1. *Plot of log* $k_4/k_2^{\frac{1}{2}}$ *against* $\frac{1}{T}$.

is also produced by Reaction (3*b*). We therefore have to subtract the ethane produced by disproportionation from the total amount of $C_2H_4D_2$ found. The ethane produced by disproportionation is equal to the $C_2H_2D_2$ produced. A simple subtraction of $C_2H_2D_2$ from $C_2H_4D_2$ would, however, not do since at high temperatures, as is already indicated and will be shown in the next section, $C_2H_2D_2$ is also produced by other reactions. In Section *A*, however, it was shown that

$$k_2/k_4 = \frac{R_{C_2D_2H_2}}{R_{C_4}} \sim 0.1.$$

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To obtain the amount of $C_2H_4D_2$ produced by Reaction (5) only, we have, therefore, subtracted 1/10 of the amount of C_4 produced from the total amount of $C_2H_4D_2$. We thus obtain Equation II

$$k_5/k_2^{\frac{1}{2}} = \frac{R_{C_2H_2D_2} - 1/10\ R_{C_4}}{R_{C_4}} \times \frac{R_{C_4}^{\frac{1}{2}}}{(D)}. \qquad \text{II}$$

The values of $k_5/k_2^{\frac{1}{2}}$ obtained are given in Column 7 (Table III). It will be seen that the equation holds very approximately, which is not surprising in

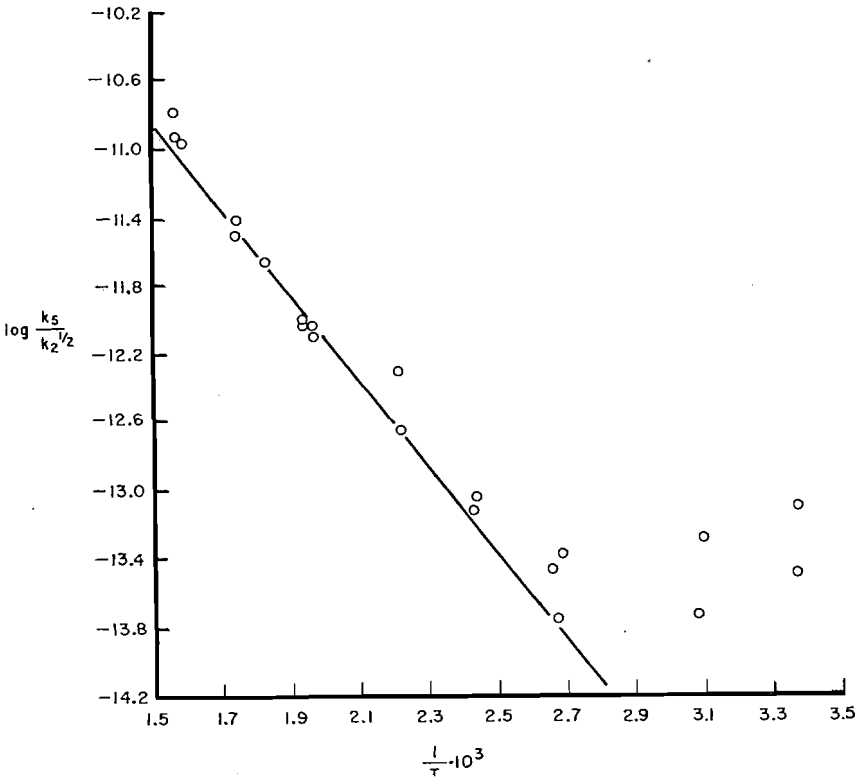

FIG. 2. *Plot of log* $k_5/k_2^{\frac{1}{2}}$ *against* $\frac{1}{T}$.

view of the approximate nature of the method of calculation. If log $k_5/k_2^{\frac{1}{2}}$ is plotted against $1/T$ (Fig. 2) we obtain as activation energy for Reaction (5) (assuming $E_2 = 0$) $E_5 = 11.7$ kcal. The amount of $C_2D_2H_4$ produced by Reaction 5 is at low temperatures very small, and hence there is a large scatter at low temperatures in Fig. 2. At higher temperatures, however, the plot is reasonably linear. The value of E_5 thus obtained is certainly much less precise than that of E_4 where the calculation is straightforward. There seems to be no doubt, however, that E_5 is considerably greater than E_4. This point will be discussed later.

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C. Thermal Decomposition of the Pentanonyl Radical

$$CH_3CDCOCD_2CH_3 = C_2H_3D + CO + CD_2CH_3 \quad (6)$$

$$CH_2CD_2COCD_2CH_3 = C_2H_2D_2 + CO + CD_2CH_3 \quad (7)$$

The increase of $R_{C_2H_4}/R_{C_4H_{10}}$ at high temperatures and/or low intensity has in the photolysis of diethyl ketone been explained by a thermal decomposition of the $C_2H_4COC_2H_5$ radical. The present investigation throws considerably more light on this decomposition. Owing to various experimental complications, however, the results discussed in this section are open to some doubt, and the conclusions drawn are, therefore, somewhat speculative.

The pentanonyl radical is formed by Reactions (4) and (5) above. The amount of ethylene produced by thermal decomposition of the radicals $CH_3CDCOCD_2CH_3$ and $CH_2CD_2COCD_2CH_3$ can thus never exceed the amount of $C_2D_3H_3$ and $C_2D_4H_2$ produced. Table I shows that C_2DH_3 is always smaller than $C_2D_3H_3$. At high temperatures, however, the amount of $C_2D_2H_2$ exceeds the amount of $C_2D_2H_4$, indicating that $C_2D_2H_2$ is not formed solely by Reaction (5). (The amount of $C_2D_2H_2$ formed by disproportionation is negligible at these temperatures.)

It may be seen from Table I that at high temperatures (except for Runs 48 and 53 at low intensities) the amount of $C_2D_3H_3$ formed is always larger than $C_2D_2H_4$. It would, therefore, be expected that more C_2H_3D would be formed than $C_2H_2D_2$, but the reverse is the case. It is difficult to see why this should be true, and the situation is too complex to permit definite conclusions. Possible explanations are:

(*a*) A higher activation energy for the decomposition of $CH_3CDCOCD_2CH_3$ than for $CH_2CD_2COCD_2CH_3$.

(*b*) A reaction of the type
$CH_3CDCOCD_2CH_3 + CH_3CD_2COCD_2CH_3 = CH_3CHDCOCD_2CH_3 + CH_2CD_2COCD_2CH_3$.
The abstraction of a primary rather than a secondary hydrogen in such a reaction might be favored on steric grounds.

(*c*) An internal exchange, or isomerization, of the pentanonyl radical
$CH_3CDCOCD_2CH_3 = CH_3CHDCOCD_2CH_2$.

(*d*) Rearrangement of the radical on decomposing
$CH_3CDCOCD_2CH_3 = CH_2CD_2 + CO + CH_3CHD$.

On the above basis we may write for the decomposition of the radical, in addition to (6) and (7) also

$$CH_3CDCOCD_2CH_3 = C_2H_2D_2 + CO + C_2H_4D. \quad (8)$$

If Reaction (8) occurs it will lead to an increase in C_2H_5D at high temperatures as is found.

If the mechanism is assumed to include Reactions (1) to (8), together with the obvious recombination reactions

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TABLE IV

Expt. No.	Temp., °C.	Relative intensity	$R_{C_4}.10^{12}$	$R_{C_2D_2H_2}.10^{12}$	$R_{C_2DH_3}.10^{12}$	$\left(\frac{R_{C_2D_2H_2}-1/10\,R_{C_4}}{(D)}\right).10^{8}$	$\frac{R_{C_2DH_3}}{(D)}.10^{8}$
27	138	10	0.904	0.095	0.035	0.67	5.1
28	138	10	0.665	0.071	0.0096	0.89	1.9
1	180	100	9.57	0.62	0.117	–	17.4
3	180	10	0.675	0.128	0.024	9.2	3.6
10	236	100	6.16	1.24	0.178	107	30.7
13	236	26.5	0.88	0.277	0.050	31.9	8.5
11	236	10	0.310	0.122	0.0206	15.7	3.5
12	236	10	0.214	0.106	0.0118	25.2	3.5
44	250	100	5.87	0.92	–	59	–
46	250	30	1.03	0.463	0.067	64	11.9
45	250	10	(0.214)	0.175	0.045	27	7.9
47	250	3	(0.026)	0.062	0.0145	10.1	2.5
14	273	100	3.80	1.64	0.296	214	50
23	300	100	2.74	2.84	0.81	470	148
24	300	100	2.82	2.62	0.72	485	149
50	300	30	(0.378)	1.41	0.383	230	64.4
54	300	10	(0.077)	0.645	0.230	109	39
52	300	3	(0.0086)	0.322	0.139	55	24
56	331	100	(2.72)	5.27	2.27	930	427
40	350	100	3.40	13.3	5.79	2390	1070
25	365	100	2.28	17.0	7.35	3360	1475
26	365	100	3.40	18.1	6.42	3370	1220
51	365	30	(0.83)	9.56	3.66	1880	727
48	365	10	(0.18)	6.15	2.66	1155	500

$$CH_3CD_2 + CH_3CDCOCD_2CH_3 = X \quad (9)$$

and

$$CH_3CD_2 + CH_2CD_2COCD_2CH_3 = X, \quad (10)$$

then a steady state treatment leads to

$$\frac{R_{C_2DH_3}}{[D]} = \frac{k_6k_4(CH_3CD_2)}{k_7 + k_8 + k_9\ (CH_3CD_2)}. \quad \text{III}$$

The values obtained for $R_{C_2DH_3}/(D)$ are given in Table IV for experiments at higher temperatures where the decomposition of the pentanonyl radical becomes important. Except at low temperatures where the amount of C_2DH_3 is very small the results are consistent, and at a given temperature $R_{C_2DH_3}/D$ decreases with decreasing temperature as required by Equation III.

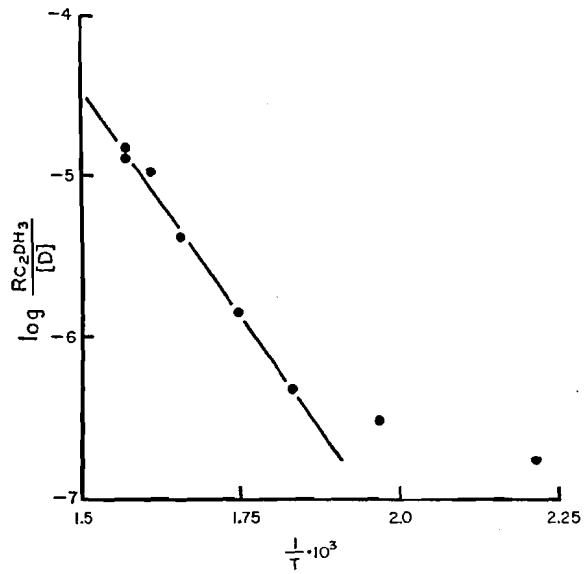

FIG. 3. *Plot of log* $\frac{R_{C_2DH_3}}{[D]}$ *against* $\frac{1}{T}$.

At the highest intensities it may be assumed that $k_7 + k_8$ will be negligible compared with $k_9(CH_3CD_2)$. Equation III then becomes

$$\frac{R_{C_2DH_3}}{[D]} \backsim \frac{k_6k_4}{k_9}. \quad \text{IV}$$

This is not a very good approximation, but is about the only thing that can be done. In Fig. 3 log $\frac{R_{C_2DH_3}}{(D)}$ is plotted against $1/T$ for experiments at the highest intensity. The activation energy thus obtained is

$$E_6 + E_4 - E_9 = 25.7 \text{ kcal.}$$

Taking $E_4 = 8.7$ kcal. as found above, and assuming $E_9 = 0$ as usual, this gives $E_6 \sim 17$ kcal., which seems a reasonable value.

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Discussion

The most important conclusion from the present work concerns the mechanism of disproportionation. There are two plausible possibilities for this reaction, a "head to tail" mechanism

$$CH_3.CH_2- + H.CH_2.CH_2- = C_2H_6 + -CH_2.CH_2- \qquad (A)$$

leading to the formation of the bimethylene radical, and a "head to head" mechanism

$$CH_3.CH_2- + H.CH.CH_3 = C_2H_6 + \rangle CH.CH_3 \qquad (B)$$

leading to the ethylidene radical. If the biradicals thus formed had an appreciable existence the reaction would be similar to an ordinary hydrogen-abstraction reaction, and would be expected to have an activation energy of the order of 7-10 kcal. If, however, the biradicals isomerize to ethylene simultaneously with the primary step the disproportionation reaction will be strongly exothermic, and might be expected to have an activation energy of approximately zero, as found. It would appear much easier for ethylene to be formed directly in (*A*) than in (*B*) which involves a hydrogen transfer. Hence the fact that the activation energy is approximately zero strongly favors mechanism (*A*). The isotopic composition of the ethane formed by disproportionation in the present investigation gives a direct proof of the "head to tail" mechanism.

For the ratio of the rate constants of the disproportionation and recombination reactions the value obtained is $k_3/k_2 \backsim 0.1$, in agreement with the value obtained with light diethyl ketone (2).

For the hydrogen-abstraction reactions the activation energies found are $E_4 = 8.7$ kcal., $E_5 = 11.7$ kcal. The results thus indicate a considerably lower activation energy for the abstraction of a secondary hydrogen as compared with a primary hydrogen. It should be noticed that in one case a D– and in the other an H-atom is abstracted. Isotopic effects will influence the relative magnitudes of the activation energies obtained and will probably even enlarge this difference.

In the reaction $C_2H_5 + C_2H_5COC_2H_5 = C_2H_6 + C_2H_4COC_2H_5$ there is no means of deciding where the H-atom has been abstracted. The relatively low activation energy ($E = 7.4$ kcal. (2)) however indicates that the activation energy measured is the one for abstraction of a secondary hydrogen.

The fact that the activation energy for the abstraction of a secondary hydrogen is considerably lower than that for a primary hydrogen is in line with the results for methyl radical reactions (4). It is also in line with chemical evidence that the "activity" of hydrogen atoms is enhanced by the presence of a neighboring carbonyl group.

The fact that the activation energy of Reaction (4) is higher than the similar

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one in $C_2H_5+ C_2H_5COC_2H_5$ agrees with results obtained in the photolysis of acetone. Dr. T. G. Majury (3) of this laboratory obtained $E = 9.6$ kcal. for the abstraction of an H atom from acetone by a CH_3 radical, and $E = 11.4$ for the abstraction of a D atom from heavy acetone by a CD_3 radical. Accepting for the collision diameters of diethyl ketone and the $C_2H_3D_2$ radical, 6 and 4×10^{-8} cm. respectively, the following values are obtained for the steric factor ratios $P_4/P_2^{\frac{1}{2}} \backsim 5.10^{-4}$ and $P_5/P_2^{\frac{1}{2}} \backsim 3.10^{-3}$. The corresponding ratio was found to be $\sim 10^{-3}$ in the photolysis of light diethyl ketone (2).

Acknowledgment

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AN EVALUATION OF OSMOTIC PRESSURE MEASUREMENTS USING POLYVINYL ACETATE SYSTEMS[1]

By L. A. McLeod[2] and R. McIntosh[3]

Abstract

Measurements of osmotic pressures of polyvinyl acetate solutions in various solvents have been made. These pressures are precise to ±0.005 cm. of solvent and can be repeated on successive samples to 0.02 cm. In five solvents, plots of reduced osmotic pressure (π/C_2) against concentration show distinct upward curvature which differs significantly from theoretical equations derived by Flory and by Huggins. The evidence suggests that further refinement of these theoretical equations is required to bring them into exact agreement with experimental data.

Introduction

Since polymer solutions were first found to depart from the behavior predicted by van't Hoff's law, attempts have been made to rationalize their observed osmotic behavior. The most satisfactory description of the behavior of such solutions is the equation proposed by Huggins (5) and derived independently by Flory (3) and Miller (7). They suggested a quadratic dependence of reduced osmotic pressure on concentration, usually used in the form

$$\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3}C_2^2 = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2}(1/2 - \mu_1)C_2$$

where π is osmotic pressure, C_2 is solute concentration, d_1 and d_2 are densities of solvent and solute respectively, M_1 and M_2 are molecular weights of solvent and solute respectively, μ_1 is a constant for a particular polymer–solvent system, R is the molar gas constant, and T is the absolute temperature. This equation has served to express the osmotic pressure data reported for many polymer solutions.

Attempts to determine accurate osmotic pressure values led Sirianni, Wise, and McIntosh (9) to the conclusion that metal osmometers of the usual design were inadequate. These authors showed that the use of a membrane as a gasket may lead to erroneous results; they also observed a difference in osmotic behavior for different types of membrane but their evidence was at variance with the results published by Robertson, McIntosh, and Grummitt (8). These discrepancies were of such a fundamental nature that it was decided to continue the study of the measurement of osmotic pressure *per se*. The purpose of the following investigation has therefore been to develop a technique of osmotic measurements of sufficient precision to show whether or not the osmotic pres-

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sure is influenced by the nature of the membrane; whether the intercepts of the π/C_2 vs. C_2 curves are identical for different solvents; whether van't Hoff's law describes the effect of temperature on the limiting value of π/C_2; and other such basic questions. The effect of solvent type is discussed in the present report.

Two points of interest arise in the analysis of experimental osmotic data. The first is the form of the π/C_2 vs. C_2 curve. The slope of this line and the presence or absence of curvature are directly related to the solvent–polymer interaction forces. Reference has already been made to the theoretical equation derived by Flory, Huggins, and Miller to relate π/C_2 to C_2. By modifying his original assumptions, Flory (4) has recently deduced another equation for osmotic behavior, which he states in the form

$$\frac{\pi}{C_2} = \frac{RT}{M_2}\left[1 + \Gamma C_2 + \tfrac{5}{8}\Gamma^2 C_2^2\right]$$

where Γ is a constant and the other symbols are the same as in the first equation. The ability of these equations to fit experimental osmotic data should be a reflection of the validity of their underlying assumptions.

The second point of interest in the analysis of the data is the value of $(\pi/C_2)_{C_2=0}$ since this leads directly to the molecular weight of the solute. Extrapolation of the π/C_2 vs. C_2 curve to this intercept is much more difficult if curvature exists. Extrapolation may be done visually but with this method it is difficult to be completely objective; an empirical equation may be derived for the range in which data are available and used to calculate $(\pi/C_2)_{C_2=0}$. Bawn, Freeman, and Kamaliddin (1) have outlined a convenient procedure for this treatment; extrapolation of the curve would be most reliable if the experimental data could be fitted to a theoretical equation.

The data obtained in the present investigation are considered sufficiently dependable to assess the merits of the two theoretical equations and to compare the various ways of obtaining the extrapolated intercept.

Experimental

The Osmometer

The osmometer is only a minor adaptation of that described by Sirianni, Wise, and McIntosh (9). Their experience showed the need for a ridge surrounding the cell to enable the membrane to be fully submerged in solvent during assembly. Their difficulties attributed to corrosion of the brass cell have been largely eliminated by gold-plating the cell. Other changes have also been incorporated into the design:

1. Since cold flow of the "Composition" lead foil gave rise to leakage after about 10 days of use, this foil was replaced by a Teflon gasket which has given excellent service.

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2. A more convenient method of controlling evaporation of the cell contents was to connect the two measuring capillaries together. This did not improve the drop of liquid level reported by Sirianni, Wise, and McIntosh but was a simpler method.
3. The Fernico bushings used to seal the measuring capillaries to the brass cell were found to rust in water and were replaced by copper–nonex seals.
4. It has not been possible to eliminate the trouble caused by air bubbles although the gold-plating of the cell has given a marked improvement in behavior. In spite of very careful oscillation of the liquid levels in the cell, coupled with a rocking motion of the cell itself and a slight (2-3°) warming of the cell contents, bubbles still appear occasionally and for no apparent reason. Their presence is usually manifested by a rise in levels in both capillaries.

With these relatively minor changes, the cell design described by Sirianni, Wise, and McIntosh (9) has been accepted as adequate. Another cell of the same design has been made of stainless steel (S.A.E. No. 303) but its chief advantage over the gold-plated cell lies in its resistance to the action of mercury.

Membranes

Preparation of a semipermeable membrane still constitutes a serious problem for the systems involved in this work. It was finally found necessary to fractionate the polymer to the extent described below in order to eliminate solute leakage. Dried "Cellophane" (No. 600 P.T. not waterproofed, obtained through the courtesy of Canadian Industries Ltd.), has been used throughout the present investigation but care is necessary to select sheets which are free from air bubbles. The membranes were swollen in 5% sodium hydroxide according to the procedure previously outlined (9) but the various times of swelling and accommodation to solvent were not found to be critical and the results did not appear to depend on the amount of sodium hydroxide left in the membrane. As in the case of the earlier investigations (8, 9), these caustic-swollen "Cellophane" membranes showed no evidence of adsorption of solute.

A very rigorous test for semipermeability was used. Membranes intended for use with Gelva V360 (molecular weight 300,000) were tested overnight with a 3% acetone solution of Gelva V15 (molecular weight 45,000). The contents of the solvent side were then poured into an equal volume of water. Any cloudiness caused the membrane to be rejected.

Materials

Commercial polyvinyl acetate (provided through the courtesy of Shawinigan Chemicals Ltd.) was used. A partial fractionation procedure was used in order to remove the very small and very large polymers. A 5% solution of the crude polymer in acetone was filtered through a sintered glass funnel. The polymer was precipitated from the filtrate by slow addition of water to the solution until only a faint cloudiness resulted from further addition of water. The

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polymer was allowed to settle out, decanted, redissolved in acetone, and reprecipitated in the same manner. After redissolving the polymer in acetone, the final precipitation was effected by slow addition of the acetone solution to a large excess of water. This produced a very spongy type of polymer which, after partial drying, was sliced thin and dried *in vacuo* at room temperature.

Reagent grade solvents stored over Drierite were used without further treatment.

Preparation of Solutions

Concentrations were measured either from known weights of solute and solvent or by evaporation to constant weight of an aliquot of the solution. Results from the two methods agreed within 1% when used on the same solutions. It was thus possible to use the second method with confidence to measure concentrations of solutions obtained by dilution from a stock solution. Concentrations are probably reliable to 0.2% in the upper range and 0.5% at the lower range.

Temperature Control

Measurements were made at 30°C. in a water thermostat controlled to ±0.002°C. (i.e. no fluctuation was observed on a Beckmann thermometer). This control can be achieved by using an American Instrument Co. Metastatic thermoregulator and any convenient electronic relay, provided the regulator is vibrated periodically to prevent sticking at the mercury surface.

Measurements

For greatest precision the cell was used as a static osmometer. Equilibrium pressures approached from above and below were averaged. The two readings usually agreed to ±0.005 cm. of the mean. Equilibrium was attained in about five hours and was followed overnight to detect any drift due to solute leakage. If a drift occurred overnight, the reading was rejected and the membrane was tested again with Gelva V15.

Periodically the cell was rinsed with solvent and a measurement taken of the "cell zero". If repeated washing with solvent did not reduce the "cell zero" to less than 0.01 cm., the readings were rejected and the cell was tested for failure of the gasket since a large "cell zero" can usually be attributed to leakage at this location (1, 9).

Results

Three polymer samples were used in this work and are designated Gelvas V360, V360A, and V 360B respectively. They are the result of three similar preparations from the same commercial sample. Gelvas V360 and V360B appeared to have the same molecular weight and so are treated as identical samples; Gelva V360A showed a slightly lower molecular weight and was dealt with separately. The two osmometers (the gold-plated brass cell and the stainless steel cell) were used interchangeably except in the case of Gelva V360A in benzene where an unaccountable difference in slope but not in intercept was

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TABLE I

μ_1 VALUES FOR POLYVINYL ACETATE IN VARIOUS SOLVENTS

Solvent	McLeod and McIntosh	Sirianni, Wise, and McIntosh(9)	Masson and Melville(6)	Browning and Ferry(2)
Acetone	0.439 (30°)	0.439 (30°)		0.437 (25°)
Methyl ethyl ketone	0.435 (30°)			0.429-0.44 (25°)
Benzene	0.427-0.430 (30°)	0.427 (30°)	0.44 (20°)	
Chloroform	0.338-0.345 (30°)	0.377 (30°)		
Ethyl acetate	0.412-0.423 (30°)		0.415 (20°)	

observed. A total of five solvents was used: acetone, benzene, methyl ethyl ketone, chloroform, and ethyl acetate.

The data were plotted on graphs of π/C_2 vs. C_2 and in every case upward curvature was evident (Fig. 1). However, all curves could be readily extrapolated to a common intercept which was 0.735 for Gelvas V360 and V360B and 0.875 for Gelva V360A.

The data were then plotted in the form $\left(\frac{\pi}{C_2} - \frac{RTd_1}{3M_1d_2^3}C_2^2\right)$ vs. C_2. According to the Flory–Huggins theory this treatment should yield a straight line but it failed to remove all the curvature in the present data. The μ_1 values

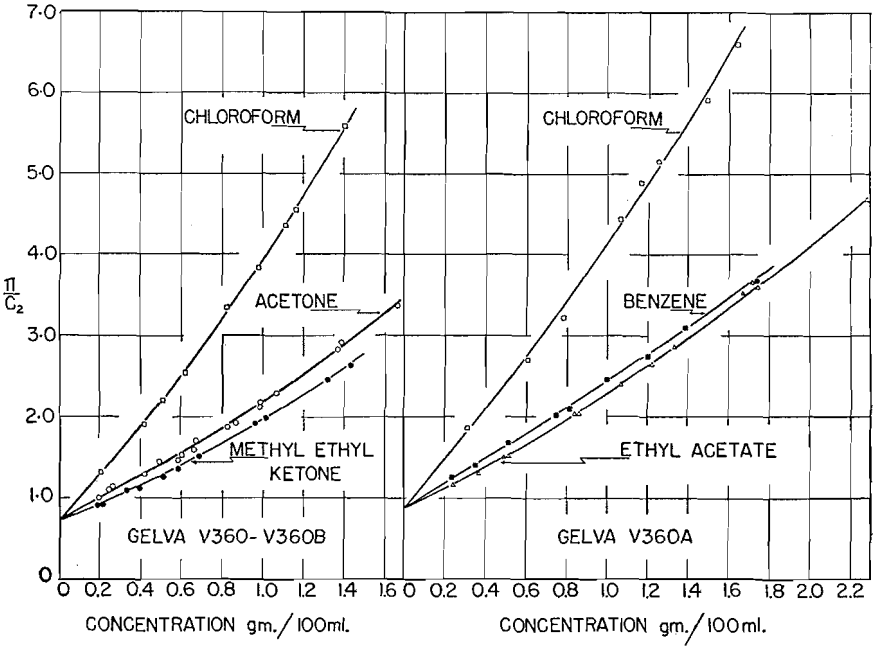

FIG. 1. *Representative graphs of reduced osmotic pressure as a function of concentration.*

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obtained from these curves are listed in Table I and are in excellent agreement with the results of Sirianni, Wise, and McIntosh (9), Masson and Melville (6), and Browning and Ferry (2) for comparable systems.

This residual curvature in the Flory–Huggins plot (reported also by Masson and Melville(6)) suggests that the Flory–Huggins equation does not adequately describe the concentration dependence of π/C_2. An attempt was therefore made to define the curvature of the π/C_2 vs. C_2 plot in the following manner. The experimental data were fitted by the method of least squares to three quadratic equations having the general form $\pi/C_2 = a_0 + a_1C_2 + a_2C_2^2$. In the first case, (the Flory–Huggins equation) $a_0 = \frac{RT}{M_2}$, $a_1 = \frac{RTd_1}{M_1d_2^2}$ $(\frac{1}{2} - \mu_1)$, and $a_2 = \frac{RTd_1}{3M_1d_2^3}$. The symbols have the same significance as outlined above.

TABLE II

DERIVED CONSTANTS FOR THEORETICAL PARABOLAS

Solvent	Huggins		Flory		Least squares		
	a_0	μ_1	a_0	Γ	a_0	a_1	a_2
Gelva V360-V360B							
Acetone	0.644	0.439	0.891	0.890	0.776	1.107	0.276
Methyl ethyl ketone	0.615	0.435	0.789	0.917	0.684	1.065	0.206
Benzene	0.641	0.428	0.857	0.890	0.774	1.011	0.298
Chloroform	0.441	0.345	1.092	1.363	0.742	2.524	0.651
Ethyl acetate	0.659	0.423	0.881	0.854	0.841	0.866	0.344
Gelva V360A							
Benzene—brass	0.748	0.427	1.012	0.785	0.888	1.112	0.236
Benzene—steel	0.971	0.430	1.137	0.735	1.043	1.144	0.216
Chloroform	0.518	0.338	1.456	1.058	0.921	2.689	0.504
Ethyl acetate	0.685	0.413	1.055	0.758	0.785	1.359	0.155

Values of d_1 were obtained from Reference (10). For the Flory equation, $a_0 = \frac{RT}{M_2}$, $a_1 = \frac{RT}{M_2}\Gamma$, and $a_2 = \frac{5}{8}\frac{RT}{M_2}\Gamma^2$ where Γ is a constant. In the third case, a_0, a_1, and a_2 are not assigned any predetermined relationship. The calculated constants for these three equations are listed in Table II and the differences between the experimental points and the calculated values appear in Table III.

A representative set of data from Table II is shown graphically in Fig. 2. On this graph are plotted the experimentally determined values of π/C_2 vs. C_2 for Gelva V360 in chloroform and in ethyl acetate, together with the best fitting curves for the three equations calculated from these experimental data. It is seen that the parabola represented by the Flory–Huggins equation does not have enough curvature to fit the experimental points whereas the curvature required by the new Flory equation is too great to fit the experimental facts. The parabola whose constants are unrestricted by any arbitrary relationship gives very good agreement with the experimental data. The same general

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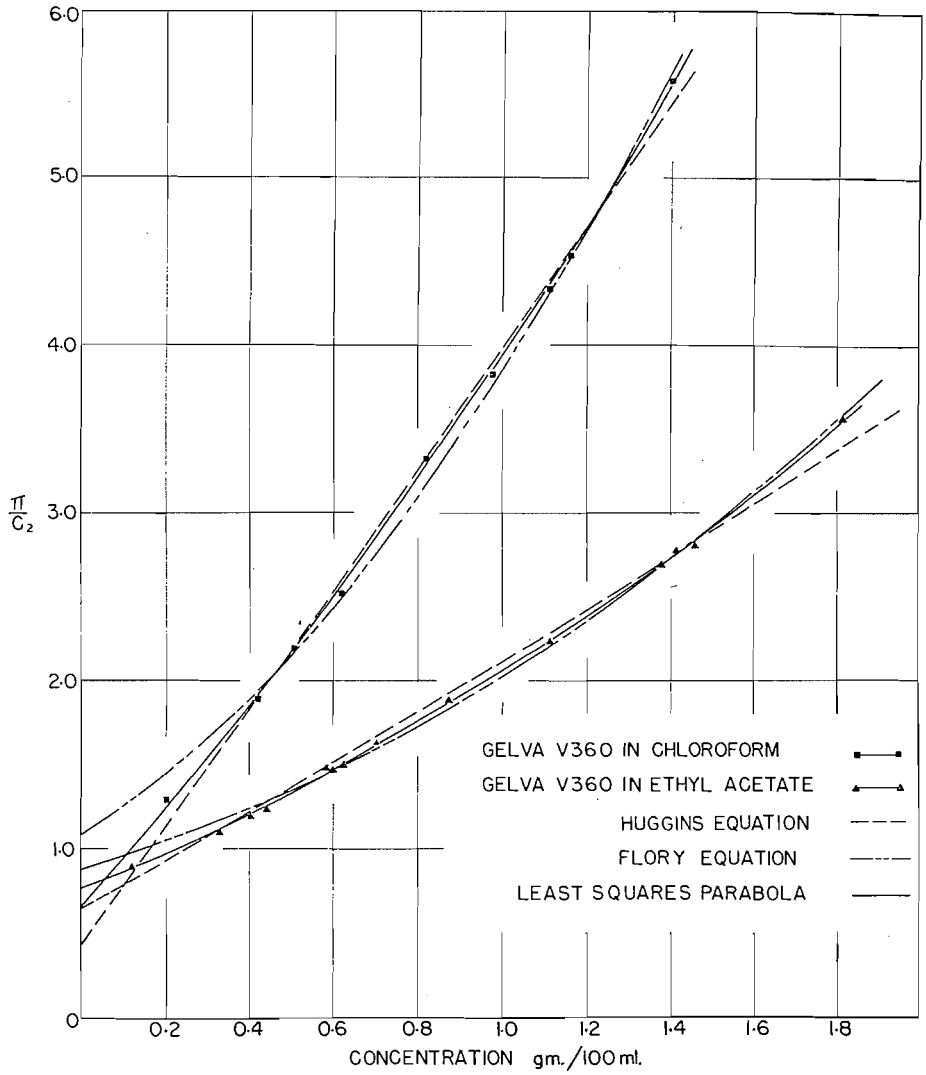

FIG. 2. *Comparison of theoretical equations derived from experimental osmotic data.*

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statement applies to the intercepts on the π/C_2 axis. For both the Flory and the Flory–Huggins equations the spread in the intercepts is much greater than for the unrestricted quadratic equation.

The disagreement of the two theoretical equations with the experimental facts is illustrated much more graphically by the data of Table III. It is immediately obvious that the average deviation of the experimental points from the curve representing an unrestricted quadratic is approximately ±0.030 cm. The average deviation from the Flory–Huggins equation and from the Flory equation is about ±0.050 cm. This in itself suggests that the unrestricted equation is a better representation of the experimental data than is either the

TABLE III

π/C_2 VALUES FOR POLYVINYL ACETATE SYSTEMS

Gelva V360–V360B					Gelva V360–V360B				
C_2, gm./100 ml.	π/C_2 obs.	(π/C_2 obs.−π/C_2 calc.)			C_2, gm./100 ml.	π/C_2 obs.	(π/C_2 obs.−π/C_2 calc.)		
		Huggins	Flory	Least squares			Huggins	Flory	Least squares
Acetone					Benzene – brass				
1.667 B*	3.370	.055	−.069	−.018	1.860	3.658	.113	−.085	−.028
1.667 S	3.359	.044	−.080	−.029	1.451	2.899	.027	.042	.031
1.390 B	2.913	.068	.068	.065	1.382	2.820	.059	.099	.080
1.370 S	2.837	.026	.032	.026	1.320	2.593	−.069	−.010	−.035
1.067 S	2.279	−.031	.040	.008	1.162	2.308	−.102	−.008	−.043
.989 B	2.166	−.017	.059	.025	.821	1.823	−.051	.054	.018
.989 S	2.105	−.078	−.002	−.036	.751	1.690	−.076	.021	−.011
.870 B	1.920	−.071	.005	−.028	.549	1.423	−.034	.019	.004
.870 S	1.899	−.092	−.016	−.049	.504	1.330	−.059	−.019	−.029
.830 B	1.866	−.060	.013	−.019	.343	1.159	.012	−.010	.003
.830 S	1.949	.023	−.004	.064	.336	1.129	−.007	−.032	−.018
.678 B	1.701	.017	.070	.046	.278	1.084	.034	−.018	.006
.666 S	1.591	−.054	−.024	−.045	.205	.974	.033	−.057	−.020
.606 B	1.532	−.039	−.002	−.016	.176	1.006	.107	.002	.045
.587 S	1.469	−.073	−.039	−.052					
.496 B	1.452	.053	.059	.059	Mean		.056	.034	.027
.422 B	1.290	.006	−.014	−.002					
.391 B	1.354	.118	.085	.103	Chloroform – brass				
.391 S	1.111	−.125	−.158	−.140	1.405	5.583	.140	−.103	.010
.267 S	1.137	.091	.003	.046	1.165	4.548	−.023	.001	−.019
.249 S	1.101	.082	−.015	.033	1.115	4.347	−.043	.019	−.019
.200 B	1.001	.056	−.066	−.007	.980	3.839	−.064	.071	−.003
.200 S	.981	.036	−.086	−.027	.825	3.339	−.009	.156	.070
					.622	2.534	−.091	.026	−.031
Mean		.057	.044	.041	.511	2.204	−.007	.020	.002
					.425	1.906	−.022	−.048	−.027
Methyl ethyl ketone – brass					.207	1.307	.144	−.147	.015
1.438	2.634	.030	−.053	−.007					
1.321	2.445	.011	−.023	−.005	Mean		.060	.066	.022
1.020	1.994	−.008	.036	.009					
1.017	1.990	−.008	.036	.010	Ethyl acetate				
.965	1.920	−.004	.047	.016	1.819 B*	3.572	.174	−.006	.018
.691	1.511	−.031	.024	−.007	1.462 B	2.817	−.016	−.022	−.025
.588	1.374	−.026	.016	−.007	1.419 S	2.776	.009	.019	.013
.518	1.271	−.034	−.004	−.020	1.381 S	2.704	−.003	.018	.011
.400	1.120	−.025	−.025	−.023	1.353 S	2.588	−.076	−.046	−.055
.337	1.089	.029	.009	.023	1.117 B	2.248	−.052	.026	.010
.219	.918	.015	−.049	−.009	.880 S	1.891	−.051	.037	.022
.190	.911	.047	−.030	.017	.709 B	1.640	−.046	.024	.012
					.630 S	1.509	−.060	−.005	−.014
Mean		.022	.029	.013	.603 B	1.479	−.050	−.002	−.009
					.588 B	1.492	−.015	.030	−.023
					.525 S	1.467	.053	.080	.076
					.445 B	1.244	−.053	−.051	−.050
					.407 S	1.201	−.042	−.053	−.050
					.334 B	1.114	−.023	−.063	−.054
					.230 S	1.159	.172	.084	.101
					.122 B	.917	.085	−.062	−.035
					Mean		.058	.037	.034

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TABLE III—*Concluded*

Gelva V360A					Gelva V360A				
C_2, gm./100 ml.	π/C_2 obs.	(π/C_2 obs.$-\pi/C_2$ calc.) Huggins	Flory	Least squares	C_2, gm./100 ml.	π/C_2 obs.	(π/C_2 obs.$-\pi/C_2$ calc.) Huggins	Flory	Least squares
Benzene – brass					Chloroform – steel				
1.818	3.691	.073	−.053	.001	1.800	7.502	.249	−.027	.108
1.551	3.170	−.003	−.012	−.011	1.644	6.587	−.067	−.155	−.117
1.517	3.131	−.014	.017	.013	1.490	5.916	−.148	−.097	−.130
1.503	3.087	−.007	.000	−.005	1.257	5.147	−.031	.145	.050
1.125	2.416	−.065	.017	−.022	1.169	4.878	.032	.229	.125
1.103	2.408	−.037	.045	.006	1.063	4.443	−.003	.203	.094
.846	2.010	−.028	.047	.012	.782	3.220	−.174	−.063	−.112
.844	1.971	−.063	.011	−.024	.609	2.696	−.055	−.075	−.050
.610	1.639	−.030	−.003	−.015	.317	1.864	.190	−.182	.040
.582	1.681	.055	.075	.066					
.444	1.378	−.036	−.063	−.050	Mean		.105	.131	.092
.422	1.426	.045	.009	.027					
.275	1.231	.073	−.029	.019	Ethyl acetate – brass				
.271	1.179	.027	−.077	−.028	2.286	4.682	.081	−.181	−.020
					1.749	3.599	−.034	−.012	−.037
Mean		.040	.033	.021	1.724	3.650	.061	.090	.061
					1.675	3.525	.024	.067	.029
Benzene – steel					1.335	2.847	−.060	.049	−.028
1.743	3.656	.046	−.104	−.037	1.237	2.753	.015	.129	.050
1.387	3.092	.049	.057	.047	1.222	2.646	−.066	.048	−.031
1.205	2.739	−.020	.037	.004	1.068	2.395	−.053	.054	−.018
1.000	2.454	.011	.097	.051	.863	2.027	−.073	.000	−.046
.815	2.089	−.074	.016	−.030	.842	2.031	−.033	.034	−.008
.748	2.024	−.038	.047	.004	.819	2.041	.015	.077	.039
.517	1.679	−.039	.007	−.013	.515	1.513	−.008	−.054	−.013
.353	1.392	−.086	−.088	−.082	.495	1.502	.014	−.042	.006
.236	1.251	−.057	−.105	−.074	.489	1.486	.009	−.051	−.001
.149	1.270	.087	.000	.052	.367	1.288	.010	−.112	−.017
.148	1.296	.115	.027	.079	.240	1.147	.076	−.122	.027
Mean		.057	.053	.043	Mean		.040	.070	.026

* *B—refers to results obtained in brass cell.*
S—refers to results obtained in steel cell.

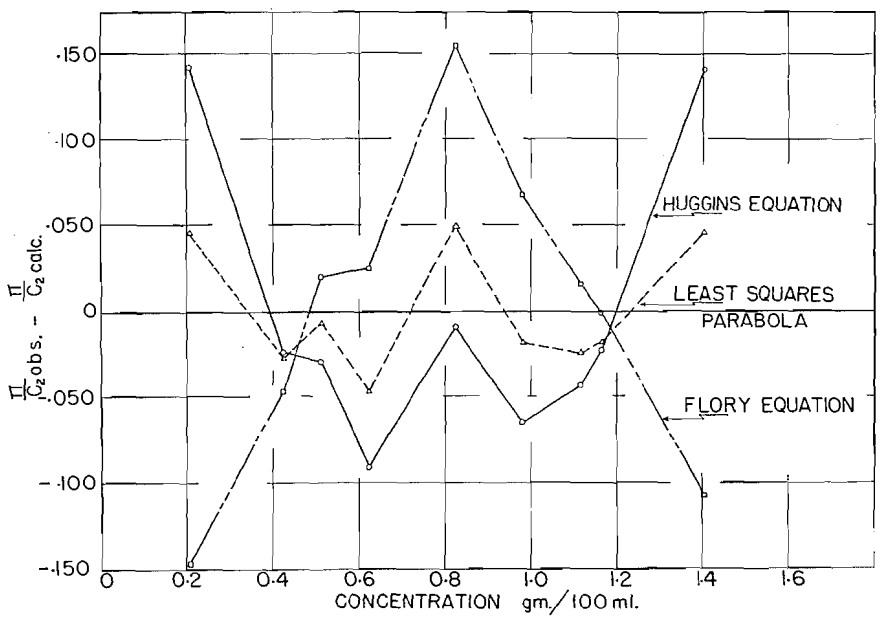

FIG. 3. *Deviations of experimental osmotic data from theoretical equations.*

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Flory or the Flory–Huggins equation. Further evidence for this conclusion is shown in Fig. 3 which is a graph of deviation of the experimental value of π/C_2 from each calculated equation plotted against concentration. The data for Gelva V360 in chloroform have been chosen as representative. It is evident that the deviations are random about the unrestricted equation but follow a distinct trend in both the other cases.

Rather than base conclusions on this evidence, it was decided to make a careful statistical analysis of the data to determine whether these apparent differences were indeed significant. As an arbitrary criterion for rejection of data it was decided to include all values of π/C_2 whose deviation from the unrestricted quadratic equation was less than three times the standard deviation for all values of π/C_2 in the same solvent. On this basis it was not possible to reject any data even though certain values are open to considerable suspicion.

The results of the statistical analysis may be briefly summarized. The standard error was calculated for the intercept on the π/C_2 axis for each unrestricted quadratic equation. A "*t*-test" was then used to determine whether the calculated intercept differed significantly from the common intercept obtained by visual extrapolation of the curves (0.735 for Gelva V360-V360B and 0.875 for Gelva V360A). In three solvents (Gelva V360 in methyl ethyl ketone, Gelva V360B in ethyl acetate, and Gelva V360A in benzene (steel cell)) there was a significant difference in the intercepts at the 5% level but in no case was there a significant difference at the 1% level. However, a similar analysis showed that the intercepts predicted by the Flory and the Flory–Huggins equations were almost invariably significantly different from the intercepts predicted by the unrestricted parabola and hence were probably different from the common intercept extrapolated visually.

Equations for the visually-fitted curves were determined following the procedure of Bawn, Freeman, and Kamaliddin (1) and the dispersions of the experimental values about these lines were compared by means of an "*F*-test" with the dispersions about the least squares parabolas. The visually-fitted equations were found to be not significantly different from the simple least squares equations at the 1% level of significance. A similar test was used to compare the simple parabola with the Flory and the Flory–Huggins equations. The evidence is not conclusive but indicates a somewhat lower dispersion about the unrestricted parabola.

Discussion

1. An osmotic cell has been developed whose operation is reliable and whose results show good precision. For any one solvent, the average deviation of experimental values of π/C_2 about a simple quadratic equation fitted by the method of least squares is approximately ± 0.03 cm. This would correspond to an uncertainty of 4% in the molecular weights measured in this test. In different solvents, however, the intercepts obtained by extrapolating these least squares equations cover a range of ± 0.06. This uncertainty is apparently

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consistent with the experimental precision and does not indicate a significant dependence of molecular weight on solvent. It appears, therefore, that the uncertainty in molecular weight is about 10% even though the experimental measurements are precise to ± 0.03 cm.

2. Caustic-swollen "Cellophane" membranes are suitable for use with polyvinyl acetate solutions.

3. Available theoretical equations do not describe the π/C_2 vs. C_2 curve in the concentration range usually employed and consequently are not satisfactory in predicting the value of the π/C_2 intercept at $C_2 = 0$.

It should be noted that the method of curve-fitting suggested by Flory for his recent equation is a visual one involving a log–log plot which will tend to obscure the differences between his equation and the simple empirical equation. Further experimental data may well prove that Flory's equation is required to account for the curvature of the π/C_2 vs. C_2 plot in the extremely dilute region but at present it seems to be inferior to the unrestricted quadratic equation.

4. A simple quadratic equation, whose constants are evaluated empirically, is adequate in describing the curvature of the π/C_2 vs. C_2 curve and predicts a common intercept for different solvents consistent with experimental error.

5. A smooth curve fitted visually to the experimental data is equally satisfactory in representing the curvature and in predicting the value of the intercept. Bawn has described a convenient method of analyzing such a curve.

6. There seems to be no effect of solvent on the value of the π/C_2 intercept in the polyvinyl acetate systems reported here.

Acknowledgment

The authors are pleased to acknowledge the assistance of Mr. P. J. D'Arcy who carried out all the osmotic measurements and of Mrs. W. Stewardson who performed some of the calculations. Guidance in the statistical analyses was given by Dr. J. W. Hopkins and Mr. C. Reimer of the Biology Division, National Research Council, and Dr. N. R. Legge and Mr. J. Curran of Polymer Corporation.

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A COMPARISON OF THE PROTECTIVE COLLOID INDEX AND POLAROGRAPH WAVE FOR NORMAL AND CANCER SERA[1]

By L. A. Munro and D. J. Boyd

Abstract

The protective colloid indices have been determined on the sera of 83 normal rats and on 74 rats with transplanted Walker carcinosarcoma. As previously found with humans, the sera from tumor animals have much less of the protective colloids than the sera of normals. When 0.12 ml. of serum was used, 82% of the cancerous animal gave residual dye of less than 51γ per ml., whereas 100% of the normals gave concentrations above this value. Half of the false negative tests were from rats having tumors less than 15 gm. in weight. When 0.10 ml. of serum was used, 89.2% had an index below 15γ with an average of 7.8γ while the index of 91% of the normals was above 15γ with an average of approximately 42γ. The protective indices and polarograms have been compared for the sera of 43 cancerous and 47 normal rats. In 91% of the cancerous animals characteristic curves were obtained having a wave height greater than 50 mm., with 4.2% false positives in the normal group. The two tests are of approximately equal value in classifying the sera. The serum constituents responsible for the polargraph wave are different from those indicated by the protective colloid index.

Protective Colloids in Cancer

In 1944 a study was made of the protective colloid index of the blood sera of cancer patients and normal individuals (6). The protective index of a lyophilic colloid is defined by the residual concentration of a standard sol in micrograms per milliliter after its treatment with an electrolyte in the presence of a given amount of the protecting colloid, under standard conditions. Cancer serum was found to give a much lower index than normal serum. Seventy of seventy-eight cancer patients (approximately 90%) gave values less than 15γ per ml. when 0.075 ml. of serum was used as compared with 3 from 70 normal individuals (approximately 4%). When a 0.10 ml. portion of serum was used in each test, the frequency – colloid index curves were very different, 86% of the normals gave values greater than 100γ per ml. whereas 80% of the cancer patients were below this range. The cancer group included a wide variety of cancer types in all stages of development.

The present work was undertaken to see whether transplanted tumors in animals would bring about a similar lower protective colloid index, and, if so, to establish the quantitative values for normal and tumor animals.

Methods

The colloid used in the test was Congo red purified by recrystallization from hot aqueous ethyl alcohol (10 gm. of dye + 150 ml. 95% ethyl alcohol + 150 ml. water). The mixture was filtered while hot through a Buchner using No. 1 Whatman paper, and the filtrate allowed to crystallize. The crystallized pro-

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Contribution from the Department of Chemistry, Queen's University, Kingston, Ont. Presented before Section III of the Royal Society of Canada June 5, 1950.

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duct was removed by filtration, washed with cold 95% ethyl alcohol, and the procedures repeated until the maximum adsorption was obtained with the Beckman quartz spectrophotometer.

The coagulating electrolyte was U.S.P. grade quinine monohydrochloride. Other electrolytes could be used, but this was found in the previous study to be the most satisfactory. Aluminum salts cannot be employed owing to the color changes produced in the dye at the pH of the hydrolyzed salt.

The rats were of the Wistar strain. The tumor, Walker carcinosarcoma 256, was implanted subcutaneously by trocar method into the groin of the animal. Blood samples were obtained by decapitation.

Procedure

The technique of the test is exacting. The glassware must be scrupulously clean. The adsorption of chromic ions from cleaning solution was found to influence the test and consequently a sulphuric acid – nitric acid mixture was substituted. Accurate pipetting is necessary since as little as 0.01 ml. of serum has a very great effect on the result. In subsequent experiments the serum was diluted and an equivalent amount used.

The chosen amount of serum was transferred to each of three conical centrifuge tubes containing 5 ml. of 0.10% Congo red. Five milliliter portions of a 0.30% solution of quinine monohydrochloride were then pipetted into separate tubes. At zero minus two minutes the electrolyte was dumped into the first tube and the whole mixed by pouring back and forth four times. This method of mixing was found to be better than shaking the tubes. At zero minus one minute the electrolyte was dumped into the second tube and at zero time the third tube was mixed. All tubes were then placed in a constant-temperature bath at 30°C.

After 30 min. in the bath, the tubes were removed and centifuged at 2400 r.p.m. for four minutes. The color in the supernatant was then evaluated in a Klett photelometer using a blue filter No. 42, from a standard curve for Congo red.

In the present study, the results reported are a mean of from two–five determinations depending on the amounts of sera available and the agreement obtained.

Preliminary trials, using human cancer and normal sera, were made. The marked differences reported by one of us were again observed. This indicated that the reagents and technique were satisfactory for the present work.

Results

P.C. Index

The results, using 0.10 ml. of serum for 74 cancer and 83 normal rats, are summarized in Table I and Fig. 1.

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TABLE I

PROTECTIVE COLLOID INDEX USING 0.10 ML. SERUM

Residual dye, γ/ml.	Normals		Cancer	
	No. in group	Per cent of total	No. in group	Per cent of total
0–5	0	0	37	50.0
6–10	4	4.82	23	31.1
11–15	5	6.04	6	8.1
16–20	8	9.64	3	4.0
21–25	7	8.44	3	4.0
26–30	3	3.62	1	1.3
31–35	4	4.82	1	1.3
36–40	6	7.23	0	0
41–45	5	6.04	0	0
46–50	2	2.41	0	0
> 50	39	46.8	0	0
Total	83	99.9	74	99.8

The values for residual dye are given in micrograms (γ) of Congo red per milliliter.

Table II gives the results when 0.12 ml. of serum was used. The distribution curves are shown in Fig. 2.

It will be noted that the distribution curves are very different for cancer and normal sera. Using 0.10 ml. of serum, no cancerous animal, no matter how small the tumor, gave residual dye greater than 35γ. Only two of the 74 cancer animals gave a protective colloid index of greater than 25γ. If 15γ is taken as the dividing index between the protective value of cancer and normal sera as was done with humans, 89.3% of all cancer animals gave final dye concentrations below this figure. Four of the eight cancer sera which showed higher

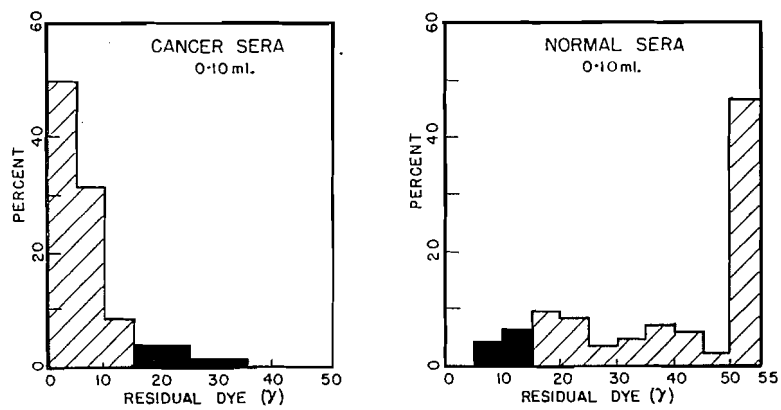

FIG. 1

FIG. 1. *Distribution curves for residual dye using 0.10 ml. of serum from cancerous and normal animals.*

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TABLE II

PROTECTIVE COLLOID INDEX USING 0.12 ML. SERUM

Residual dye, γ/ml.	Normals		Cancer	
	No. in group	Per cent of total	No. in group	Per cent of total
0–5	0	0	8	14.8
6–10	0	0	17	31.5
11–15	0	0	10	18.5
16–20	0	0	4	7.4
21–25	0	0	3	5.5
26–30	0	0	1	1.9
31–50	0	0	1	1.9
> 50	61	100	10	18.5
Total	61	100	54	100

protective value had small tumors (less than 15 gm.). In the 70 animals with tumors greater than 15 gm., 94% had a protective colloid index below 15γ. On the other hand, 89% of the normal animals gave residual dye greater than 15γ per ml. when 0.10 ml. of sera was used. The average concentration of residual dye was 7.8γ per ml. for the cancer animals and approximately 42γ per ml. for the normals.

Examination of the results obtained for 0.12 ml. of serum reveals that with well developed tumors (tumors of the order of 30 gm. or more), the cancer sera were much less effective as protective agents than the normal sera. Indeed 100% of the "non-takes" gave values for the residual dye of at least 50γ per ml., i.e. there were no false positives, while in the case of the advanced tumor rats, only five of the 48 (10.6%), gave values of 50γ per ml.

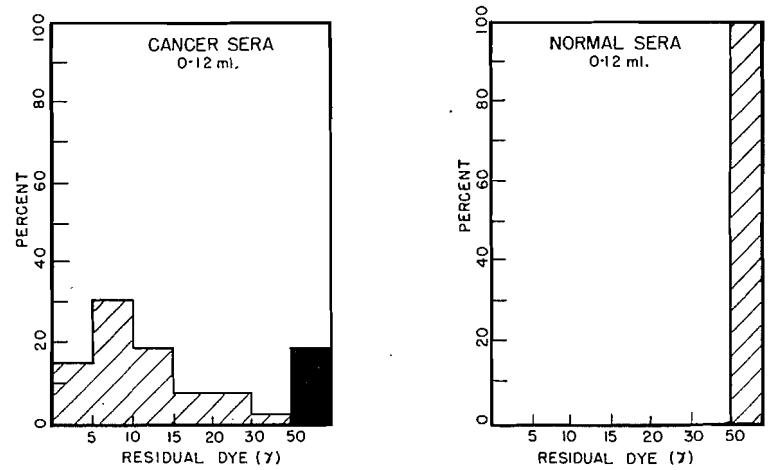

FIG. 2

FIG. 2. *Distribution curves for residual dye using 0.12 ml. of serum from cancerous and normal animals.*

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Polarograph Studies

It seemed of interest to obtain the polarograms on the sera of rats bearing the Walker carcinosarcoma 256, and to compare the relative accuracy of the protective colloid index and the polarographic waves in indicating malignancy using the same animals, especially since the former involves the whole serum and the latter a specific fraction of the serum.

The polarograph has been used extensively to indicate differences between normal humans and cancerous individuals. According to the comprehensive survey of Winzler and Burk (10) 93% of some fourteen hundred cancer patients gave polarograph waves significantly higher than normal. There are very few papers in the literature dealing with polarographic studies in cancerous rats. Klatt *et al.* (3, 4) have studied the sera of tumor bearing rats and mice. They report a difference in the height in the waves for the cancerous and normal animals.

Winzler and Burk used three different tumors; the Jensen sarcoma, hepatoma 31, and a chemically induced primary hepatoma. They noted a marked increase in the serum proteose as indicated by the polarogram, with each of the above tumors. The sera of animals with hepatoma 31 were found to give a good correlation between tumor size and wave height until a maximum was reached about 15 days after implantation.

Methods

Polarograms were made using a technique similar to that of Waldschmidt-Leitz (9). By this method, 0.5 ml. of serum was pipetted into a centrifuge tube and the serum proteins were then precipitated using 1 ml. of a 25% solution of 5-sulphosalicylic acid. One milliliter of distilled water was next added and the mixture stirred. After centrifuging for 10 min. at 2400 r.p.m. the supernatant was poured into a No. 50 Whatman filter paper and allowed to drain. (By centrifuging first, the filtration was greatly accelerated.) An aliquot of the filtrate, 0.5 ml., was then measured into a polarograph vessel, containing 4 ml. of cobalt buffer solution and 8 ml. of distilled water.

A stream of nitrogen, which had been passed over heated copper shavings (450°C.) to remove traces of oxygen, was next allowed to bubble through the solution for approximately 10 min. The dropping cathode was then attached to the vessel and the cell connected to the instrument—a model XX Sargent Polarograph.

The polarograms were then made using a span potential of 2.0 v. In each case the bridge was initially set at about 0.6 v., since the double wave was completely recorded in this range (0.6–2.0). This was the only part of the curve in which we were interested. A sensitivity setting of 2–55 on this instrument was used for all polarograms. This sensitivity proved to be the most satisfactory, since it allowed good magnification of the second wave without the

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pen running off the chart paper. By using the same sensitivity every time, the wave heights all became directly comparable.

Polarographic Results

The heights of the polarographic second waves were measured as indicated in the accompanying figure (Fig. 3). These polarograms are typical ones obtained from normals and from tumor bearing animals. Not only is the height of the wave greater with cancer serum but the appearance of the wave is different.

TABLE III

Cancer animals			Normal animals		
Wave height, mm.	Number	%	Wave height, mm.	Number	%
11–20	0	0	11–20	5	10.6
21–30	1	2.3	21–30	18	38.3
31–40	0	0	31–40	18	38.3
41–50	3	6.9	41–50	4	8.5
51–60	3	6.9	51–60	1	2.1
61–70	12	27.9	61–70	1	2.1
71–80	9	20.9	71–80	0	0
81–90	10	23.3	81–90	0	0
91–100	4	9.3	91–100	0	0
101–110	1	2.3	101–110	0	0
Total	43	99.8		47	99.9

The summarized data for 43 tumor rats and 47 healthy animals are given in Table III. The average height of the double wave with tumor serum is 77 mm. as compared with 31 mm. obtained with normal serum.

These results are embodied in the distribution curves given in Fig. 4.

Comparison and Discussion

A study of Table III and Fig. 4 reveals that in the majority of cases of well developed tumors, the polarographic double wave is higher than in normal animals. Thus in the 43 cancer sera examined polarographically, 39 (90.7%) gave wave heights greater than 50 mm. Five of the normals gave wave heights between 40–60 mm. It appears that the sera which gave waves less than 50 mm. are to be classified as normals. Those from 40–60 mm. might be classified as doubtful, while those producing wave heights greater than 60 mm. are definitely pathological.

Tables IV and V contain values obtained by both tests when made on the same sera samples for 41 cancer animals and 39 normals. A correct diagnosis is indicated by a + sign. Conversely, a − sign indicates a negative or incorrect finding. '*D*' indicates a doubtful diagnosis.

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PLATE I

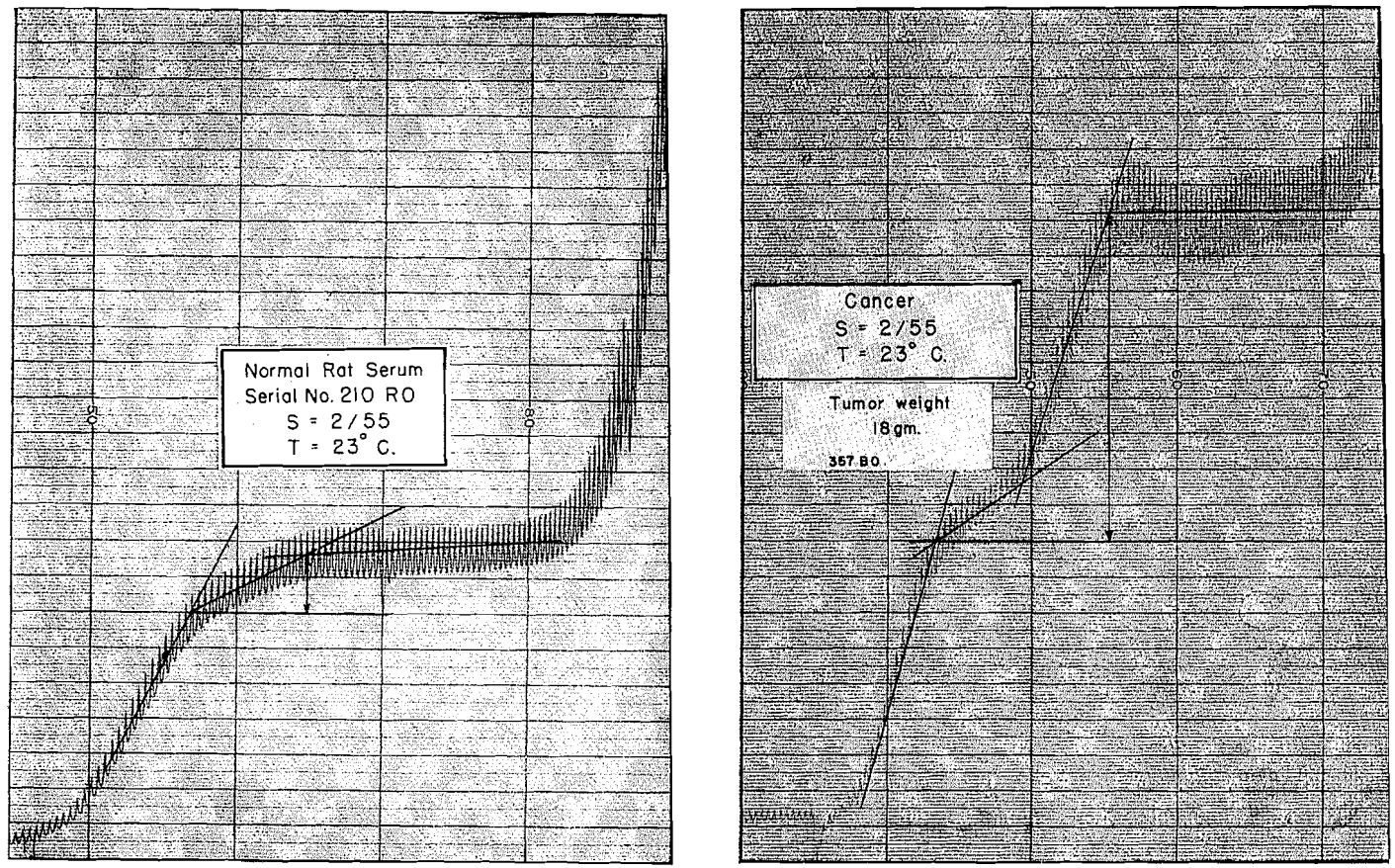

FIG. 3. *Typical polarograms for: (a) normal rat serum; (b) cancerous rat serum.*

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With the protective colloid index, values under 15γ for 0.10 ml. portions are considered as being indicative of cancer. Animals giving values of 15–20γ are in a doubtful range unless the 0.12 ml. is below the ± group, in which case it would be considered as normal if the second tube is in the + group or cancerous if it is below 50γ.

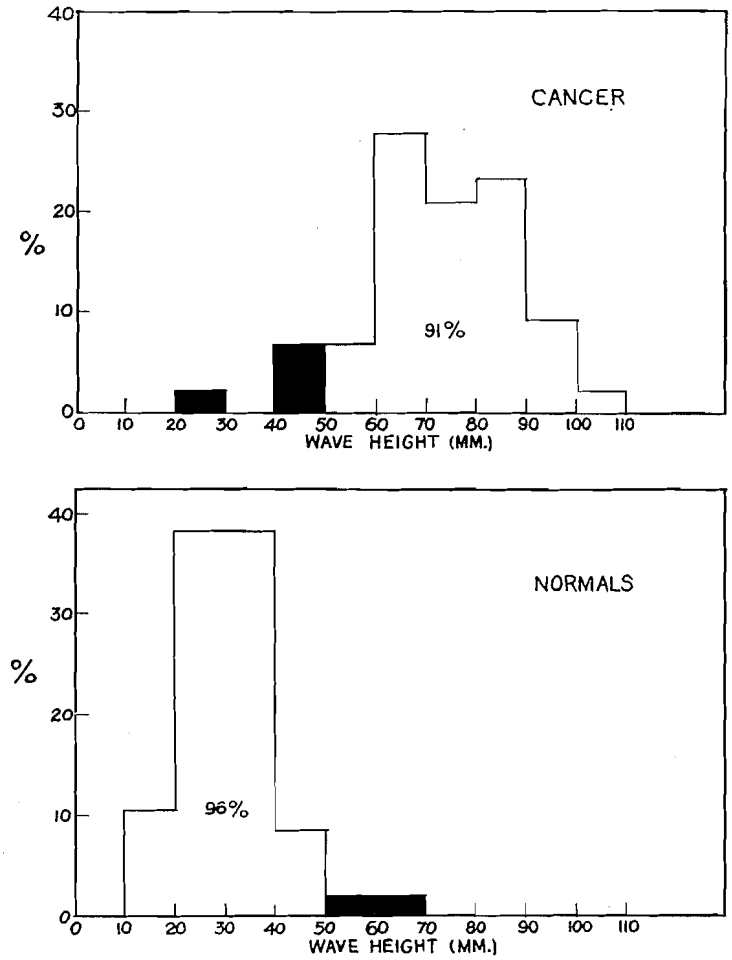

FIG. 4. *Distribution curves for wave heights of cancer and normal rat sera.*

The results embodied in Tables IV and V are summarized in Table VI.

The cancer sera diagnosed as 'doubtful' by both tests are from small tumor animals. An insufficient number of these cases has been examined to permit any final conclusions on the relative merits of the tests in detecting early stages of the disease. More work on this aspect of the problem is therefore necessary.

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The differentiation of the cancer rats into advanced, medium, and small tumor cases is only approximate and rather arbitrary. The body weight of the animals may have a bearing on the problem. Thus, a tumor of 10 gm. may have

TABLE IV

CANCER ANIMALS

No.	Wave height, mm.	Polarograph diagnosis	Residual dye, γ/ml. (0.10 ml.)	Residual dye, γ/ml. (0.12 ml.)	P.C. Index diagnosis	Tumor weight
1	69	+	2.9	11.8	+	71
2	70	+	21.2	±	−	54
3	93	+	2.8	10.0	+	83
4	86	+	6.0	17.2	+	56
5	86	+	5.8	11.8	+	133
6	82	+	2.4	5.1	+	108
7	81	+	2.8	4.0	+	71
8	83	+	0.8	0.8	+	107
9	76	+	3.2	8.1	+	60
10	76	+	2.5	2.5	+	127
11	83	+	1.1	3.0	+	110
12	82	+	3.8	7.1	+	72
13	72	+	5.4	10	+	67
14	65	+	5.4	±	+	77
15	68	+	2.9	12.2	+	81
16	65	+	3.0	11.0	+	54
17	76	+	1.4	1.6	+	81
18	68	+	1.4	1.4	+	80
19	75	+	16.8	21.2	+	87
20	89	+	2.8	2.8	+	45
21	68	+	2.2	4.8	+	76
22	61	+	5.4	14.8	+	46
23	53	+	4.9	12.8	+	43
24	65	+	5.8	11.2	+	71
25	84	+	3.8	6.0	+	55
26	67	+	19.8	20	+	90
27	80	+	4.8	9.8	+	109
28	70	+	7.1	13.2	+	58
29	70	+	3.8	22	+	91
30	96	+	4.4	10.0	+	87
31	91	+	4.4	5.4	+	84
32	84	+	4.0	4.0	+	54
33	52	+	6.8	18.0	+	70
34	75	+	7.4	±	+	20
35	48	*D*	21.8	±	−	5
36	53	+	25	−	−	10
37	93	+	10	±	+	20
38	76	+	5.4	±	+	25
39	47	*D*	12.4	±	+	10
40	24	−	17	±	*D*	10
41	46	*D*	39	±	−	14

Note: ±indicates practically no coagulation: residual dye > 50 γ per ml.

more effect on a 125 gm. animal than on one weighing 230 gm. Pertinent data is not at hand. However, it appears that, when the tumors have attained a size of about 40 gm., the body weight of the animal is not a significant factor as regards changes in the blood serum constituents.

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TABLE V

NORMAL ANIMALS

Stock No.	Wave height, mm.	Polarograph diagnosis	Residual dye, γ/ml. (0.10 ml.)	Residual dye, γ/ml. (0.12 ml.)	P.C. Index diagnosis
1	17	+	±	±	+
2	26	+	±	±	+
3	27	+	±	±	+
4	22	+	35	±	+
5	16	+	31	±	+
6	22	+	±	±	+
7	26	+	±	±	+
8	28	+	15.2	±	*D*
9	31	+	24.2	±	+
10	63	−	±	±	+
11	37	+	±	±	+
12	46	*D*	±	±	+
13	37	+	15.2	±	*D*
14	21	+	30.2	±	+
15	32	+	±	±	+
16	29	+	±	±	+
17	35	+	41.2	±	+
18	25	+	±	±	+
19	36	+	14.8	±	−
20	30	+	±	±	+
21	25	+	±	±	+
22	35	+	±	±	+
23	26	+	±	±	+
24	44	*D*	±	±	+
25	46	*D*	±	±	+
26	33	+	±	±	+
27	33	+	20.0	±	+
28	43	*D*	22.8	±	+
29	24	+	36.2	±	+
30	32	+	24.8	±	+
31	35	+	±	±	+
32	29	+	2.12	±	+
33	35	+	±	±	+
34	40	*D*	±	±	+
35	29	+	±	±	+
36	18	+	±	±	+
37	28	+	±	±	+
38	38	+	±	±	+
39	22	+	9.8	±	−

Note: ± indicates practically no coagulation: residual dye > 50 γ per ml.

These experiments appear to indicate that the polarograph and P.C. Index are of an approximately equal value when the 256 Walker carcinosarcoma is used.

TABLE VI

	Polarograph				P.C. Index			
	Positive	Negative	Doubtful	Total	Positive	Negative	Doubtful	Total
Cancer	37	1	3	41	36	4	1	41
Normal	33	1	5	39	35	2	2	39

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It is certain that the particular serum constituents responsible for the polarograph test are not the same as those involved in the protective colloid test. The former is considered (3, 4) to be determined by and a measure of the proteoses of molecular weight 10,000 or so, containing—S-S—and S-H-linkages. It has been suggested that excessive proteose arises in cancer from the degradation of albumin possibly through the action of a proteolytic enzyme of Aberhalden. Others believe it arises through failure of the liver to metabolize normal amounts of polypetides or from impaired kidney functions.

Obviously since there is more proteose present in cancer and less of the protective colloids, the proteose cannot be the source of the protection of the Congo red against the electrolyte.

The exact nature of the changes indicated by the P.C. Index have not been determined. The most obvious suggestion is that the test depends on the decreased amount of serum albumin which is significantly low in cancer. The decrease in albumin is accompanied by an increase in α_1 and α_2 globulins and, in plasma, of fibrinogen (8).

Mider, Alling, and Morton (5) in their recent paper on plasma proteins in malignancy state that the correlation factor for decreased albumin and increased globulin indicated a high degree of variation. It was found in the previous work with human sera (6) that the A/G ratio was much less significant in indicating malignancy than the Protective Colloid Index, and that the correlation between the A/G and P.C. Index was poor.

Heubner and Jacobs (2) and also Reitstotter (7) from studies of the gold numbers of serum fractions, concluded that the euglobulin had a higher protective action than the albumin and other fractions.

Bernsohn and Borman (1) believe that one or more β-globulins and possibly α globulins are responsible for the protective action of spinal fluid on the gold sol in the Lange test, whereas gamma globulin has a coagulating action. Serum albumin, they state, is inert. We have found that the so-called albumin fraction, obtained by precipitation of the globulins with half saturated ammonium sulphate, after dialysis was approximately equal in its protective action to the whole serum on the basis of nitrogen content.

Tiselius (8) has shown the heterogeneous nature of such 'salted' fractions. It therefore seems probable that the decrease in protective colloid index in cancer is due, not to the lower concentration of albumin only, but to the conversion of albumin, euglobulin, and possibly other serum constituents, to much less active species.

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* *This author is correctly cited by T. Svedberg in Colloid Chemistry p. 231, Chem. Catalogue Co., but the author's abstract states 'Der geringste Goldzahl besitzen die Albumin, der grosste die Euglobuline . . .', although in the text of his paper (p. 22 and Table II), it is clear that the abstract should read the 'reciprocal of the gold number'. Unfortunately Chemical Abstracts repeats the error in the author's summary.*

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